The aqueous chemistry of radium

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Contribution to “Diamond Jubilee of RCA”

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The aqueous chemistry of radium

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Abstract: Available literature data on the aqueous chemistry of radium are compiled. There are limited available experimental data and a significant portion of the data has been estimated using electrostatic techniques, typically based on the corresponding data of barium. The available data are compared with the corresponding data of barium (and strontium) and a methodology for estimating additional radium thermochemical data is described.

Keywords: aqueous chemistry; radium chemistry; thermodynamic data.

1 Introduction

All the isotopes of radium are radioactive and emit high intensity radiation (often alpha particles and gamma rays) and, as such, very few laboratories are equipped to work with milligram amounts of radium that are required for the determination of good quality thermodynamic data. Consequently, the aqueous chemistry of radium is relatively unexplored and the vast majority of the chemical and thermodynamic properties of radium have been estimated, being generally based on the similarity of radium with the other alkaline earth metals, in particular, barium. Similar problems are found with other heavy elements that have no stable isotopes, especially the actinides.

Radium release from high level nuclear waste repositories is predicted to be one of the major contributors of radiation dose. Radium is also associated with uranium tailings and scale formation in the oil and gas industry. To understand the behavior of radium in these settings, it is essential to have thermodynamic data in relation to the aqueous chemistry of radium, both the stability of its aqueous species and solubility of its phases, so that its behavior in the environment can be understood.

Presently, radium finds applications in radiopharmaceutical chemistry [1, 2] where studies have shown that an aqueous solution of $^{223}RaCl_2$ (trademark Xofigo®) is an efficient bone-seeking radiopharmaceutical which can reduce pain and delay disease progression in patients with bone metastases from advanced stage prostate cancer. These encouraging successes have sparked an interest in radium chemistry and much effort has been directed towards development of organic chelating ligands that can strongly and efficiently bind $^{223}Ra^{2+}$ in mild conditions [3–5]. These radium-based molecules can be later conjugated to a biomolecule (e.g., amino acid or peptide) and can then be used to selectively target specific cancer cells. Moreover, various inorganic particles have been considered as alternative carriers for ^{223}Ra and ^{224}Ra, where the particles (e.g., surface functionalized $BaSO_4$ or $CaCO_3$ [6, 7]) labeled with radium can target various biological moieties.

Chemically, radium is similar to barium because they have similar ionic radii, however, their ionic radii are sufficiently different for measurable differences in stability/solubility to occur between Ba and Ra species/phases with the same ligand. The similar ionic radii of Ra and Ba have enabled the thermochemistry of radium to be estimated (when experimental data have not been determined) on the basis of the measured thermochemical behavior of barium and, in general, the stability of radium complexes is weaker than those of barium and radium phases less soluble. However, on occasion, it has been found that the opposite behavior occurs, where radium has a more stable complex than that of barium or its solid phase is more soluble than the corresponding phase of barium.

The present study compiles the available thermochemical data for radium and compares it to the associated data of barium. It describes how additional radium thermochemical data can be estimated depending on available measured data for both strontium and barium.

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2 Aqueous chemistry of radium

2.1 Radium ion (Ra^{2+})

The standard oxidation potential of the Ra^{2+}-Ra couple was calculated by Latimer [8] to be −2.916 V (equivalent to a $\log_{10} K = -98.6$). Parker et al. [9] list a Gibbs energy of formation for Ra^{2+} of −561.5 kJ/mol that is equivalent to an oxidation potential of −2.910 V, in agreement with the value derived by Latimer [8]. All three values are very similar to the corresponding values for barium [10]. The Gibbs energy is more negative than the value recently estimated by Kitamura and Yoshida [11] (−555.6 ± 1.8 kJ/mol [−2.879 V]) from the trend in the Gibbs energy values for the other alkaline earth couples (M^{2+}-M). This latter value is discussed further below.

2.2 Inorganic species and phases of radium

Experimental data for stability and solubility constants are only available for a relatively small number of radium species and solid phases, due to the experimental difficulties outlined above. Radium hydroxide is the most soluble of the alkaline earth hydroxide phases and, as such, is more basic than barium hydroxide [10]. This is supported by the data of Kitamura and Yoshida [11] who gave a solubility for $Ra(OH)_2(s)$ in acid of $\log_{10} K_s° = 31.2$; this solubility constant was determined from Gibbs energy data listed in the JAEA thermochemical database [12]. The formation of $RaOH^+$ has been experimentally measured [13, 14] and has also been estimated using electrostatic techniques several times [11, 15, 16]. Matyskin et al. [13] determined a stability constant for $RaOH^+$ formation of $\log_{10} {}^*K° = -13.3 \pm 0.2$ that was in good agreement with the earlier data of Zielińska and Bilewicz [14]. Brown and Ekberg [15] quoted a value of $\log_{10} {}^*K° = -13.49 \pm 0.20$ from the earlier work of Langmuir and Riese [16], who estimated their value. Brown and Ekberg [15] also estimated a value of $\log_{10} {}^*K° = -13.36$ using the unified theory of metal ion complexation (UTMIC). Finally, the Gibbs energy data estimated by Kitamura and Yoshida [11] lead to $\log_{10} {}^*K° = -13.56$. The average of these values, which are all in reasonable agreement considering the weak stability, is $\log_{10} {}^*K° = -13.42 \pm 0.23$ (equivalent to $\log_{10} K° = 0.57 \pm 0.23$ using the protonation constant of water from Brown and Ekberg [15]; where multiple data are available, the uncertainty is determined from the 95% confidence interval of the cited data).

The solubility of radium sulfate has been experimentally determined in several studies across the temperature range of 10–70 °C [17–22], with all the data being in reasonable agreement. Experimental solubility data for 25 °C are only from Matyskin [22] ($\log_{10} K_s° = -10.23$) whereas estimated values using electrostatic techniques have been derived by Brown et al. [23], Langmuir and Riese [16] (both $\log_{10} K_s° = -10.26$) and Paige et al. [19] ($\log_{10} K_s° = -10.21$). Aqueous complexes can form in solubility experiments, in this case $RaSO_4(aq)$, and data are only used in the present study where aqueous speciation has been considered (for all solubility constants). The average solubility constant is $\log_{10} K_s° = -10.24 \pm 0.05$. Use of the Gibbs energy data (where necessary, Gibbs energy data for inorganic anions are taken from the Nuclear Energy Agency series, e.g., ref. [24]) from Kitamura and Yoshida [11] leads to a solubility constant that is inconsistent with the other values listed and may question the Gibbs energy value they obtained for Ra^{2+}. The crystal structures of Ra and Ba sulfate are both orthorhombic and they easily form a solid solution with a small Gibbs energy of mixing [22]. The stability of aqueous radium sulfate has not been measured experimentally, but has been estimated using electrostatic techniques several times [11, 16, 25]. The stability of the aqueous alkaline earth sulfate complexes exhibit an unusual behavior of increasing stability with increasing size of the alkaline earth ion, although a similar trend is also observed for cations in other valences (e.g., alkali and lanthanide metals). Consequently, it has been estimated that the stability of radium sulfate is greater than that of barium sulfate. Reported stability constants for aqueous radium sulfate are $\log_{10} K° = 2.63$ [11], 2.76 [16], and 2.48 [25], with an average of $\log_{10} K° = 2.61 \pm 0.33$.

The solubility of most radium solid phases is less than that of the corresponding barium phase. However, radium carbonate is an exception with Nikitin [26] indicating that radium carbonate was 10 times more soluble than barium carbonate. Recently, Matyskin [22] conducted solubility studies from both undersaturation and oversaturation and confirmed that radium carbonate was significantly more soluble than barium carbonate, obtaining the first solubility constant for radium carbonate of $\log_{10} K_s° = -7.5$ that is one log unit more than the solubility constant of barium carbonate. This latter study noted that witherite ($BaCO_3(s)$) has an orthorhombic crystallinity whereas $RaCO_3(s)$ is cubic containing carbonate oxygen atoms that are highly disordered. This disordered nature possibly leads to the increase in solubility of $RaCO_3(s)$. Again, the stability constant of aqueous radium carbonate has not been measured experimentally, but data are available for the constant that have been determined using electrostatic techniques. The stability constants that have been derived are $\log_{10} K° = 2.5$ [16], 2.61 [11], and 2.43 [25], leading to an average value of $\log_{10} K° = 2.53 \pm 0.14$.

A solubility constant has been estimated for $RaHPO_4(s)$ using electrostatic methods with confirmation of the solubility in a biogeochemical model of metal uptake (as a surrogate for calcium) into aquatic invertebrates [27, 28]. The average of the two solubility constants was $\log_{10} K_s° = -7.55$.

Radium chloride is a relatively soluble salt. The solubility has been measured by Erbacher [29] and from the data a solubility constant of $\log_{10} K_s° = 0.35$ can be determined. In addition, from the Gibbs energy data given by Kitamura and Yoshida [11] a solubility constant of $\log_{10} K_s° = 0.29$ was determined. The latter value was estimated using electrostatic techniques, but is in very good agreement with the experimentally determined value. The average solubility constant is $\log_{10} K_s° = 0.32 \pm 0.10$ (where the uncertainty has been estimated in the present study). A stability constant has been estimated for the formation of $RaCl^+$ in two studies [11, 16]. The estimated stability constants are $\log_{10} K° = -0.10$ and -0.55 indicating that the stability of the complex is very weak, and potentially, actual formation of the complex may be questionable. The average stability constant is $\log_{10} K° = -0.32 \pm 0.23$ (where the uncertainty is selected to cover the range of the two values).

A stability constant for RaF^+ can be estimated from Kitamura and Yoshida [11] using the provided Gibbs energy data. A stability constant of $\log_{10} K° = -0.27$ was derived indicating that the stability of the species is weak. However, the stability of the corresponding barium and strontium phases might suggest that the stability of this phase is greater than indicated from the stability constant of Kitamura and Yoshida [11] and, as such, it is not considered reliable (see discussion with barium species below). In addition, recently Butkalyuk et al. [29] measured the solubility of $RaF_2(s)$. They measured a solubility of 0.763 g per 100 mL of water. Use of this value, and correction for the ionic strength of the solution (using the Davies equation; this equation has been used to correct stability or solubility constants to zero ionic strength throughout the present study) and complexation of radium with fluoride, leads to a solubility constant of $\log_{10} K_s° = -4.66$ (considering the solution speciation of RaF^+ with the stability constant listed below).

Erbacher [30] also measured the solubility of radium bromide and found that it was more soluble than radium chloride. From the data, a solubility constant of $\log_{10} K_s° = 1.39$ has been determined.

Polesitsky and Tolmatsheff [31] measured the solubility of radium iodate. They found that it was less soluble than the corresponding barium salt. The solubility constant determined from the data was $\log_{10} K_s° = -8.85$.

The solubility of radium nitrate was also measured by Erbacher [30]. Similar to the case for radium carbonate, the nitrate phase of radium is more soluble than the corresponding phase for barium. This has also been confirmed more recently by Butkalyuk et al. [32]. From the data of Erbacher [30], a solubility constant of $\log_{10} K_s° = -0.60$ is determined, indicating that expectedly that the nitrate phase is quite soluble.

2.3 Organic species of radium

The majority of data on the complexation of radium by organic ligands has come from the work of Schubert and coworkers [33, 34] and Sekine et al. [35], although other data have been published on the stability of radium with ethylenediamine *N*,*N*,*N′*,*N′*-tetraacetic acid (EDTA) [36–39]. In all of these studies, it has been found that the stability of the radium complex is less than that of the corresponding barium complex.

Matyskin et al. [39] have recently studied the complexation of both radium and barium with EDTA at two different pH values and as a function of ionic strength (0.2–2.5 mol/L) using NaCl as the medium. From the data, the stability constant of a single complex, $RaEDTA^{2-}$, was determined with a value of $\log_{10} K° = 9.13$. Previous data, when corrected to zero ionic strength [39], have been found to be in good agreement with this value, with stability constants of $\log_{10} K° = 9.22$ [36], 9.2 [37], 8.9 [38], and 9.09 [35]; the average of all five measurements is $\log_{10} K° = 9.11 \pm 0.25$. Two of these studies utilized a temperature of 20 °C [36, 38], but the difference in stability that results from use of this temperature is believed to be within the uncertainty of the measurements.

Sekine et al. [35] also determined stability constants of the alkaline earth metals, including radium, with a range of other organic ligands. The ligands included cyclohexane 1,2-diamine *N*,*N*,*N′*,*N′*-tetraacetic acid (CyDTA), diethylenetriamine *N*,*N*,*N′*,*N″*,*N″*-pentaacetic acid (DTPA), nitrilotriacetic acid (NTA), 2,2′-ethylenedioxyl bis[ethyliminodi(acetic acid)] (EGTA) and *N′*-(2-hydroxyethyl)ethylenediamine N,N,N′-triacetic acid (HEDTA). Stability constants were determined in 0.1 mol/L $NaClO_4$ and have been corrected to zero ionic strength [38] (although two [DTPA and HEDTA] have been redetermined in the present study using the correct charge for the ligand). The stability constants obtained were $\log_{10} K° = 10.09$ ($RaCyDTA^{2-}$), 9.49 ($RaEGTA^{2-}$), 10.74 ($RaDTPA^{3-}$), 6.95 ($RaHEDTA^-$), and 6.45

($RaNTA^{-}$). The latter stability constant has been corrected to zero ionic strength in the present work from $\log_{10} K = 5.1$ (0.1 mol/L $NaClO_4$).

Schubert and coworkers [33, 34] studied the complexation of radium with several other organic acids. The acids studied included citric (Cit), tartaric (Tar), malic (Mal), succinic (Suc), aspartic (Asp), pyruvic (Pyr), oxaloacetic (OxAc), fumaric (Fum), and sulfosalicylic ($SalSO_4$). The data were obtained using an ionic strength of 0.16 mol/L NaCl. They have also been corrected to zero ionic strength [39]. The stability constants obtained for zero ionic strength are $\log_{10} K° = 3.91$ and 3.55 (for $RaCit^{-}$; with an average of $\log_{10} K° = 3.73$), 2.27 and 2.23 (for RaTar(aq); with an average of $\log_{10} K° = 2.25$), 1.98 (RaMal(aq)), 2.03 (RaSuc(aq)), 1.38 ($RaAsp^{+}$), 1.41 ($RaPyr^{+}$), 2.63 (RaFum(aq)), 2.83 (RaOxAc(aq)), and 2.93 ($RaSalSO_4$(aq)).

It is clear from the data for all organic ligands that the stability, as expected, increases with increasing charge of the complexing ligand. Moreover, the stability of the neutral species is also similar to the stability of the neutrally species of radium with inorganic ligands.

2.4 Comparison with the aqueous chemistry of barium

Stability and solubility data can also be compiled for barium. The data for radium with the inorganic and organic ligands listed above are compared with those of barium, where available, in Table 1. The data are split into two; those where the barium stability or solubility constant ($\log_{10} K°$ or $\log_{10} K_s°$) is less than the corresponding radium

Table 1: Comparison of the solubility and stability constants of radium, barium, and strontium with various ligands at 25 °C and zero ionic strength.

Species	**$\log_{10} K°$**				**References for Ba**	**References for Sr**
	Ra	**Ba (Ba > Ra)**	**Ba (Ba < Ra)**	**Sr**		
MOH^{+}	0.57 ± 0.23	0.67 ± 0.07		0.84 ± 0.05	[15]	[15]
MSO_4(aq)	2.61 ± 0.33		2.40 ± 0.10^{b}	2.21 ± 0.11	[19, 40]	[40, 56]
MCO_3(aq)	2.53 ± 0.14	2.56 ± 0.10^{b}		2.81 ± 0.10^{b}	[16]	[57]
$MEDTA^{2-}$	9.11 ± 0.25	9.86 ± 0.11		10.31 ± 0.37	[39]	[58–60]
$MCyDTA^{2-}$	10.09 ± 0.10^{b}	$9.79 \pm 0.10^{a,b}$		10.71 ± 0.10^{b}	[35]	[58]
$MEGTA^{2-}$	9.49 ± 0.10^{b}	10.19 ± 0.10^{b}			[35]	
$MDTPA^{3-}$	10.74 ± 0.10^{b}	11.04 ± 0.10^{b}		11.94 ± 0.10^{b}	[35]	[61]
$MHEDTA^{-}$	6.95 ± 0.10^{b}	7.55 ± 0.10^{b}		8.15 ± 0.10^{b}	[35]	[62]
$MNTA^{-}$	6.45 ± 0.10^{b}	$6.41 \pm 0.10^{a,b}$		6.73 ± 0.10^{b}	[41] (20 °C)	[41] (20 °C)
$MCit^{-}$	3.73 ± 0.18	4.09 ± 0.05		4.41 ± 0.03	[32, 42, 43]	[33, 63]
MTar(aq)	2.25 ± 0.05	2.64 ± 0.12		2.85 ± 0.29	[33, 44]	[63, 64]
MSuc(aq)	2.03 ± 0.10^{b}	2.25 ± 0.11		2.29 ± 0.10^{b}	[33, 45]	[45]
$MAsp^{+}$	1.38 ± 0.10^{b}	1.59 ± 0.10^{b}		1.93 ± 0.10^{b}	[46]	[46]
$MPyr^{+}$	1.41 ± 0.10^{b}					
MFum(aq)	2.63 ± 0.10^{b}	$2.49 \pm 0.10^{a,b}$			[47]	
MOxAc(aq)	2.83 ± 0.10^{b}					
MMal(aq)	1.98 ± 0.10^{b}	2.31 ± 0.11		2.45 ± 0.28	[33, 44, 48]	[33, 48]
$MSalSO_4$(aq)	2.93 ± 0.10^{b}					
MCl^{+}	−0.32 ± 0.23	−0.01 ± 0.05		0.21 ± 0.10^{b}	[49–51]	[51]
MSO_4(s)	−10.24 ± 0.05	−9.96 ± 0.05		−6.62 ± 0.02	[23]	[23]
$MHPO_4$(s)	-7.55 ± 0.05^{b}	-7.46 ± 0.05^{b}		−6.97 ± 0.11	[27, 28]	[27, 28]
$M(OH)_2$(s)	$31.2 \pm 0.5^{b,c}$	30.2 ± 0.2^{b}		27.5 ± 0.2^{b}	[11]	[11]
MCO_3(s)	−7.49 ± 0.10		−8.56 ± 0.02	−9.27 ± 0.02	[23]	[23]
MCl_2(s)	0.32 ± 0.10^{b}	1.11 ± 0.10^{b}			[22]	
$M(NO_3)_2$(s)	-0.60 ± 0.10^{b}		-0.84 ± 0.10^{b}		[22]	
$M(IO_3)_2$(s)	-8.85 ± 0.10^{b}	-8.75 ± 0.10^{b}		−6.49 ± 0.08	[22]	[52, 65, 66]
MBr_2(s)	1.39 ± 0.20^{b}	2.23 ± 0.20^{b}			[22]	
MF_2(s)	-4.66 ± 0.20^{b}		−5.87 ± 0.05	−8.54 ± 0.15	[53–55]	[29, 59, 67]

[a] Although these values are less than the corresponding Ba constant, the stability behavior within the alkaline earth series (particularly that of strontium) would suggest that the constant should be larger than that of radium – see text. [b] Uncertainty estimated in the present study. [c] Estimated stability or solubility constant.

constant (there are only a few examples of this behavior) and those where it is larger. There are some examples where the barium constant is less than the radium constant, but it has been placed in the second of the two datasets. For these few cases, it is believed that either the radium or barium (or both) constant may be slightly in error and the barium constant should be the larger. In all three cases, this behavior is seen for organic acid ligands where the typical behavior for these ligands is for the barium constant to be larger than that of radium (see also discussion below).

Linear free energy relationships can be used to compare the magnitude of the solubility and stability constants of radium and barium complexes and phases. Figure 1 illustrates the relationship between the larger dataset, where the barium constant is larger than that of radium. As can be seen from the figure, there is very good correlation between the two sets of constants, with a coefficient of determination (r^2) of 0.999. As would be expected when the barium solubility and stability constants are larger than those of radium, the intercept is negative. The slope is marginally larger than unity. Given that the stability and solubility constants are displayed in logarithmic form, the relationship extends over more than 40 orders of magnitude in stability.

The relationship between the much smaller dataset, where the radium constant is larger than that of barium is shown in Figure 2. Again, there is an excellent correlation between the two sets of data, with a coefficient of determination of 0.9988. Even considering the small amount of data in the relationship, the correlation between the data indicates that the fit is significant. Converse to the behavior for the larger set of data, as might be expected for this dataset the intercept is greater than zero. The slope is significantly less than unity. For this set, the relationship spans about 10 orders of magnitude.

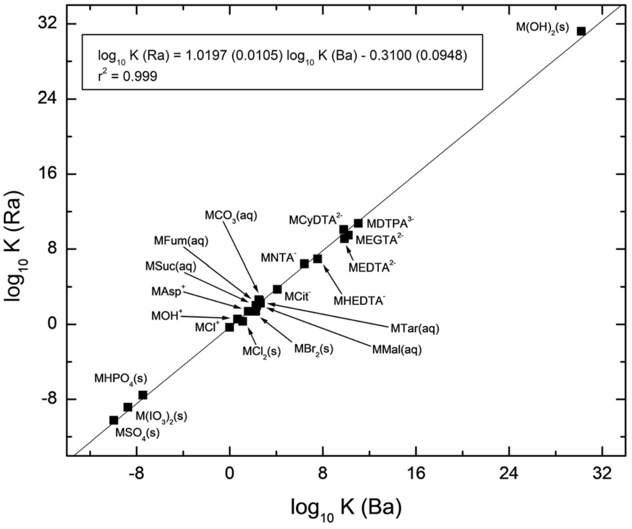

Figure 1: Correlation of the stability and solubility of Ba and Ra complexes and phases where the Ba constant is greater than that of Ra.

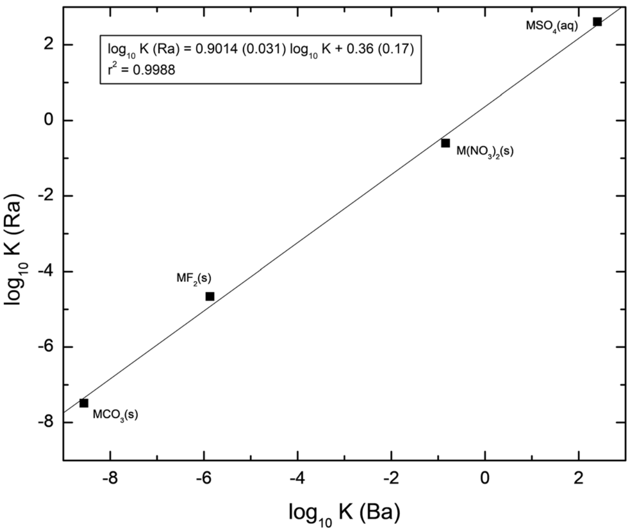

Figure 2: Correlation of the stability and solubility of Ba and Ra complexes and phases where the Ba constant is less than that of Ra.

It is important to note that a similar linear free energy relationship is not observed between the stability and solubility constants of radium with those of strontium. For example, the solubility constant of strontium with iodate has been determined to be $\log_{10} K_s° = -6.48$ [52], whereas that for the solubility of strontium with sulfate is quite similar with $\log_{10} K_s° = -6.62$ [23]. As can be seen in Table 1, the solubility constants for these two ligands both differ by more than an order of magnitude for both radium and barium.

What is always consistent from the data shown in Table 1, that further enables the selection of whether the solubility or stability constant of barium is greater than that of radium, is that when the Ba constant is greater than that of Ra then the corresponding constant of strontium is always greater than that of barium. Conversely, if the constant of barium is less than that of radium then the constant of strontium will always be less than that of barium. For example, at 25 °C, strontium is the least soluble of the alkaline earth carbonate phases. The stability or solubility constants of radium and strontium rarely overlap ensuring that the occurrence of the Ba constant being greater or less than the corresponding Ra constant can be easily ascertained.

Further, it is probable that when Ba and Ra phases have the same crystal structure that the solubility of the Ra phase will be less than that of the corresponding Ba phase.

Conversely, when they are different and the radium phase may have a disordered structure, then the solubility of the Ra phase will be greater than that of the barium phase.

Stability constant data are available in the literature for the complexation of the alkaline earth metals, except radium, with fluoride. For magnesium the data span an ionic strength range of 0–1 mol/L ($NaClO_4$), whereas there are less data for the heavier alkaline earth metals. However, the data that are available enable estimates to be made for all the metals at zero ionic strength. The data so derived indicate that the zero ionic strength stability constants decrease with increasing alkaline earth metal ion size, with BaF^+ having a stability constant of $\log_{10} K° = 0.63$. Based on this stability, the decreasing stability down the series and the regression equation listed in Figure 1, the calculated stability constant for RaF^+ is $\log_{10} K° = 0.33$. This stability constant is substantially more positive than that proposed by Kitamura and Yoshida [11] ($\log_{10} K° = -0.27$). This may appear to again question the Gibbs energy derived for Ra^{2+} in this latter work, however, using the Gibbs energy listed in the present work actually leads to a more negative stability constant for RaF^+. Use of the stability constants for SrF^+ and BaF^+ derived in the present study to determine Gibbs energy of reaction values, and combining them with the Gibbs energy values given by Kitamura and Yoshida [11] for Sr^{2+} and Ba^{2+} and that for F^- from the NEA series [24], leads to Gibbs energy of formation values for both SrF^+ and BaF^+ that are 4.4 kJ/mol more negative than indicated by Kitamura and Yoshida [11]. Based on the prediction methodology used in the latter study [11], then the predicted Gibbs energy of formation value for RaF^+ would also be 4.4 kJ/mol more negative, leading to a stability constant of $\log_{10} K° = 0.49$, in closer agreement with the stability constant derived in the present study.

The regression equations given in Figures 1 and 2 can be used to estimate stability and solubility constants for either radium or barium complexes or phases where they have not been previously measured experimentally. However, before undertaking such calculations it is worthwhile to show the difference that occurs between the regression equations of the two figures. For this purpose, the solubility of radium carbonate is an excellent example. If the solubility of radium carbonate was consistent of a phase that was less soluble than the corresponding barium phase, then the regression equation shown in Figure 1 would indicate a solubility constant of $\log_{10} K_s° = -9.03$. This is about 1.5 orders of magnitude less soluble than has been observed experimentally [22] and also estimated using electrostatic techniques [23]. There is a clear chemical behavior difference when radium solubility or stability constants are greater than the corresponding barium constants. Importantly, as indicated above, when the stability or solubility constant of radium is greater than that of barium, then also the constant of barium will be greater than that of strontium.

These important relationships between the stability and solubility constants in the strontium, barium and radium series can then be used to derive constants that have not, to date, been measured experimentally. As a first example, the stability of thiosulfate complexes with the alkaline earth metals exhibits the same behavior as that of the sulfate complexes. The average stability constant for the barium species, $BaS_2O_3(aq)$, determined from literature data [68, 69] is $\log_{10} K° = 2.27$. It is noted that the solubility constant for barium is greater than that of strontium which, in turn, is greater than that of calcium. Based on this information, and using the regression equation given in Figure 2, the calculated solubility constant for $RaS_2O_3(aq)$ is $\log_{10} K° = 2.41$, i.e., larger than that for $BaS_2O_3(aq)$.

Similarly, data from Stary [70] indicate that the solubility of alkaline earth metals with oxalate increases with increasing ionic size of the alkaline earth metal ion. Stary [70] measured a solubility constant for BaOx(s) of $\log_{10} K_s° = -6.0$ (using 0.1 mol/L $KClO_4$), from which a zero ionic strength solubility constant of $\log_{10} K_s° = -6.43$ can be derived. In the same study, the solubility of the strontium salt was found to be less than that of the barium salt and, in addition, that of the strontium salt less than that of the corresponding calcium salt. Regarding this behavior, the solubility of RaOx(s) is calculated, using the regression equation given in Figure 2, to be $\log_{10} K_s° = -5.43$.

As shown in Table 1, there are a few ligands where stability constants have been determined for radium complexes, but no similar measurements have been made for barium complexes. Given that these complexes are all with organic acids, it is expected that the stability of the barium complexes will be greater than those of the radium complexes. Consequently, using the regression equation given in Figure 1, the following stability constants are calculated, $\log_{10} K° = 1.69$ ($BaPyr^+$), 3.08 (BaOxAc(aq)), and 3.18 ($BaSalSO_4$(aq)).

There are also multiple examples of where the stability or solubility constant of barium is greater than that of radium. The following are some examples of prediction of the solubility or stability constant of radium complexes where not only is the stability of the barium complex larger than that of radium, but also the strontium complex stability is larger than that of barium. The data derived are for both inorganic and organic ligands. The stability constants derived for the various radium complexes are: $RaAc^+$ ($\log_{10} K° = 0.44$ [based on an average stability constant for $BaAc^+$ of $\log_{10} K° = 0.74$ [71–73]; where Ac is acetate]); RaOx(aq)

($\log_{10} K = 1.09$ [based on a stability constant for BaOx(aq) of $\log_{10} K = 0.58$ [74]; and corrected to zero ionic strength using other related data]); $RaProp^+$ ($\log_{10} K^\circ = -0.16$ [based on a stability constant for $BaProp^+$ of $\log_{10} K^\circ = 0.15$ [71]; where Prop is propionate]); $RaGly^+$ ($\log_{10} K^\circ = 0.47$ [based on a stability constant for $BaGly^+$ of $\log_{10} K^\circ = 0.77$ [75]; where Gly is glycine]); $RaATP^{2-}$ ($\log_{10} K^\circ = 4.87$ [based on a stability constant for $BaATP^{2-}$ of $\log_{10} K = 3.29$ [76] and corrected to zero ionic strength; where ATP is adenosine triphosphoric acid]); $RaHQSO_4$(aq) ($\log_{10} K^\circ = 2.05$ [based on a stability constant for $BaHQSO_4$(aq) of $\log_{10} K^\circ = 2.31$ [77]; where $HQSO_4$ is 8-hydroxyquinoline-5-sulfonic acid]); RaDiPic(aq) ($\log_{10} K^\circ = 4.10$ [based on a stability constant for BaDiPic(aq) of $\log_{10} K = 3.43$ [78] and corrected to zero ionic strength; where DiPic is dipicolinic acid]); and $RaP_3O_{10}{}^{3-}$ ($\log_{10} K^\circ = 4.10$ [based on a stability constant for $BaP_3O_{10}{}^{3-}$ of $\log_{10} K^\circ = 4.33$ [79]; where $P_3O_{10}{}^{5-}$ is the triphosphate ion]).

3 Conclusions

Available literature data for the aqueous chemistry of radium shows that in the majority of cases that the stability or solubility (with respect to $\log_{10} K^\circ$ or $\log_{10} K_s{}^\circ$) of a radium species/phase is less than the corresponding barium species/phase. This would indicate that the aqueous species are less stable, but also that the solid phases are less soluble. However, there are a limited number of cases where the opposite behavior is observed. Nevertheless, in all cases, the same trend that is observed between strontium and barium will also be observed between barium and radium. These trends enable the estimation of thermochemical data for radium if the corresponding data are available for strontium and barium.

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