



Weak barium and radium hydrolysis using an ion exchange method and its uncertainty assessment



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ABSTRACT

The hydrolysis of Ba²⁺ and Ra²⁺ was studied at 25 °C in aqueous mixtures of NaOH and NaClO₄ using an ion exchange method and radiotracer and batch techniques. The distribution of ¹³³Ba and ²²⁶Ra between solid (ion exchange resin) and aqueous (mixture of NaOH and NaClO₄) phases was measured via gamma spectrometry and liquid scintillation counting. The total ionic strength was kept constant and the concentration of NaOH in the aqueous phase was varied from 0 (pure NaClO₄) to pure NaOH from sample to sample. It was shown that an increase of the Ba²⁺ or Ra²⁺ concentration in the aqueous phase with an increase of the NaOH concentration cannot be explained solely by Ba²⁺ or Ra²⁺ activity coefficient differences in the NaOH and NaClO₄ media (salting out) and that weak BaOH⁺ and RaOH⁺ ion pairing occurs in the systems studied. A model for weak ion association was developed and apparent BaOH⁺ and RaOH⁺ stability constants were derived assuming the formation of weak aqueous NaOH(aq) ion pairs via non-linear curve fitting. It was demonstrated that systematic uncertainties have a much greater contribution to the NaOH(aq), BaOH⁺ and RaOH⁺ stability constant uncertainty budget compared to stochastic uncertainties and a method for estimation of the systematic uncertainties was proposed. The method combines fitting, restricted primitive model computations with surveyed literature data that resulted in a stability constant for NaOH(aq) that ranged from 0 to 1 at ionic strengths below 5 mol·kg⁻¹ (i.e. $K_{\text{NaOH}} = 0.5 \pm 0.5$, where the uncertainty is a systematic 95% confidence interval). The variation of K_{NaOH} allowed the estimation of the systematic 95% confidence interval in the apparent stability constants of BaOH⁺ and RaOH⁺. The specific ion interaction theory was used to extrapolate the derived logarithms of the BaOH⁺ and RaOH⁺ apparent stability constants to zero ionic strength ($\log_{10}K = 0.7 \pm 0.2$ for both ion pairs) and obtain the relevant ion interaction parameters. It was shown that both the Ba²⁺ and Ra²⁺ ions have similar activity coefficients and undergo similar short-range interactions in aqueous NaOH–NaClO₄ media.

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1. Introduction

Water is the most abundant chemical compound on the Earth. It hydrolyses virtually all metal ions to result in the formation of various metal hydroxide complexes. As a consequence, the mobility of toxic metal ions in the environment can be enhanced if the metal hydroxide complexes formed are soluble in aqueous media.

Radium is one of the most radiotoxic metals present in the environment [1]. It has no stable isotopes and can be found in natural uranium and thorium ores and minerals as part of the ²³⁸U, ²³⁵U and ²³²Th natural decay chains. Enhanced radium concentrations can be found in different waste streams: uranium and other metal

mining [2–4], fossil fuel combustion [5], oil and gas production [6] and others. Moreover, radium ingrowths occur in spent nuclear fuel, which makes it a critical element for long-term safety assessments of final nuclear waste repositories [7]. According to Langmuir and Riese [8], radium hydrolysis should influence its migration from man-made waste streams. This provokes strong interest in the environmental science and geochemistry of radium.

Radium is the last of the alkaline-earth metals and its complexation is similar to barium. This is due to the fact that both metal ions have the same charge (+2) and similar effective ionic radii (1.48 Å for Ra²⁺ and 1.42 Å for Ba²⁺ in 8-fold coordination [9]). Until quite recently, Ba(OH)₂ was considered as a strong, completely dissociated electrolyte but nowadays, there is consensus that BaOH⁺ is formed in strong alkaline media and comprehensive reviews on barium hydrolysis are available [10,11]. However, it is also known

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that the BaOH^+ complex is weak and its first hydrolysis constant at zero ionic strength is less than 10 ($K^0 < 10$). Similar values and trends can be expected for RaOH^+ .

Weak complex formation often referred to as ion pairing or ion association is a special case of equilibrium. A review defining the “state of the art” by Marcus and Hefter [12] and other valuable works [13–16] throw light on what has been done for the past 130 years in the area of ion pairing. In general, all the methods that are widely used to study strong complex formation (emf, conductivity, spectroscopy, solubility, distribution measurements and others) can also be used to study weak ion pairing, but dielectric and ultrasonic relaxation allow different types of weak complexes or ion pairs to be distinguished [12]. These methods are difficult to apply in studying the weak ion pairing of radium due to its radioactive nature. For example, the minimum concentration of radium required in solution in the case of conductivity measurements is $0.5 \cdot 10^{-3} \text{ mol} \cdot \text{L}^{-1}$. Such a high radium concentration would result in the radiolysis of water and require extensive radiation protection. Radium ion pairing can be studied using under saturation solubility measurements of its sparingly soluble salt – radium sulfate ($^{226}\text{RaSO}_4$). In this case, relatively small amounts of $^{226}\text{RaSO}_4$ are needed and the radiolysis of water can be neglected. However, such experiments are still challenging and require extensive radiation protection because $^{226}\text{RaSO}_4$ powder must be handled in hot cells or in negative pressure glove boxes due to ^{222}Rn emissions.

Only trace concentrations of radium (approximately $1 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$ of ^{226}Ra) are required to study its complex formation using distribution methods, for example, ion exchange. In this case, the method entails measuring the change in the distribution of a metal ion at trace levels between an ion exchange resin and the aqueous phase containing an inert background electrolyte as a function of changes in the concentration of a complexing agent. The change in a metal ion concentration in the aqueous phase resulting from a change of the complexing agent concentration can be explained solely by its complex formation with the ligand if only negligible amounts of background electrolyte (less than 10% [17]) were substituted with the complexing agent. In this case, the activity coefficients of the metal ion were kept constant and the principle of constant ionic media, implemented by Niels Bjerrum [18], is observed. As a result, the stability constant for a metal complex at a particular ionic strength (constant concentration of inert background electrolyte) can be derived.

However, in the case of weak ion pairing it is necessary to carry out experiments at moderate ionic strength ($I > 0.1 \text{ mol} \cdot \text{L}^{-1}$) and to substitute significant amounts (more than 10%) of background electrolyte with the complexing agent (*i.e.* NaClO_4 with NaOH in the system described here) to be able to detect any weak ion pairing. In this case, the principle of constant ionic media is violated and a change in the metal ion concentration (Ba^{2+} or Ra^{2+}) in the aqueous phase as a result of a change in the complexing agent concentration can be explained by two effects: weak metal-ligand ion pairing and/or differences in the activity coefficient of the metal ion in the varying medium. In other words, the metal ion will not only form weak ion pairs with the added ligand but may also undergo short-range specific ion interactions due to activity coefficient changes in the varying medium. These specific short-range interactions can lead to either a change of the metal ion concentration in the aqueous phase (salting out) or in the ion exchange resin (salting in). Thus, it is necessary to distinguish between these two effects.

Moreover, ion pair formation between components of the background media may also occur due to significant substitution of the background electrolyte with the complexing agent. When studying radium or barium hydrolysis by ion exchange, because of the weak complexation that occurs, significant amounts of NaClO_4 have to be substituted with NaOH which may lead to the formation of aqueous

$\text{NaOH}(\text{aq})$ ion pairs. However, the existence of the aqueous $\text{NaOH}(\text{aq})$ complex is debatable and no consensus has been reached with respect to the formation of weak aqueous ion pairs with stability constants at zero ionic strength less than 2 ($K^0 < 2$) [12]. For example, the semi-empirical Pitzer model [19,20] is widely used to extrapolate apparent stability constants measured at high ionic strength (above $3.5 \text{ mol} \cdot \text{kg}^{-1}$) to zero ionic strength. In this model, the deviation of an apparent stability constant from its thermodynamic stability constant at zero ionic strength is described by virial coefficients that can be explained solely by electrostatic long- and short-range ion interactions (activity coefficients). Ion pairing of 1:1 or 1:2 or 2:1 electrolytes is not considered directly in the Pitzer model. On the other hand, there is some experimental evidence for the existence of ion pairs in aqueous solutions of some concentrated 1:1 electrolytes [12].

Another important issue associated with the experimental determination of the stability constants of weak ion pairs is uncertainty assessment. The stochastic uncertainties for the stability constants can be determined using a methodology that has been used before [21,22] but, to the best of our knowledge, no method for systematic uncertainty assessment of weak ion pairing has yet been developed. It is likely that systematic uncertainties associated with the stability constants of weak ion pairs are very high. Therefore, any study of weak ion pairing is not a trivial task. In the only experimental study of radium hydrolysis [23], no distinction was made between Ra^{2+} activity coefficient differences in NaOH and NaClO_4 media or weak RaOH^+ ion pairing, and the possible formation of the aqueous $\text{NaOH}(\text{aq})$ ion pair. Further, no systematic uncertainty assessment was undertaken.

In this work, the hydrolysis of radium and barium were experimentally studied using a suitable ion exchange method and radiotracer technique. The experimental data obtained were critically analysed and the hypothesis that no BaOH^+ or RaOH^+ ion pairing takes place in the studied systems was tested. A model which can be used to derive the stability constants of BaOH^+ or RaOH^+ ion pairs was proposed and a detailed assessment of stochastic and systematic uncertainties was carried out.

2. Experimental

2.1. Sample preparation

The hydrolysis of Ba^{2+} and Ra^{2+} was extensively studied (360 samples) via an ion exchange method with radiotracer (^{133}Ba and ^{226}Ra) and batch techniques in an aqueous mixture of NaClO_4 and NaOH . The distribution of ^{133}Ba and ^{226}Ra was studied in polypropylene tubes as a function of the concentration of NaOH . The ionic strength was kept constant, but the ionic medium was not, and 40–100% of the background electrolyte (NaClO_4) was substituted with the complexing agent (NaOH). All samples were kept at a constant temperature ($25.1 \pm 0.1 \text{ }^\circ\text{C}$). Preliminary kinetic and sorption studies showed that the equilibria were achieved within 24 h and that Ba^{2+} and Ra^{2+} sorption on the tubes is negligible under the experimental conditions used. Molar concentrations of NaOH and NaClO_4 solutions were converted to molal using densities. The densities of non-radioactive NaOH – NaClO_4 mixtures (without Ba^{2+} and Ra^{2+} , concentration of Ba^{2+} and Ra^{2+} in all samples was below $1 \cdot 10^{-6} \text{ mol} \cdot \text{L}^{-1}$ and $1.5 \cdot 10^{-5} \text{ mol} \cdot \text{L}^{-1}$, respectively) were measured gravimetrically using 1 mL pycnometer. The densities for pure NaOH and NaClO_4 solutions measured in this work were in close agreement (0.5% difference) with the literature values, taken from [24] and [25], respectively.

First only barium hydrolysis (barium samples) and then the hydrolysis of both barium and radium (barium/radium samples) was studied and the experimental details are listed in Table 1.

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