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Complexation of calcium and magnesium with glutarimidedioxime: Implications for the extraction of uranium from seawater

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ABSTRACT

Complexation of calcium and magnesium with glutarimidedioxime, a ligand of importance in the sorption of uranium from seawater by functionalized sorbents, in aqueous solutions was investigated with potentiometry and calorimetry. The stability constants of the complexes and the enthalpies of complexation were determined. Results show that calcium(II) and magnesium(II) form much weaker complexes with glutarimidedioxime than uranium(VI). However, due to the very high concentrations of calcium and magnesium in seawater, small but significant fractions of the sorption sites on the glutarimidedioxime-functionalized sorbent are expected to be occupied by calcium and magnesium. Results also show that the dominant complexation reactions of calcium and magnesium with glutarimidedioxime at seawater pH are endothermic processes, implying that the complexation, as well as the sorption of calcium and magnesium on the glutarimidedioxime-functionalized sorbent, would be enhanced at higher temperatures.

1. Introduction

The global supply of uranium derived from conventional terrestrial sources is estimated to be 7.1 million tons, enough to power the world's nuclear reactors for a little over 100 years [1]. However, this estimate does not take into account the increase in demands for uranium due to the expansion of nuclear power in countries such as China and India. In addition to increasing the exploration of new potential mining sites, attempts to meet the growing demand for uranium have involved exploring unconventional sources such as phosphate rocks, black shale, mill tailings, and coal ash. One unconventional source of uranium that could vastly increase the global inventory of uranium is the ocean, which contains 4.5 billion tons of uranium – nearly a thousand times more than the entire known terrestrial supply [2].

Although there is essentially a limitless supply of uranium in the ocean, several factors complicate the efforts to efficiently and economically extract uranium. Firstly, the uranium is present at an extremely low concentration ($3.3\ \mu g\ L^{-1}$) along with a number of other elements that can compete with uranium for an extractant (Table 1) [3]. Secondly, due to the overwhelmingly high concentrations of calcium, magnesium, and carbonate in seawater, uranium exists primarily in the forms of very stable tris(carbonato) species that include the $Ca_2[UO_2(CO_3)_3]^0(aq)$, $Ca[UO_2(CO_3)_3]^{2-}$, $Mg[UO_2(CO_3)_3]^{2-}$, and $UO_2(CO_3)_3^{4-}$ species [4]. Lastly, the pH and temperature of seawater can vary by location, ranging from pH 7.5–8.5 and 12–40 °C, respectively [5–7]. Therefore, it is evident that a suitable extraction technique must employ an extractant that can bind uranium very strongly and selectively at slightly alkaline pH and in a relatively wide range of temperatures.

Though many extraction techniques have been investigated over the past five decades, the most advanced technology is the use of polymeric sorbents, particularly those that have been functionalized with the amidoxime ($-C(NH_2)NOH$) moiety developed in the 1990s in Japan [8]. The efficacy of poly(acrylamidoxime) sorbents for the extraction of uranium was demonstrated by Japanese scientists in marine tests more than a decade ago, in which the uranium uptake was 1.5 g U/kg adsorbent after 30 days [8]. More recently, another series of marine tests using newly developed amidoxime-based sorbents were conducted in the United States, achieving 3.3 g U/kg adsorbent after 8 weeks [9]. Using the current technology, it is roughly estimated that the cost for implementing the amidoxime-based sorption system on a large scale would range from $610/kg U to $1000/kg U, still much higher than the cost of recovering uranium terrestrially (⩽$260/kg U) [1]. To further reduce the cost and make the extraction of uranium from seawater economically viable, research at both the fundamental and practical levels is underway with the objectives of improving the sorption efficiency, selectivity, and recyclability of the sorbents.

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Table 1
Concentrations of selected elements in seawater [12,13].

Element	Concentration ($\mu g\ L^{-1}$)
Na	1.08×10^7
Mg	1.290×10^6
Ca	411,000
U	3.3
Fe	3.4
V	1.6
Cu	0.9
Ni	6.6
Pb	0.03

The efficiency and selectivity of the amidoxime-based sorbents can be assessed by quantifying the binding strength of the amidoxime ligands with uranium and comparing these with the binding strengths with other major competing seawater cations. Recently, in an effort to provide a rigorous thermodynamic explanation for the high uptake of uranium by amidoxime-based sorbents, we have determined the thermodynamic stability constants for complexes of uranium with a series of amidoxime ligands that could represent the functional groups on the poly(acrylamidoxime) sorbents used for uranium collection from seawater. Among the ligands, a cyclic imidedioxime, glutarimidedioxime (Fig. 1, denoted as H_2A in this paper), was found to form strong complexes with uranium at seawater pH [10], and is expected to be responsible for the sorption of uranium from seawater. Building on this work, the thermodynamics of complexation of glutarimidedioxime with a number of other competing cations was studied [11]. Data indicated that the binding strength of glutarimidedioxime with the metal cations in seawater followed the order: $Fe^{3+} > UO_2^{2+} \sim Cu^{2+} > Pb^{2+} > Ni^{2+}$ [11]. The thermodynamic results have helped to predict and interpret the sorption behavior of these cations in the process using the poly(acrylamidoxime) sorbents.

It has been noticed that previous thermodynamic studies do not include the alkali and alkaline earth metals – most notably, Na^+, Ca^{2+}, and Mg^{2+} – that are present in seawater at the highest concentrations (Table 1). Though calcium and magnesium are expected to form weak complexes with glutarimidedioxime, they could still be sorbed on a significant fraction of the binding sites of the poly(acrylamidoxime) sorbents because of their exceedingly high concentrations relative to uranium in seawater. To evaluate the competition of calcium and magnesium with uranium for sorption, thermodynamic data including stability constants and enthalpies of complexation for the complexes of calcium and magnesium with glutarimidedioxime (H_2A) are needed. Therefore, the present work focused on the determination of thermodynamic parameters ($\log\beta$, ΔH, and ΔS) for the complexation of calcium and magnesium with glutarimidedioxime by potentiometric and calorimetric experiments. Using the thermodynamic data for calcium and magnesium in conjunction with the data for uranium and other cations from previous studies, the competition of all major cations in seawater (except Na) with uranium for sorption can be quantitatively evaluated. The interactions of glutarimidedioxime with Na, which are expected to be much weaker than those of Ca and Mg and could possibly be evaluated using specific ion interaction theory (SIT), are not the focus of this study.

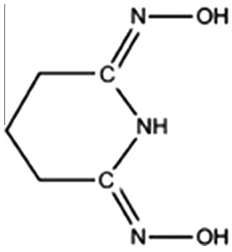

Fig. 1. Glutarimidedioxime (H_2A).

2. Experimental

2.1. Chemicals

Freshly boiled/cooled Millipore water was used to prepare all solutions. Glutarimidedioxime (H_2A) was synthesized according to previous procedures [10] and checked for purity by NMR and potentiometric titrations with a standard sodium hydroxide solution. Sodium chloride (J.T. Baker) was recrystallized from water and was used to adjust the total ionic strengths (I) of all solutions to 0.5 M. This ionic strength was selected because it is similar to the NaCl salinity in seawater. Stock solutions of sodium hydroxide were prepared from a 1.00 N volumetric solution (Metrohm) and standardized against potassium hydrogen phthalate (99.95–100.05%, Sigma Aldrich). Stock solutions of hydrochloric acid were prepared using a 1.00 N volumetric solution (Metrohm) and subsequently standardized against tris(hydroxymethyl)aminomethane (TRIS, 99.9995%, Fluka). Stock solutions of calcium chloride and magnesium chloride were prepared from 1.0 M $MgCl_2$ and 1.0 M $CaCl_2$ volumetric solutions (Fluka), respectively, and standardized against ethylenediaminetetraacetic acid (EDTA, 99.995%, Aldrich) at pH 10 using Eriochrome Black T as the indicator according to known methods [14].

2.2. Potentiometry

Potentiometric titrations were carried out using an automated titration system that consists of a thermostated glass cell, Metrohm model 713 pH meter, and a Metrohm model 765 Dosimat. The temperature was maintained at 25 ± 0.01 °C using a circulating water bath and the solutions were blanketed with a gentle stream of argon to minimize the ingress of CO_2. A Metrohm Unitrode pH electrode was used to measure the electrode potentials in the titrations. The electrode potentials can be described using Eqs. (1) and (2) for the acidic and basic regions, respectively:

$$E = E^0 + 2.303 \times (RT/F)\log[H^+] + \gamma_H[H^+] \quad (1)$$

$$E = E^0 + 2.303 \times (RT/F)\log(Q_w/[OH^-]) + \gamma_{OH}[OH^-] \quad (2)$$

where E^0 is the standard electrode potential, $Q_w = [H^+][OH^-]$, $2.303 \times RT/F = 59.16$ mV for the hydrogen ion at 25 °C, and the terms $\gamma_H[H^+]$ and $\gamma_{OH}[OH^-]$ are the electrode junction potential corrections in the acidic and basic regions, respectively. Prior to each protonation or complexation titration, the parameters Q_w, E^0, γ_H, and γ_{OH} were determined from the electrode potentials by titrating a standard HCl solution with a standard NaOH solution. These values were then used to convert the measured potentials in the subsequent titration to the concentrations of H^+ for data analysis.

Multiple titrations were performed to determine the protonation constants of glutarimidedioxime and the stability constants of its complexes with Ca^{2+} and Mg^{2+} at a constant ionic strength ($I = 0.5$ M NaCl). For a typical protonation titration, twenty milliliters of a glutarimidedioxime solution (0.01–0.02 M glutarimidedioxime and 0.06 M NaOH) were titrated with 0.0994 M HCl. For the complexation titrations, the stability constants for Ca^{2+} and Mg^{2+} complexes with glutarimidedioxime were determined from several titrations using different concentrations of the metal cation (C_M), ligand (C_A), and total protons (C_H). Usually a basic solution containing the metal cation (Ca or Mg) and glutarimidedioxime