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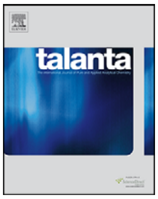

Kinetic study of uranium speciation in model solutions and in natural waters using Competitive Ligand Exchange Method

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ABSTRACT

Kinetic speciation of uranium in model solutions containing uranium and humic acid (HA) and in natural waters has been investigated by Competitive Ligand Exchange Method (CLEM). In alkaline freshwaters, most of uranium species were uranium–carbonate species, which were labile in the CLEM experiment. The uranium speciation of every sample was characterized either as “labile” or “non-labile” uranium complexes depending on the dissociation rate coefficients of the complexes. The results showed that as the U(VI)/HA ratio was decreased, the dissociation rate coefficients decreased and the labile fraction decreased as well. When the U(VI)/HA ratio was 0.1, the labile fraction of the U(VI)-HA increased with increasing pH; however, there was no pH effect on the dissociation of U(VI)-HA complexes at lower U(VI)/HA ratios. Chelex-100 had some limitations in its use for the study of dissociation of U(VI)-HA complex at very low U(VI)/HA ratios. By developing an analytical method and procedure for quantitative determination of kinetic parameters for the dissociation of uranium-HA complexes in model solutions and natural waters, this work has made a substantial contribution to analytical chemistry.

1. Introduction

Uranium is one of the heaviest naturally occurring elements on Earth. It has 16 known isotopes, all of which are radioactive. In nature, U consists of a mixture of three isotopes, ^{238}U (99.276%), ^{235}U (0.718%), and ^{234}U (0.0056%) [1]. The chemical toxicity of uranium in natural water systems depends not only on the total uranium concentration, but also on the chemical speciation of uranium [2]. Uranium exists as various chemical species in natural waters, including the free metal ions (UO_2^{2+}), and complexes with inorganic and organic ligands (both anion and cation) [3]. Humic substances (fulvic acid, humic acid, and humin), which represent typically 40–99% of dissolved organic carbon (DOC) [4], are important complexing agents for uranium in natural waters at neutral or low pH. Fulvic acid (FA) apparently reduces the bioavailability of U with increasing pH, by reducing the activity of UO_2^{2+} [5]. The binding of U(VI) by humic acid (HA) is stronger than that by fulvic acid and exhibits a larger pH-dependence [6]. Several kinetic studies of other metals complexation with humic substances have been done using Competitive Ligand Exchange Method (CLEM) [7–10]. However, published literature on the kinetics of uranium binding to the humic substances is relatively scarce. This work presents the results of our investigation of kinetics of uranium binding to humic acid, studied using CLEM combined with inductively coupled plasma mass spectrometry (ICP-MS).

2. Competitive Ligand Exchange Method

The kinetic model proposed by Olson and Shuman [11] was adapted to the study of speciation of uranium(VI) complexes as described below.

Consider a metal complex, ML_i, undergoes a first-order or pseudo-first-order dissociation, as follows:

$$ML_i \underset{k_{f,i}}{\overset{k_{d,i}}{\rightleftarrows}} M + L_i \quad \text{(slow)} \qquad (1)$$

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where M is a metal ion and L_i is a complexant such as $CO_3{}^{2-}$ or humic acid, $k_{\mathrm{d},i}$ and $k_{\mathrm{f},i}$ are the rate coefficients of dissociation and formation of ML_i, respectively. The charges have been omitted for simplicity.

Assuming that the metal reacts with a large excess of a competing ligand, Chelex-100 chelating resin, resulting in the formation of a strong M–Chelex complex:

$$\mathrm{M} + \mathrm{Chelex} \underset{k_{d,\mathrm{M\text{-}Chelex}}}{\overset{k_{f,\mathrm{M\text{-}Chelex}}}{\rightleftarrows}} \mathrm{M\text{-}Chelex} \quad (\mathrm{fast}) \tag{2}$$

where $k_{\mathrm{f,M-Chelex}}$ and $k_{\mathrm{d,M-Chelex}}$ are the rate coefficients of formation and dissociation of M–Chelex, respectively. Since the competing ligand has been added in large excess, the net reaction, Eq. (3), lies far to the right, and is considered as pseudo-first-order and irreversible

$$\mathrm{ML}_i + \mathrm{Chelex} \rightarrow \mathrm{M\text{-}Chelex} + \mathrm{L}_i \tag{3}$$

The concentration of ML_i can be described by a pseudo-first-order rate law.

$$-\frac{\mathrm{d}c_{\mathrm{ML}_i}}{\mathrm{d}t} = k_{\mathrm{d},i}c_{\mathrm{ML}_i} \tag{4}$$

Integrating Eq. (4) and get Eq. (5):

$$c_{\mathrm{ML}_i}(t) = c^0_{\mathrm{ML}_i}exp(-k_{\mathrm{d},i}t) \tag{5}$$

where $c^0_{\mathrm{ML}_i}$ is the initial concentration of the ML_i complex and $c\mathrm{ML}_i(t)$ is the concentration of the ML_i complex at any time, t, $k_{\mathrm{d},i}$ is dissociation rate coefficient of ML_i.

Since it has been assumed that the ML_i complexes dissociate simultaneously and independently, the total concentration of metal c_{M} remaining in the solution, at any time, t, is shown by Eq. (6)

$$c_{\mathrm{M}}(t) = \sum_{i=1}^{n} c^0_{\mathrm{ML}_i}exp(-k_{\mathrm{d},i}t) \tag{6}$$

In M-HA system, Eq. (6) can be simplified as consisting of two components: fast (labile) and slow (non-labile) component, and re-written as Eq. (7)

$$c_{\mathrm{M}}k(t) = c_1\exp(-k_{\mathrm{d}1}t) + c_2\exp(-k_{\mathrm{d}2}t) \tag{7}$$

where c_1 and c_2 are the initial concentrations of the fast and the slow component and $k_{\mathrm{d}1}$ and $k_{\mathrm{d}2}$ are the dissociation coefficients of these components, respectively. The percentage of the total metal remaining in the solution, $C_{\mathrm{M}}(t) = c_{\mathrm{M}}(t)/c_{\mathrm{M}}(0) \times 100\%$, at any time t, was used in this work to avoid the bias error. Eq. (7) can be re-written as:

$$C_{\mathrm{M}}(t) = C_1\exp(-k_{\mathrm{d}1}t) + C_2\exp(-k_{\mathrm{d}2}t) \tag{8}$$

where C_1 and C_2 are the percentage of the fast and the slow component, respectively, in the initial solution; $C_1 = c_1/c_{\mathrm{M}}(0) \times 100\%$ and $C_2 = c_2/c_{\mathrm{M}}(0) \times 100\%$.

3. Experimental

3.1. Reagents

Chelex-100 chelating resin (Bio-Rad 100–200 mesh) was conditioned for the work by soaking Chelex-100 resin sequentially in methanol, 1 mol/L HCl, 3 mol/L NH_4OH and 0.1 mol/L HCl [12]. The ICP-MS/AES uranium standard solution (SCP SCIENCE, 1000 mg/L) was used to prepare uranium model solutions in ultra pure water of resistivity of 18.2 MΩ cm, obtained direct from a Milli-Q Academic (Millipore, USA) ultrapure water system. Nitric acid (Optima, Fisher Scientific) and sodium hydroxide (Caledon Laboratories Ltd.) were used to adjust the pH. Ammonium acetate (BDH Inc.) was used to prepare 0.01 mol/L ammonium acetate solutions.

Humic acid was supplied by Dr. Les Evans (University of Guelph, Guelph, Ontario), who characterized and purified the HA according to the procedure recommended by the International Humic Substances Society. The bidentate complexing capacity of HA was calculated to be 4.88 mmol/g [13]. A stock solution of 1.0 g/L HA was prepared by dissolving approximately 1.0 g HA in sodium hydroxide, and the solution was made up to 1 L of ultrapure water. The solution was stored in the dark at 4 °C.

3.2. Model solutions, the synthetic lake water sample, and the natural water sample

A series of model solution was prepared by spiking known amounts of uranium standard solution into the HA solutions to make the concentration ratio of U(VI)/HA 0.1, 0.01 and 0.001. The total uranium concentration in these solutions was fixed at 20 μg/L (8.4×10^{-8} mol/L), whereas the HA concentration was varied: 0.2, 2.0 and 20 mg/L. The above concentration range corresponded to the range found in natural waters. Ammonium acetate was added to those model solutions as pH buffer (final concentration 0.01 mol/L). The mole/mass ratio of U(VI)/HA in the above three solutions was 0.42, 0.042 and 0.0042 mmol/g. The pH of these model solutions was adjusted to 6.0, 7.0 or 8.0, using aqueous solutions of NaOH and HNO_3. The model solutions were then equilibrated for 48 h in the dark at room temperature.

Samples of natural waters (surface waters) were collected from St. Lawrence River at Morrisburg (Ontario, Canada), using 2.2 L Teflon bottles. Major cations and anions were quantitatively determined by using atomic emission spectrometry (AES) and ion-exchange chromatography (IEC), respectively. Total dissolved organic carbon and inorganic carbon were determined using TOC Analyzer (Shimadzu TOV-V_{CPH}). The synthetic lake water sample simulating the natural lake water was prepared in our laboratory by adding inorganic chemicals and humic acid to ultrapure water of resistivity 18 MΩ cm.

300 mL of the test sample of above solutions was stirred with a Teflon-coated magnetic stirring bar in a Teflon reactor. About 3 g Chelex 100 resin (1 g/100 mL), which had been soaked in 0.01 mol/L ammonium acetate buffer at the same pH as that of the test sample solution, was added to the test sample. The test sample was filtered with a 8 μm polycarbonate membrane filter (Whatman), which was placed at the end of the reactor tube to filter out the Chelex 100 resin before introducing the filtrate into Elan 6100 DRC ICP-MS (PerkinElmer SCIEX). The total experimental time was 1–2 h.

4. Results and discussion

The U(VI)-HA systems were very complex, even in a simple model solution. The complexation kinetics of U(VI)-HA could be influenced by many factors, such as the deprotonation of HA at different pH, the hydrolysis of uranyl ion and the formation of uranyl complexes. The experimental data were analyzed using Marquardt–Levenberg algorithm, an advanced non-linear regression algorithm. All the data were fitted using one, two or three distinct components to find the best-fitting curve, using SigmaPlot 10 computer program (Systat Software Inc.).

The kinetic curves and kinetically distinguishable components are presented in Figs. 1–3 and Tables 1–3. The error bars in the figures represent standard deviation of the average of three measurements. In the kinetic curves, the initial steep part represents the fast component, which is the labile fraction (C_1), whereas the plateau part is the slow component or non-labile fraction