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Thermodynamic studies of U(VI) complexation with glutardiamidoxime for sequestration of uranium from seawater†

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Glutardiamidoxime (H_2B), a diamidoxime ligand that has implications in sequestering uranium from seawater, forms strong complexes with UO_2^{2+}. Five U(VI) complexes were identified in 3% NaCl solution. The stability constants and the enthalpies of complexation were measured by potentiometry and microcalorimetry. The competition between glutardiamidoxime and carbonate for complexing U(VI) in 3% NaCl was also studied in comparison with the cyclic glutarimidedioxime ligand (H_2A) previously studied.

Introduction

The ocean is an important source of uranium because it contains about 4.5 billion tons of uranium, a thousand times as much as the amount of uranium in terrestrial ores.[1,2] However, it is extremely difficult to extract uranium from seawater, because uranium compounds exist in extremely low concentrations as very stable carbonate complexes,[2] and because the ocean also contains many other metal ions (Na, K, Ca, Mg, Al, and transition metals), some of which are in overwhelmingly higher concentrations. To make the extraction process economically competitive, the extracting agents must be highly efficient and selective, robust and inexpensive.[3]

Screening studies in 1980s showed that, among more than 200 functionalized adsorbents, the materials with the amidoxime group, $RC(NH_2)(NOH)$, were highly selective towards uranium.[4,5] Based on these studies, a radiation-induced grafting process was developed in Japan to functionalize a nonwoven polyethylene fabric with amidoxime groups. In this process, the irradiated polyethylene fabric was grafted with acrylonitrile ($CH_2{=}CHCN$) and then reacted with hydroxylamine (NH_2OH), resulting in the sorbents functionalized with amidoxime (or related moieties) that could form strong complex(es) with uranium under seawater conditions. The sorbent materials were used in the marine tests in 1999–2001, and about 1 kg uranium was collected.[6–8]

Though the amidoxime-fuctionalized materials have been shown to be capable of extracting uranium from seawater,[4–8] the configurations of the functional groups on the materials were not identified and the coordination modes in the complexes with uranium are not well understood. Based on the knowledge of the reaction between acrylonitrile and hydroxylamine, we have hypothesized that at least two configurations, a cyclic imide dioxime and an open-chain diamidoxime, could form if the conditions of the grafting process were not well-controlled, and that the yields of the two configurations would affect the efficiency of the sorbents because the cyclic imide dioxime and the open-chain diamidoxime may have different binding strengths towards uranium. Quantification and comparison of the binding strengths of the cyclic imide dioxime and the open-chain diamidoxime towards uranium could help to optimize the grafting process and improve the efficiency of the extraction of uranium.

To quantify and compare the binding strengths of different functional groups towards uranium, two small molecular ligands, glutarimidedioxime (H_2A) and glutardiamidoxime (H_2B), were synthesized and used as the water-soluble surrogates of the cyclic imide dioxime and the open-chain diamidoxime on the sorbent (Scheme 1). The results for the cyclic ligand (H_2A) have been summarized in a recent publication from this group.[9] The present study is focused on the complexation of uranium with the diamidoxime ligand (H_2B) in comparison with H_2A. Conditions for synthesizing the ligands were optimized to obtain high yields of each. The binding strength with UO_2^{2+} and the enthalpy of complexation were investigated by potentiometry, spectrophotometry and microcalorimetry. The most probable coordination modes in the uranyl/H_2B complexes were discussed based on the

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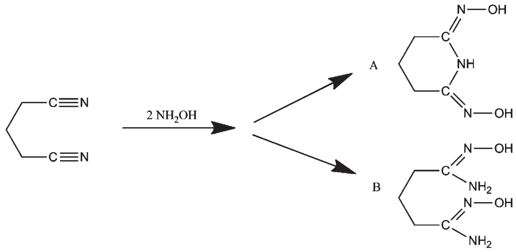

Scheme 1 Preparation routes for glutarimidedioxime (H_2A, upper) and glutardiamidoxime (H_2B, lower).

thermodynamic data and the crystal structures of related complexes. Besides, spectrophotometric experiments were conducted to evaluate the ability of glutardiamidoxime to compete with carbonate for binding UO_2^{2+} under seawater conditions.

Experimental

Chemicals

All experiments were conducted at 25 °C and an ionic strength of 0.5 M (NaCl), close to the seawater condition of 3% NaCl. Hydroxylamine (50 wt% solution in water) and glutaronitrile (99%) from Sigma-Aldrich were used as received. Boiled/cooled Milli-Q water was used in preparation of all solutions. The stock solution of U(VI) was prepared by dissolving UO_3 in HCl and standardized by fluorimetry[10] using standard solutions of U(VI) in 1 M H_3PO_4. The concentration of free H^+ in the U(VI) stock solution was determined by the Gran titration.[11]

The same procedure[12–14] that was used to prepare the cyclic glutarimidedioxime (H_2A)[9] was used to prepare the open chain glutarimidedioxime (H_2B), except that the reactions were conducted at different temperatures (Scheme 1). Using the same starting materials at the molar ratio of 1 : 2 (glutaronitrile and hydroxylamine), the cyclic glutarimidedioxime (H_2A) was obtained at 80–90 °C[9] while the open chain glutardiamidoxime (H_2B) was obtained at room temperature. To obtain H_2B in high yields, 9.4 g glutaronitrile (99%) and 14.5 g hydroxylamine (50% in H_2O) were dissolved in 200 mL of 1/1 (V/V) ethanol/water and reacted at room temperature with stirring for 5 days, resulting in H_2B as colorless crystals with >90% yield.

Ligand H_2B was characterized by ^{1}H-NMR (pyridine-d_5): $-CH_2-C\boldsymbol{H}_2-CH_2-$, 2.19 ppm, 2H; $-CH_2-C\boldsymbol{H}_2-C(NOH)NH_2$, 2.51 ppm, 4H; $-C(NOH)N\boldsymbol{H}_2$, 5.98 ppm, 4H; $-CH_2-C(NH_2)-NO\boldsymbol{H}$, 10.97 ppm, 2H. The purity was determined to be >99.5% with potentiometry by titrating the H_2B solution with standard NaOH. The crystal structure of $H_2B\cdot H_2O$ was also obtained (see ESI†).

Potentiometry

The procedures for potentiometric titrations have been described elsewhere.[9] Multiple titrations were conducted with solutions of different concentrations of U(VI) (C_U as total [U(VI)]), ligand (C_B as the total ligand concentration including H_4B^{2+}, H_3B^+, H_2B, HB^-, and B^{2-}), and acidity (C_H for the total hydrogen ion, where $-C_H = C_{OH}$). For determining the protonation constant of the ligand, 20 mL of the ligand solution (C_B = 0.01 to 0.02 M; C_H = (−0.02) to (−0.04) M) was titrated with 1.0 M HCl. 50–100 data points were collected in each titration. For determining the stability constants of the U(VI) complexes, 20 mL of U(VI)/H_2B solutions (C_U = 0.20–0.50 mM; C_H = 2.0–4.0 mM: C_B = 1.0–2.0 mM) were titrated with 0.100 M NaOH. About 40–50 data points were collected for each titration. A nonlinear regression program Hyperquad 2008[15] was used to calculate the protonation constants of the ligand and the stability constants of U(VI) complexes.

Spectrophotometry

Two types of spectrophotometric titrations were performed using a Cary 6000i spectrophotometer (Varian Inc.) from 500 to 200 nm with an interval of 1.0 nm: (1) addition of a buffered ligand solution to the U(VI) solution; (2) addition of HCl to the solution containing both U(VI) and the ligand. Usually, 15–20 additions were made in each titration, generating a set of 16–21 spectra for calculation.

Microcalorimetry

An isothermal microcalorimeter (Model: ITC 4200, Calorimetry Sciences Corp.) was used to determine the enthalpy of the reactions. The calorimeter was calibrated with the same procedures in the literature.[16] Multiple titrations with different concentrations of U(VI), ligand and acidity were performed to reduce the uncertainty of the results. For the protonation of the ligand, 0.9 mL solution containing the ligand was placed in the reaction cell and titrated with 0.1 M HCl. For the complexation of U(VI) with the ligand, 0.9 mL solution containing U(VI), the ligand and H^+ was titrated with a solution of NaOH. A titration usually contains 40–50 additions (0.005 mL each) of the titrant to the reaction vessel. The observed total heat ($Q_{ex,j}$, j = 1 to n, n = 40–50) values were corrected for the heats of titrant dilution ($Q_{dil,j}$) that were measured in a separate run. The net reaction heat at the jth point ($Q_{r,j}$) was obtained from the difference: $Q_{r,j} = Q_{ex,j} - Q_{dil,j}$. The value of $Q_{r,j}$ is a function of the concentrations of the reactants (C_U, C_B, and C_H), the equilibrium constants, and the enthalpies of the reactions that occurred in the titration. The computer program HypDeltaH[17] was used to calculate the enthalpy of ligand protonation and complexation with U(VI). In the calculation, the protonation constants and the stability constants of U(VI) complexes obtained by potentiometry were used.

Results and discussion

Protonation of glutardiamidoxime

A typical potentiometric titration for the protonation of glutardiamidoxime (H_2B) is shown in Fig. 1. Differing from the protonation titration curve for the ligand H_2A system where three steps of protonation are involved,[9] the titration curve in Fig. 1 can be fitted with four steps of protonation, from B^{2-}, through

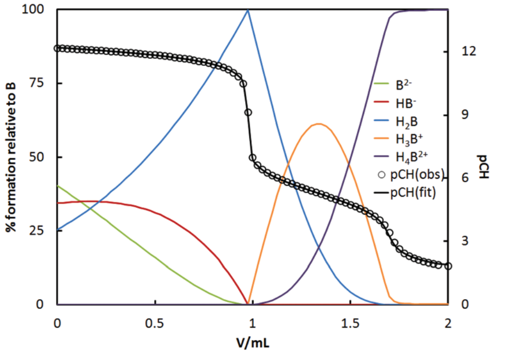

Fig. 1 Protonation titration of glutardiamidoxime in 3% NaCl. V^0 = 20 mL, $C_B{}^0$ = 0.0181 M, $C_H{}^0$ = −0.0127 M. Titrant: 1 M HCl.

HB^-, H_2B, H_3B^+, to H_4B^{2+}. The calculated protonation constants are listed in Table 1. It is interesting to compare the stepwise protonation constants of the two ligands (H_2B and H_2A). For H_2B, the first protonation constant ($10^{12.13}$) is typical for the oxime group (–NOH)[18,19] and the second protonation constant ($10^{12.06}$) is essentially the same as the first one, indicating that the two oxime groups in H_2B are independent and the protonation or deprotonation of one group has little effect on the basicity of the other group. In contrast, the protonation constants of the two oxime groups in H_2A are $10^{12.06}$ and $10^{10.7}$, respectively, suggesting that the protonation of one oxime group reduces the basicity of the other oxime group.[9] In addition, the third and fourth stepwise protonation constants of H_2B ($10^{5.8}$ and $10^{4.8}$ for the amide nitrogen) are significantly higher than that for the imide nitrogen of H_2A ($10^{2.1}$).[9] Obviously, the basicity of the amide nitrogen in H_2B is much higher than that of the imide nitrogen in H_2A.

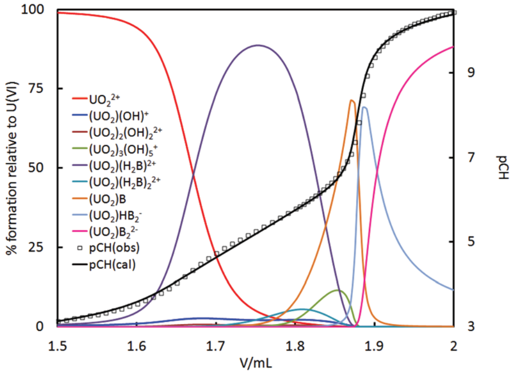

Fig. 2 Potentiometric titration for the complexation of H_2B with U(VI) in 3% NaCl. V^0 = 20 mL, $C_U{}^0$ = 0.0553 mM, $C_B{}^0$ = 0.535 mM, $C_H{}^0$ = 0.011 mM. Titrant: 0.106 M NaOH.

Complexation of U(VI) with glutardiamidoxime

Stability constants. A representative potentiometric titration of the complexation of U(VI) with glutardiamidoxime is shown in Fig. 2. The data were best fitted with the model including the formation of five U(VI) complexes, UO_2B, $UO_2H_2B^{2+}$, $UO_2B_2{}^{2-}$, $UO_2HB_2{}^-$ and $UO_2H_4B_2{}^{2+}$, shown by eqn (1):

$$UO_2{}^{2+} + mH^+ + nB^{2-} = UO_2H_mB_n{}^{(2n-m-2)-} \tag{1}$$

where (m,n) = (0,1), (2,1), (0,2), (1,2) and (4,2). Table 1 shows the calculated stability constants for the five complexes.

The complexation of U(VI) with glutardiamidoxime was also studied with spectrophotometric experiments. The spectra of the ligand under different conditions are compared in Fig. 3a. Spectra 1, 2 and 3 represent three solutions of 0.1 mM glutardiamidoxime in the absence of U(VI) at different acidities. Based on the protonation constants of H_2B (Table 1), the major species in the three solutions are H_4B^{2+}, H_2B, and B^{2-}, respectively. Obviously, the absorption spectra of the ligand species with various degrees of protonation differ from each other, but all their absorption bands are in the wavelengths below 300 nm. In the presence of 0.05 mM U(VI) (spectra 4 in Fig. 3a), two new bands associated with the complexation with U(VI) appear at about 300 nm and 350 nm.

Table 1 Thermodynamic parameters of the protonation and complexation of glutardiamidoxime at 25 °C and 0.5 M ionic strength (NaCl)

Ligand	Reaction	log β	ΔH (kJ mol^{-1})	ΔS (J K^{-1} mol^{-1})
Glutardiamidoxime (H_2B)	$H^+ + B^{2-} = HB^-$	12.13 ± 0.12	−52 ± 2	58 ± 7
	$2H^+ + B^{2-} = H_2B$	24.19 ± 0.07	−103 ± 3	117 ± 10
	$3H^+ + B^{2-} = H_3B^+$	29.98 ± 0.07	−124 ± 6	158 ± 20
	$4H^+ + B^{2-} = H_4B^{2+}$	34.77 ± 0.07	−151 ± 8	159 ± 26
	$UO_2{}^{2+} + B^{2-} = UO_2B$	17.3 ± 0.3	−49 ± 6	167 ± 19
	$2H^+ + UO_2{}^{2+} + B^{2-} = UO_2(H_2B)^{2+}$	29.2 ± 0.3	−102 ± 6	217 ± 21
	$UO_2{}^{2+} + 2B^{2-} = UO_2B_2{}^{2-}$	26.1 ± 0.3	−123 ± 7	88 ± 23
	$H^+ + UO_2{}^{2+} + 2B^{2-} = UO_2(HB)B^-$	36.4 ± 0.3	−133 ± 8	251 ± 27
	$4H^+ + UO_2{}^{2+} + 2B^{2-} = UO_2(H_2B)_2{}^{2+}$	56.3 ± 1.0	−207 ± 16	384 ± 51
Glutarimidedioxime (H_2A)[a]	$H^+ + A^{2-} = HA^-$	12.06 ± 0.23	−36.1 ± 0.5	110 ± 2
	$2H^+ + A^{2-} = H_2A$	22.76 ± 0.31	−69.7 ± 0.9	202 ± 3
	$3H^+ + A^{2-} = H_3A^+$	24.88 ± 0.35	−77 ± 6	218 ± 14
	$UO_2{}^{2+} + A^{2-} = UO_2A$	17.8 ± 1.1	−59 ± 8	142 ± 19
	$H^+ + UO_2{}^{2+} + A^{2-} = UO_2(HA)^+$	22.7 ± 1.3	−71 ± 6	197 ± 14
	$UO_2{}^{2+} + 2A^{2-} = UO_2A_2{}^{2-}$	27.5 ± 2.3	−101 ± 10	188 ± 24
	$H^+ + UO_2{}^{2+} + 2A^{2-} = UO_2(HA)A^-$	36.8 ± 2.1	−118 ± 6	309 ± 14
	$2H^+ + UO_2{}^{2+} + 2A^{2-} = UO_2(HA)_2$	43.0 ± 1.1	−154 ± 25	307 ± 59

[a] Data from ref. 9.

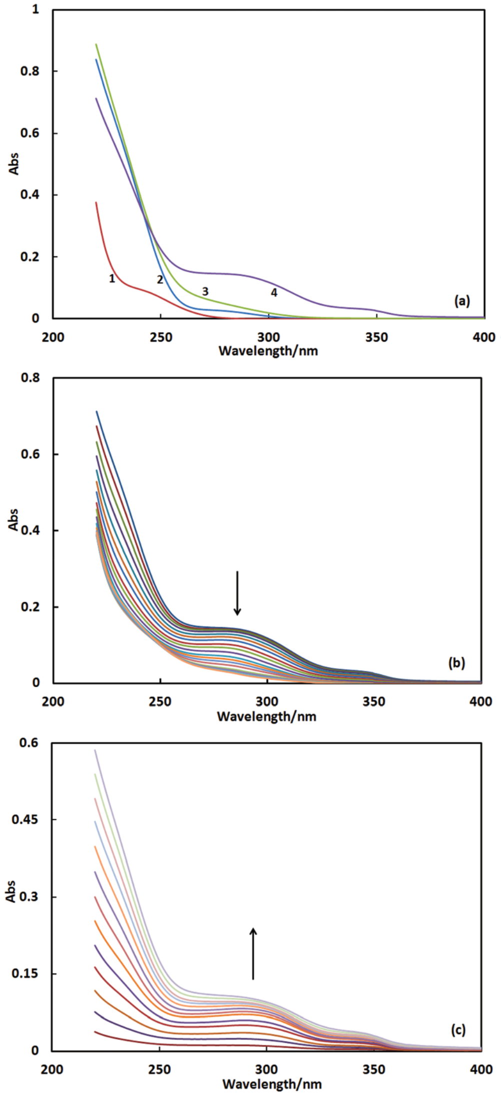

Fig. 3 Spectrophotometry for the complexation of U(VI) with H_2B in 3% NaCl. (a) 1 - 0.1 mM Na_2B/0.01 M HCl; 2 - 0.1 mM H_2B; 3 - 0.1 mM Na_2B/0.01 M NaOH; 4 - 0.1 mM Na_2B/0.05 mM U(VI). (b) V^0 = 2 mL, $C_U{}^0$ = 0.05 mM, $C_H{}^0$ = 0 mM, $C_B{}^0$ = 1 mM; titrant: 0.01 M HCl (V_{added} = 1.505 mL). (c) V^0 = 2 mL, $C_U{}^0$ = 0.025 mM, $C_H{}^0$ = 0.027 mM; titrant: 1 mM Na_2B (V_{added} = 0.13 mL). Spectra in (b) and (c) are normalized to the initial volume.

Fig. 3b shows a spectrophotometric titration in which a solution of U(VI) and neutralized H_2B was titrated with HCl. Initially, the two absorption bands at 300 nm and 350 nm were observed, showing the presence of U(VI)/H_2B complexes in the beginning of the titration. As the acid was added, the intensity of the two bands decreased, indicating the dissociation of the U(VI)/H_2B complexes due to the competition of H^+ with U(VI) for the ligand. In addition, the intensity of the bands at shorter wavelengths (<300 nm) also decreases as the acidity was increased, suggesting a higher degree of protonation of the ligand along the titration. The last spectra in the titration (Fig. 3b) were very similar to spectra 1 shown in Fig. 3a, corresponding to the solution of 0.1 mM Na_2B/0.01 M HCl with H_4B^{2+} as the major ligand species.

Fig. 3c shows a spectrophotometric titration in which a solution of U(VI) was titrated with Na_2B. The molar ratio of the ligand to uranium (C_B/C_U) was increased from 0 to 2.6 in the titration. The spectra changes can be discussed in two different phases: (1) In the early part of the titration, as shown by the first 6 spectra where C_B/C_U = 0–2, the two absorption bands at 300 nm and 350 nm appeared and became more intense, indicating the formation of the U(VI)/H_2B complexes. In the meantime, the absorption bands at shorter wavelengths were intensified because the concentration of the uncomplexed ligand was also increased along the titration. (2) In the late part of the titration where C_B/C_U > 2, as more ligands were added, the intensities of the 300 and 350 nm bands increased only slightly while the intensities of the bands at shorter wavelengths continued to increase significantly. The observation suggested that, under the experimental conditions, the 1 : 2 metal/ligand complexes were the limiting species of the U(VI)/H_2B complexes and the complexes were considerably strong. At C_B/C_U = 2, most of U(VI) was complexed with the ligand. Further additions of Na_2B only slightly increased the amounts of U(VI)/H_2B complexes, but significantly elevated the concentration of the free ligand. As a result, the spectra in the late part of the titration were nearly unchanged at 300–350 nm, but significantly intensified at shorter wavelengths.

Efforts were made to calculate the stability constants of U(VI)/H_2B complexes or validate the stability constants obtained by potentiometry with the spectrophotometric data, but were unsuccessful. The reason for the failure probably lies in the fact that we were monitoring the absorption spectra of the ligand. The absorption spectra of the ligand in different U(VI) complexes, including $UO_2H_4B_2{}^{2+}$, $UO_2H_2B^{2+}$, UO_2B, $UO_2HB_2{}^-$ and $UO_2B_2{}^{2-}$, could be too similar to be distinguished from each other.

Enthalpy of complexation. A representative calorimetric titration of U(VI) complexation with glutardiamidoxime is shown in Fig. 4. The enthalpies, calculated from the calorimetric data, and the entropies of complexation calculated accordingly are summarized in Table 1.

Coordination modes in the complexes. Attempts to prepare crystals of the U(VI)/H_2B complexes of good quality have not been successful. The following discussions on the probable coordination modes are based on the reported crystal structures of U(VI) complexes with other amidoxime-related ligands and the thermodynamic parameters of the complexation (Table 1). The thermodynamic parameters help to form hypothesis on where the protonation occurs in the complexes and what the most probable coordination modes are.

Single-crystal structures[9,20–22] and computations[21] have shown that amidoxime-related ligands could bind $UO_2{}^{2+}$ with three coordination modes: monodentate coordination with the oxygen of the oxime group without the participation of the amide group in bonding,[20] η^2 coordination with the N–O bond,[21,22] and multi-dentate coordination with the oxygen of the oxime group and the nitrogen of the imide group.[9] The first two coordination modes were observed in the complexes

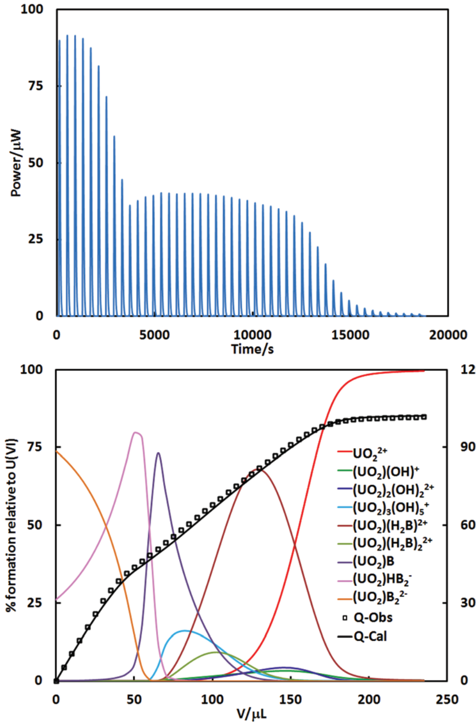

Fig. 4 Calorimetric titration of the complexation of U(VI) with H_2B in 3% NaCl at 25 °C. V^0 = 0.9 mL, $C_U{}^0$ = 0.246 mM, $C_B{}^0$ = 0.97 mM, $C_H{}^0$ = 0.257 mM; titrant: 0.01 M HCl (5.0 μL per addition). (upper) thermogram; (lower) total heat (right *y* axis) and speciation of U(VI) (left *y* axis) *vs.* the titrant volume.

that crystallized from non-aqueous solutions such as nitromethane,[20] mixtures of methanol/nitromethane[21] or a hydrophobic ionic liquid.[22] The third coordination mode was observed in the complexes that crystallized from aqueous solutions.[9] In either the monodentate mode[20] or the multidentate mode,[9] an intra-molecular proton transfer occurs within the oxime group (–NOH) from the oxygen to the nitrogen in the absence of a strong base in the solution.[9,20]

In the UO_2B and $UO_2B_2{}^{2-}$ complexes, the ligand is fully deprotonated. The most probable coordination modes for these two complexes in aqueous solutions are shown in Fig. 5a and 5c, where the deprotonation occurs on the two oxime groups. The stability constants of UO_2B ($10^{17.3}$) and $UO_2B_2{}^{2-}$ ($10^{26.1}$) are very reasonable values for successive 1 : 1 and 1 : 2 (metal/ligand) complexes (Table 1).

The stability constant of the protonated $UO_2H_2B^{2+}$ complex is $10^{29.2}$ (Table 1). Combining this with the stability constant of UO_2B ($10^{17.3}$), we can estimate the equilibrium constant for the "double" protonation of UO_2B (eqn (2)) to be $10^{11.9}$, a reasonable value for the two-step protonation of the nitrogen atom in the oxime group.

$$2H^+ + UO_2B = UO_2(H_2B)^{2+} \tag{2}$$

Based on this analysis and the observed intra-molecular proton transfer from the oxygen to the nitrogen within the oxime group (–NOH) in crystal structures,[9,20] we hypothesize

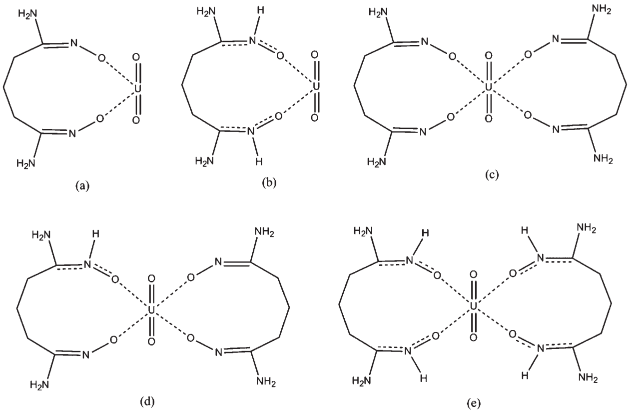

Fig. 5 Hypothesized coordination modes. (a) UO_2B, (b) $UO_2(H_2B)^{2+}$, (c) $UO_2B_2{}^{2-}$, (d) $UO_2HB_2{}^-$, (e) $UO_2H_4B_2{}^{2+}$.

that the probable coordination mode in $UO_2(H_2B)^{2+}$ is as shown in Fig. 5b.

Following the same analysis of the thermodynamic parameters, the equilibrium constants of the following protonation reactions could be estimated to be $10^{9.7}$ and $10^{30.2}$ for eqn (3) and (4), respectively.

$$H^+ + UO_2B_2{}^{2-} = UO_2HB_2{}^- \tag{3}$$

$$4H^+ + UO_2B_2{}^{2-} = UO_2H_4B_2{}^{2+} \tag{4}$$

Again, these protonation constants are not unreasonable for the protonation of the nitrogen of the oxime group. Therefore, the probable coordination modes in $UO_2HB_2{}^-$ and $UO_2H_4B_2{}^{2+}$ could be hypothesized as shown in Fig. 5d and 5e. Future efforts will be made to identify the structures so that the above hypothesis can be validated or disputed.

It should be pointed out that η^2 coordination[21,22] could also occur in these complexes, especially if the complexes form in non-aqueous media. However, the structures obtained in non-aqueous media, though highly informative, are less relevant to the issue of U(VI) complexation in seawater.

The ability of glutardiamidoxime to compete with carbonate for the sequestration of U(VI) under seawater conditions

The predominant species of uranium is the stable tricarbonato U(VI) complex, $UO_2(CO_3)_3{}^{4-}$, under the seawater conditions (pH ~ 8.3, 2.3 mM total carbonate). As a result, an effective sequestering agent must be able to compete with carbonate for complexing U(VI) at seawater pH. Using the stability constants of U(VI) complexes with glutardiamidoxime from this work and with carbonate from the literature,[23] the speciation of U(VI) under seawater conditions (C_U = 3.3 ppb, $C_{\text{carbonate}}$ = 0.0023 M) is calculated and shown in Fig. 6. The speciation was calculated at two ligand concentrations: C_B = 0.001 M and 0.01 M.

In the presence of 0.001 M glutardiamidoxime (Fig. 6, upper), nearly all U(VI) is complexed by carbonate at pH 8.3 (98.6% $UO_2(CO_3)_3{}^{4-}$ and 1.1% $UO_2(CO_3)_2{}^{2-}$). Only when pH is above 11, glutardiamidoxime starts to be competitive for complexing uranium. In the presence of 0.01 M glutardiamidoxime (Fig. 6,

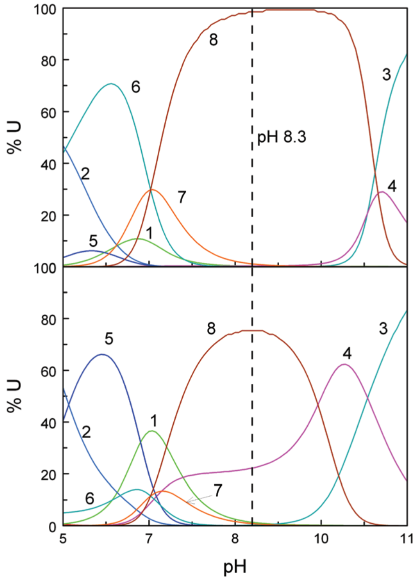

Fig. 6 Speciation of U(VI). C_U = 3.3 ppb, $C_{carbonate}$ = 0.0023 M, C_B = 0.001 M (upper) and 0.01 M (lower). 1 – UO_2B, 2 – $UO_2H_2B^{2+}$, 3 – $UO_2B_2^{2-}$, 4 – $UO_2HB_2^{-}$, 5 – $UO_2H_4B_2^{2+}$, 6 – $UO_2(CO_3)$, 7 – $UO_2(CO_3)_2^{2-}$, 8 – $UO_2(CO_3)_3^{4-}$.

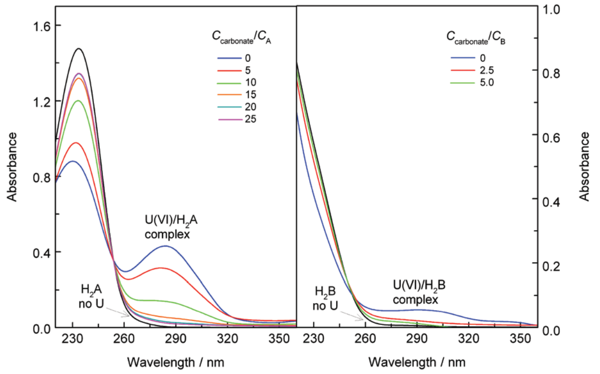

Fig. 7 Absorption spectra showing the competition of H_2A (left) and H_2B (right) with carbonate for complexing uranium. C_U = 0.05 mM. (left) C_A = 0.10 mM, $C_{carbonate}/C_B$ = 0–25; (right) C_B = 0.10 mM, $C_{carbonate}/C_B$ = 0–5. Data for the left figure are from ref. 9.

lower), about 77% U(VI) is still complexed by carbonate at pH 8.3 (76% $UO_2(CO_3)_3^{4-}$ and 1% $UO_2(CO_3)_2^{2-}$). Only about 22% U(VI) is complexed by glutardiamidoxime in the form of $UO_2HB_2^{-}$.

In contrast, a previous study[9] on the related ligand, glutarimidedioxime (H_2A), indicates that, even in the presence of the lower concentration (0.001 M H_2A), U(VI) is dominantly complexed by the glutarimidedioxime (>80%) and only minor amounts of U(VI) are in the carbonato complexes at pH 8.3. This means that, though glutardiamidoxime (H_2B) and glutarimidedioxime (H_2A) form U(VI) complexes with comparable strength (Table 1), the former (H_2B) is a much weaker competing ligand with carbonate than the latter (H_2A) for complexing U(VI) at seawater pH. The reason for the weaker competing ability of H_2B with carbonate at pH 8.3 lies in the fact that H_2B has higher tendency for protonation (higher overall pK_a values) than H_2A. At pH higher than 8.3 when more H_2B is deprotonated, the ability of H_2B to compete with carbonate for complexing U(VI) is expected to be stronger. In fact, the speciation diagrams in Fig. 6 show that nearly 100% U(VI) would be complexed by H_2B at pH 11 when C_B = 0.001 M, and at pH 10.5 when C_B = 0.01 M.

The competition between glutardiamidoxime (H_2B) and carbonate can be further illustrated by the optical absorption spectra of U(VI) in the presence of glutardiamidoxime (H_2B) and carbonate (Fig. 7, right). The spectra showing the competition between glutarimidedioxime (H_2A) and carbonate from a previous study[9] are also shown in Fig. 7 (left) for comparison. At the same concentration of the ligands ($C_A = C_B$ = 0.1 mM), the left figure shows that, when the ratio of $C_{carbonate}/C_A$ is as high as 10, the intensity of the band for the U(VI)/H_2A complexes (~290 nm) is still significant. In contrast, the right figure shows that the bands for the U(VI)/H_2B complexes (~300 nm and 350 nm) are barely identifiable when the ratio of $C_{carbonate}/C_B$ is as low as 2.5. Obviously, glutardiamidoxime (H_2B) is a much weaker competing ligand with carbonate for complexing U(VI) than glutarimidedioxime (H_2A) under these conditions.

Summary

Glutardiamidoxime (H_2B) was synthesized and studied as the small water-soluble molecular surrogate for the amidoxime-based sorbents that have been used for the sequestration of uranium from seawater. Glutardiamidoxime (H_2B) forms fairly strong complexes with U(VI), but it cannot effectively compete with carbonate for complexing U(VI) under seawater pH. In contrast, glutarimidedioxime (H_2A), a previously studied cyclic ligand related to glutardiamidoxime (H_2B), was shown to be a strong complexing ligand that can effectively compete with carbonate for U(VI) under seawater pH. On the basis of these findings, we plan to conduct further studies on the thermodynamics of the complexation of H_2A and H_2B with transition metals (Fe, Cu, Pb, Ni, V) to evaluate the competition between U(VI) and transition metals.

In the amidoxime-based sorbents that are prepared by the current radiation-induced grafting/reaction process, various configurations of the functional groups could exist, including those represented by the cyclic glutarimidedioxime (H_2A) and "open" glutardiamidoxime (H_2B). Combining the data from the present and previous work,[9] we have demonstrated that the cyclic glutarimidedioxime (H_2A) is the preferred configuration for sequestration of uranium from seawater. Results suggest that, to improve the efficiency of the sequestration of uranium from seawater, the grafting/reaction process should be conducted at 80–90 °C to achieve higher yield of the cyclic imidedioxime (H_2A).

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