



Thermodynamics of U(VI) and Eu(III) complexation by unsaturated carboxylates

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ABSTRACT

The thermodynamic parameters (ΔG , ΔH and ΔS) of complexation of U(VI) and Eu(III) by unsaturated dicarboxylic acids, namely, maleic and fumaric acid, has been determined by potentiometric and microcalorimetric titrations at fixed ionic strength ($I = 1.0$ M) and temperature (298 K). The results show formation of 1:1 complexes by both the ligands with Eu(III). In the case of U(VI), maleate forms both 1:1 and 1:2 complexes, while only 1:1 complex was formed with fumarate. The fluorescence emission spectra of Eu(III)–dicarboxylate solutions at varying ligand to metal ratio were also used to obtain their stability constants. In addition, the fluorescence lifetimes reveal higher dehydration of Eu(III)–maleate compared to Eu(III)–fumarate which corroborates the ΔS values. The thermodynamic quantities suggest charge polarization effects in the case of U(VI) and Eu(III) complexes of fumarate, which is further corroborated by theoretical calculations. For the same ligand, U(VI) complexes were found to be more stable which was mainly due to higher entropy term.

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1. Introduction

Studies on the complexation of actinides by carboxylic acids (mono, di, hydroxy) have attracted considerable interest during the recent past mainly due to two reasons. (i) Carboxylic acids present in the natural waters may play important role in influencing the migration of actinides in the aquatic environment around the deep geological repository [1–3]. They are also used as model compounds to investigate the mechanism of binding of actinides by humic substances in the natural waters [4–6]. (ii) Hybrids containing rare earths and organic moieties have been found to enhance the optical properties of rare earth elements. For instance, luminescence of Eu(III) was found to be sensitized by complexation with carboxylic acids [7–9].

Actinides present in the nuclear waste are considered most important from waste management point of view due to their long half life and alpha emitting properties. The fate of actinides in environment depends on their interaction with various organic and inorganic ligands present in the aquatic environment. Among the organic ligands, humic acid, fulvic acid and some of the simple carboxylates are most predominant. Though a lot of data on stability constant is available, the complete thermodynamic parameters are scarcely available. These parameters not only help in understanding the coordination of actinides in complexed form but are also required to determine $\log K$ at higher temperatures.

Kirishima et al. recently studied the complexation of Eu(III) and U(VI) with various mono-carboxylates, di-carboxylates and hydroxy carboxylates using potentiometry and calorimetry [10]. Complexation of U(VI) by oxalate and gluconate have been studied recently by the Berkeley group led by Rao [1,2]. Kitano et al. determined the thermodynamic parameters of the complexation of Eu(III) by di-carboxylates and hydroxyl-carboxylates and obtained linear correlation between the entropy of complexation and the number of coordinated water molecules around the central metal ion [11]. We have recently studied the thermodynamics of complexation of Eu(III) by carboxylates using isothermal titration calorimetry [12]. Time resolved fluorescence spectroscopy was also used to obtain the stoichiometry of the Eu(III) complexes along with the stability constants [6]. With the availability of intense light sources in the form of synchrotrons, there has been resurgence in the determination of molecular structure of actinide complexes. X-ray absorption fine structure spectroscopy (XAFS), time resolved fluorescence spectroscopy (TRFS) and NMR spectroscopy are being widely used to understand the mechanism of coordination of the metal ion by the ligands [13–15]. The complexation of actinides by unsaturated carboxylates is relatively less understood. The rigidity in unsaturated ligand and ease of charge polarization makes their chemistry interesting and different from saturated carboxylates. Choppin et al. have determined thermodynamic parameters (ΔG , ΔH and ΔS) of Eu(III) complexation with maleate and fumarate and attributed the higher stability of some of the carboxylates to charge polarization [16]. Ramamoorthy and Santappa determined the stability constants of U(VI) complexes with maleate and fumarate [17]. The data on enthalpy and entropy of U(VI)

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complexes with these carboxylates are not available in the literature. The coordination of UO_2^{2+} by the carboxylate anion occurs in the equatorial plane unlike in the case of Eu(III) where coordination occur through spherical coordination space. With this in view thermodynamic parameter of complexation of U(VI) by maleate and fumarate were determined by potentiometry and calorimetry. Though the thermodynamic data for Eu(III) complexation with maleate and fumarate are known. They were determined under same experimental condition as for U(VI) for comparison purpose. The time resolved fluorescence studies on Eu(III) complexes were also carried out to determine their stability constants. In addition the fluorescence lifetime data have been used to obtain information about inner sphere coordination of Eu(III) in complexes. Eu(III) is commonly used as a chemical analogue of trivalent actinides, with regard to their environmental chemistry. In order to understand charge distribution on ligands and complexes, ab initio calculation for charge distribution on all the atoms of ligand as well as complex has been carried out by natural population analysis in TURBOMOLE. The stability constants have been compared with that for other carboxylates to investigate the mechanism of the complex formation. The enthalpy and entropy of complexation have been explained in terms of the hard acid–hard base theory of actinide carboxylate complexation.

2. Experimental

2.1. Reagents

Analytical reagent grade Eu_2O_3 (Merck) was used to prepare the stock solution of Eu(III) (~ 0.1 M) in dilute perchloric acid. Uranium stock solution (~ 0.1 M) was prepared from the spectroscopically pure U_3O_8 . Analytical reagent grade (Merck) maleic acid and fumaric acid were used for preparation of the ligand solutions. MilliQ water having resistivity of $18\text{ M}\Omega\text{ cm}$ was used to prepare all solutions. Ionic strength of the solutions was maintained using analytical reagent grade NaClO_4 as a supporting electrolyte. The pH of the solutions was adjusted by addition of 0.1 M HClO_4 or 0.1 M NaOH . The concentration of the Eu(III) stock solution was determined accurately by complexometric titration of the metal ion solution with EDTA solution of known concentration and using Xylenol orange as an indicator. U(VI) stock solution was standardized by spectrophotometry using bromo-PADAP as a chromogenic reagent.

2.2. Potentiometric titrations

All the potentiometric titrations were carried out at 298 K using the Metrohm autotitrator (Model no.716 DMS Titrimo). The electrolyte solution of the glass electrode (KCl) was replaced by 1 M NaCl solution to prevent precipitation of KClO_4 and hence clogging of the frit. Prior to each potentiometric titration the glass electrode was calibrated using titration of standard HClO_4 (~ 0.01 M) and standard NaOH (~ 0.1 M). The emf of the electrode was recorded as a function of the volume of the base and the emf ($e.m.f$) vs. pH showed a linear plot representing Eqs. (1) and (2) for acidic and basic regions respectively.

$$e.m.f = e.m.f.^0 + \frac{RT}{F} \ln[\text{H}^+] + \gamma_{\text{H}}[\text{H}^+] \quad (1)$$

$$e.m.f = e.m.f.^0 + \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln[\text{OH}^-] + \gamma_{\text{OH}}[\text{OH}^-] \quad (2)$$

where $\gamma_{\text{H}}[\text{H}^+]$ and $\gamma_{\text{OH}}[\text{OH}^-]$ are electrode junction potential for hydrogen ion and hydroxide ion. R is the gas constant, F is the Faraday constant and T is the temperature in Kelvin.

The acid concentration of the Eu(III) stock solution was determined by titration of the solution with standard NaOH (~ 0.1 M)

Table 1

Titration conditions for Eu(III) and U(VI) complexation with fumarate and maleate at $I = 1.0$ M and 25°C .

S. No.	Cup solution		Titrant	
	C_M (mM)	C_H (M)	C_L (M)	C_H (M)
(a) Potentiometric titration (cup volume = 20.0 ml)				
Eu(III)–fumarate	1.00	0.007	0.500	0.186
	3.00	0.012	0.500	0.186
	4.95	0.016	0.500	0.186
Eu(III)–maleate	3.00	0.011	0.500	−0.009
	5.00	0.016	0.500	−0.009
U(VI)–fumarate	3.00	0.022	0.499	0.150
	5.00	0.023	0.499	0.150
U(VI)–maleate	0.99	0.022	0.500	0.077
	3.04	0.022	0.500	0.077
	4.99	0.022	0.500	0.070
(b) Calorimetric titration (cup volume = 2.7 ml)				
Eu(III)–fumarate	3.00	0.012	0.500	0.186
	4.95	0.016	0.500	0.186
Eu(III)–maleate	3.00	0.011	0.500	−0.009
	5.00	0.016	0.500	−0.009
U(VI)–fumarate	3.00	0.022	0.499	0.150
	0.99	0.022	0.500	0.077
U(VI)–maleate	3.04	0.022	0.500	0.077

solution and following Gran's method [18]. The protonation constant of the di-carboxylic acids was determined by the potentiometric titration of the acid solution (~ 0.005 M) by NaOH (~ 0.1 M) or potentiometric titration of sodium dicarboxylate (~ 0.005 M) with standard HClO_4 (~ 0.1 M). For complexation constants the metal ion solution in pH range 1–2 were titrated with ligand solution. The conditions of potentiometric titrations for complexation are given in Table 1a. The potentiometric titration data were analysed using the software HYPERQUAD 8.0 [19] to obtain the stepwise stability constants ($\log K_j$) of the complexes.

2.3. Calorimetric titrations

The calorimetric experiments were conducted with an isothermal titration calorimeter system (Nanocalorimeter TAM-III, Thermometric AB, Sweden). It is a twin thermopile heat conduction type calorimeter and differential power signal measured is dynamically corrected for the thermal inertia of the system. The titration assembly consists of 4 ml reaction vessel and a reference vessel. The heat capacity of reaction vessel and reference vessel is balanced by keeping the same volume of solutions in both sides in order to minimize the short-term noise. The titrant is delivered in the reaction vessel through a stainless steel injection needle (length 1 m and internal diameter 1.5×10^{-4} m) connected to the Hamilton syringe containing the titrant. The syringe was driven by Lund Syringe pump. The temperature of the bath was maintained at $25.0000 (\pm 0.0001)^\circ\text{C}$. The instrument was calibrated electrically and the performance of the instrument was tested by measuring $\log K$ and ΔH for the reaction between BaCl_2 and 18C6 in water. The details of the calorimeter are given in [20].

Calorimetric titration of sodium maleate and sodium fumarate solutions (0.01 M) with standard HClO_4 was carried out to determine the enthalpy of protonation of the acids. For the calorimetric titration of Eu(III) or U(VI) solution with the di-carboxylate, the metal ion solution (0.001 – 0.005 M) at the desired pH and ionic strength was taken in the reaction vessel and was titrated with the ligand solution (Table 1b). The heat of dilution of titrant was determined by in a separate calorimetric titration of the blank electrolyte solution ($I = 1.0$ M NaClO_4) with the titrant solution. At each step of titration, the net reaction heat Q_r^T , was calculated using the

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