



Thermodynamic study of complexation of Eu(III) with carboxylates by potentiometry and calorimetry

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ARTICLE INFO

Article history:

Received 28 August 2009

Received in revised form

16 December 2009

Accepted 21 December 2009

Available online 11 January 2010

Keywords:

Europium

Carboxylate

Complexation

Potentiometry

Titration calorimetry

ABSTRACT

Complexation of Eu(III), a chemical analogue of trivalent actinides, by various carboxylate anions, namely, acetate, 2-hydroxy-2-methylpropanoate (HMP), succinate and phthalate, have been studied at $I = 1.0$ M and 25°C by potentiometry and isothermal titration calorimetry. The enthalpy of formation of all carboxylate complexes was found out to be endothermic except for HMP and for ML_2 with phthalate. The complexation reaction was found to be controlled by entropy. The dicarboxylic anions (succinate and phthalate) were found to form stronger complexes than the monocarboxylates (acetate and HMP). However, the presence of hydroxyl group in HMP increased the stability constant of the complex. The data in conjunction with the time resolved fluorescence spectroscopy measurements performed previously have been used to infer about the structure of the complexes. The thermodynamic data have been explained in terms of hard acid–hard base interaction between Eu(III) and carboxylate anions.

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1. Introduction

Americium and curium isotopes, namely, ^{241}Am ($T_{1/2} = 432$ years), ^{243}Am ($T_{1/2} = 7370$ years), ^{245}Cm ($T_{1/2} = 8500$ years) are produced during the burning of uranium in the nuclear reactor for producing electricity. During the reprocessing of the spent nuclear fuel these trivalent actinides (An(III)) are left in the high level waste which is vitrified in a suitable waste form for burying in a deep geological repository at a later date. Considering the long half-life of these alpha emitting isotopes, it is prudent to assess the possibility of release of these radionuclides from the repository to the geosphere and subsequently their fate in the aquatic environment.

Complexation of An(III) by natural organic matter, viz., humic acid and fulvic acid as well as their degradation products in the form of small organic acids has been a subject of considerable interest during the last few decades [1,2]. The geochemical codes used to assess the performance of the geological repository require the thermodynamic data on the complexation of the actinides by complexing anions present in the natural waters. Even though significant amount of data have been generated on stability constants ($\log K$) of actinide complexes with carboxylates, the complete ther-

modynamic data (viz., enthalpy of complexation ($\Delta_c H$), entropy of complexation ($\Delta_c S$), free energy of complexation ($\Delta_c G$)) are scarcely available. Further the geological disposal sites are expected to have the surrounding water temperatures as high as 100°C . It is, therefore, important to obtain the $\log K$ of actinide complexation by various complexing anions at elevated temperatures. The measured $\Delta_c H$ values can be used to determine the $\log K$ values at higher temperatures (assuming $\Delta_c H$ to be constant in that temperature range). Moreover, the hard acid–hard base type of interaction between actinide ions and carboxylates is of fundamental interest with regard to the thermodynamics of such reactions. With this in view we have studied the complexation of Eu(III), a chemical analogue of An(III) by carboxylate anions, namely, acetate (AC), HMP, succinate (SA) and phthalate (PA) by potentiometry and calorimetry at 25°C .

Kitano et al. [3] studied the complexation of Eu(III) by carboxylates, namely, AC, glycolate, malonate and malate, at 25°C . Extensive studies of complexation of U(VI) by carboxylates are available in the literature. U(VI) complexation by dicarboxylates using calorimetry has been carried out by Kirishima et al. [4,5]. The Berkeley group led by Linfeng Rao carried out systematic thermodynamic study of actinide complexation by carboxylates of UO_2^{2+} at variable temperatures. Complexation of Th(IV) [6] and U(VI) [7] by malonate at variable temperatures was studied to determine the temperature coefficient of the stability constant and enthalpy. Recently the same group studied the complexation at variable temperatures by nitrate [8] as well as by isosaccharinic acid [9]. Np(V)

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Table 1
Titration conditions for the Eu(III) complexation with ligands $I = 1.0 \text{ M}$, $T = 25^\circ \text{C}$.

Ligand	Initial condition of sample solution in the titration vessel	Titrant solution	
		Total ligand (C_{HL}) (M)	Total proton (C_H) (M)
(a) Potentiometric titration, initial volume = 20.00 ml			
AC	7.78 mM Eu(III) in 0.012 M HClO ₄	1.024	0.490
SA	7.78 mM Eu(III) in 0.012 M HClO ₄	0.498	0.576
PA	7.78 mM Eu(III) in 0.012 M HClO ₄	0.217	0.046
HMP	7.78 mM Eu(III) in 0.012 M HClO ₄	0.999	0.447
(b) Calorimetric titration, initial volume = 2.70 ml			
AC	7.78 mM Eu(III) in 0.012 M HClO ₄	1.024	0.490
SA	7.78 mM Eu(III) in 0.012 M HClO ₄	0.498	0.576
PA	7.78 mM Eu(III) in 0.012 M HClO ₄	0.217	0.046
HMP	7.78 mM Eu(III) in 0.012 M HClO ₄	0.500	0.290

complexation by dicarboxylate, such as, oxydiacetate and iminodiacetate has been studied by Jensen and Nash recently [10]. The important conclusions drawn from the above studies are that actinide complexation by carboxylates is driven by entropy, with the enthalpy term being small and endothermic in most cases.

Recently our group studied the complexation of Eu(III) by carboxylate anions using time resolved fluorescence spectroscopy (TRFS) [11,12], which showed the formation of ML_1 , ML_2 and in some cases even ML_3 type of complexes. Similar studies had been carried out by Choppin et al. [13] and Wang et al. on aliphatic as well as aromatic dicarboxylates [14,15]. However, the thermodynamic data ($\Delta_c G$, $\Delta_c H$, $\Delta_c S$) for trivalent actinide complexation by carboxylates are scarcely available in the literature. The results from the present study of Eu(III) complexation by AC, HMP, SA and PA are discussed in terms of the number of carboxylate groups in the ligand as well as the role of hydroxyl group adjacent to the carboxylate group.

2. Experimental

Reagents: Eu(III) stock solution was prepared by dissolving A.R. grade Eu₂O₃ in concentrated nitric acid. This was converted into perchlorate by evaporating to dryness and dissolving the residue in concentrated perchloric acid. The solution was evaporated to dryness thrice and finally the residue was dissolved in 0.01 M HClO₄. The Eu(III) concentration in the stock solution was determined by EDTA titration using xylenol orange as an indicator. A.R. grade acetic acid, 2-hydroxy-2-methylpropanoic acid, succinic acid and phthalic acid were used. Decarbonated NaOH was used for electrode calibration and for titration of carboxylic acids for determination of protonation constant. NaOH was standardized by potassium hydrogen phthalate. Buffered ligand was prepared by adding known amount of NaOH to carboxylic acid solution. All the conditions for potentiometric titrations and calorimetric titrations are given in Table 1.

2.1. Potentiometric titrations

The protonation constant for various ligand anions was studied by titrating $\sim 0.01 \text{ M}$ of the acid with standard NaOH potentiometrically at $I = 1.0 \text{ M}$. Analysis of titration data was carried out by Hyperquad 2008 [16]. The potentiometric titration of Eu(III) solution in dilute HClO₄ by the buffered ligand solution was carried out by autotitrator Metrohm (Model no. 716 DMS Titrino) at 25°C to obtain the stability constant data. During the potentiometric titration addition of excess ligand solution to metal ion solution resulted in appearance of turbidity due to formation of insoluble complexes. Hence titration was carried out till the solution remained clear. All the titrations were carried out in duplicate. The electrolyte solution in the glass electrode (KCl) was replaced by saturated NaCl solu-

tion to prevent precipitation of KClO₄ and hence clogging of the frit. The ionic strength in all the solutions was maintained at 1.0 M using NaClO₄ as an electrolyte. Prior to potentiometric titration, the pH meter was calibrated by titration of standard ($\sim 0.01 \text{ M}$) HClO₄ with standard ($\sim 0.1 \text{ M}$) NaOH solution. Gran's method based software Glee was used to obtain the values of E^0 , slope and carbonate impurity in alkali [17].

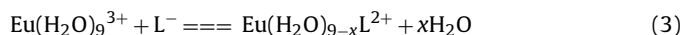
The emf of the electrode was recorded as a function of the volume of the base and the emf vs pH showed a linear plot representing Eqs. (1) and (2) for acidic and basic region, respectively

$$E = E^0 + \frac{RT}{F} \ln[H^+] + \gamma_H[H^+] \quad (1)$$

$$E = E^0 + \frac{RT}{F} \ln K_w - \frac{RT}{F} \ln[OH^-] + \gamma_{OH}[OH^-] \quad (2)$$

where $\gamma_H[H^+]$ and $\gamma_{OH}[OH^-]$ are the terms for electrode junction potential for hydrogen and hydroxide ions, respectively. The acid concentration of the Eu(III) stock solution was determined by titration of the solution with standard ($\sim 0.1 \text{ M}$) NaOH solution and following Gran's method [18]. The potentiometric titration data was analysed using the computer program Hyperquad 2008 to obtain the best model containing a set of stability constants of the individual complexes. Several chemically possible species were submitted as input to Hyperquad 2008. However software program consistently converged with the specific set of metal complex species only. Other species were ignored or rejected during the refinement process.

The formation of 1:1 complex with mono-carboxylate, can be expressed as



where L^- represents the carboxylate anion. The average number of ligands (n) bound to the metal ion (Eu^{3+}) at any concentration of the ligand was calculated using the equation [9],

$$n = \frac{C_{HL} - (K_p[H^+] + 1)[L^-]}{C_M} \quad (4)$$

where C_{HL} and C_M are total concentration of ligand and metal ion, respectively, K_p is the protonation constant obtained by potentiometric titration.

$K_p = [LH]/[H^+][L^-]$ where $[H^+]$ is proton concentration, $[LH]$ and $[L^-]$ are the protonated and free ligand concentrations, respectively. The cumulative stability constant (β_i) of the complexes (ML_i) were determined from the data of n vs $[L^-]$ using the Bjerrum equation:

$$n = \sum_{i=1}^3 (i - n)\beta_i[L^-]^i \quad (5)$$

2.2. Calorimetric titrations

The calorimetric titrations for protonation and complexation were carried out at constant temperature (25 °C) using the isothermal titration calorimeter TAM-III from Thermometric, Sweden. The 2.7 ml of titration solution was kept in the titration vessel while the titrant was added with the help of a precision syringe connected to a stainless steel cannula. The base line (power vs time) drift was <500 nW/h and short term noise of the instrument was <±50 nW. The details of the calorimeter and the calibration procedure are given elsewhere [19].

The enthalpy of protonation for HMP was determined from calorimetric titration of ~0.01 M of 2-hydroxy-2-methylpropanoic acid by standard NaOH. The power output from the calorimeter for each injection was integrated to obtain the heat output (Q_i^r). The heat obtained at each injection is related to enthalpy of protonation ΔH_p by following equation,

$$Q_i^r = \Delta H_p(v_i^{\text{HL}} - v_{i-1}^{\text{HL}}) + \Delta H_{\text{H}_2\text{O}}(v_i^{\text{HL}} - v_{i-1}^{\text{HL}}) \quad (6)$$

where v_i is the moles of corresponding species at i th injection and $\Delta H_{\text{H}_2\text{O}}$ is the enthalpy of neutralization. The $\Delta H_{\text{H}_2\text{O}}$ at $I = 1.0 \text{ M}$ was determined by calorimetric titration of strong acid by strong base and was found to be -54.89 kJ/mol , which is close to the literature value of -56.10 kJ/mol [4]. The ΔH_p for all other carboxylates were taken from the literature [2,3].

In the case of calorimetric titration of acidic Eu(III) solutions by buffered ligand, Q_i^r can be related to the enthalpy values. For instance, in case of complexation where ML , ML_2 and ML_3 are formed with dicarboxylates, Q_i^r can be given by

$$Q_i^r = \Delta_c H_1(v_i^{\text{ML}} - v_{i-1}^{\text{ML}}) + (\Delta_c H_1 + \Delta_c H_2)(v_i^{\text{ML}_2} - v_{i-1}^{\text{ML}_2}) + (\Delta_c H_1 + \Delta_c H_2 + \Delta_c H_3)(v_i^{\text{ML}_3} - v_{i-1}^{\text{ML}_3}) + \Delta H_{p1}(v_i^{\text{HL}} - v_{i-1}^{\text{HL}} - C_{\text{HL}}V_i) + (\Delta H_{p1} + \Delta H_{p2})(v_i^{\text{H}_2\text{L}} - v_{i-1}^{\text{H}_2\text{L}} - C_{\text{H}_2\text{L}}V_i) \quad (7)$$

where ΔH_{p1} and ΔH_{p2} are the enthalpy of protonation of the carboxylate anion, $\Delta_c H_i$ represent the enthalpy of stepwise complex formation for ML_i complex. C_{HL} and $C_{\text{H}_2\text{L}}$ are the concentrations of monoprotonated and diprotonated ligand in the titrant, respectively which are calculated using K_{p1} , K_{p2} , total ligand concentration (C_{HL}) and total proton concentration (C_{H}) in the burette. V_i is the volume of titrant added (dm^3) from burette at i th injection. The first three terms in Eq. (7) correspond to the heat involved due to change in concentrations of ML , ML_2 and ML_3 at i th injection. Last two terms in equation correspond to the heat involved due to protonation/deprotonation of ligand at i th injection. The stability constant K_i and protonation constant (K_p) obtained from poten-

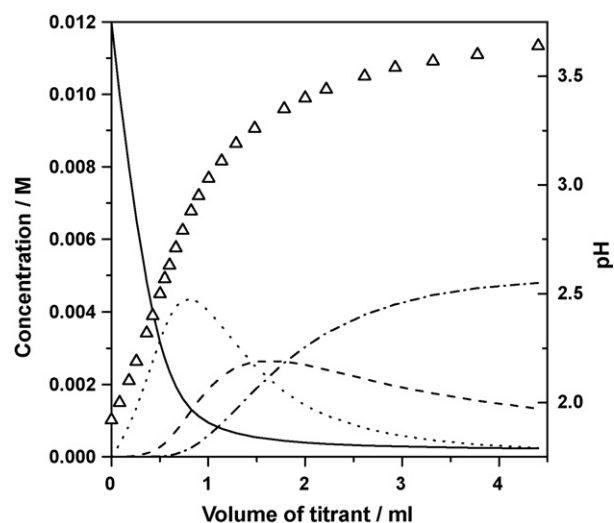


Fig. 1. Potentiometric titration data of Eu(III) with HMP. Titration vessel: 20 ml of Eu(III) (7.78 mM) + HClO_4 (0.012 M) titrant: total ligand ($C_L = 0.999 \text{ M}$) + total proton ($C_H = 0.447 \text{ M}$). (Δ) Experimental data (pH), concentration of Eu(III) species (left y axis), Eu^{3+} (solid line), EuL^{2+} (dot), EuL_2^+ (dash), and EuL_3 (dash dot).

tiometric titrations were used to calculate v_i for all species while the enthalpy of complexation ($\Delta_c H_i$) for Eu(III) carboxylates was obtained by non linear square fitting of the Q_i^r data (Eq. (7)).

3. Results and discussion

Fig. 1 shows the potentiometric data of Eu(III) titration by buffered ligand (HMP). The speciation of the different complexes ML_i ($i = 1-3$) obtained from the Hyperquad 2008 is also shown in Fig. 1. Similar analysis was carried out for other ligands also. The protonation constant (K_{pi}) and the stability constants ($\log K_i$) for the stepwise formation of ML_i complexes for all the carboxylates are given in Table 2. The stability constants for Eu(III) carboxylates obtained in the present work are in good agreement with the literature data (shown in parentheses). Table 3 gives the calorimetric titration data of Eu(III) complexation by different carboxylates. The integrated power vs time data gives Q_i^r vs volume of the titrant. The graphs of Q_i^r vs volume of the titrant for all the carboxylates are given in Fig. 2. The thermodynamic parameters for all the systems are given in Table 2. The literature values of the thermodynamic parameters wherever available are also shown in the table along with the relevant references. In calorimetric titration curve for AC

Table 2

Thermodynamic data of protonation of carboxylates (K_p) $\text{LH}_{k-1} + \text{H} = \text{LH}_k$ and Eu(III) complexation by carboxylates ($\log K_j$), $\text{EuL}_{j-1} + \text{L} = \text{EuL}_j$, at 25 °C and $I = 1.0 \text{ M}$.

Ligand	k	$\log K_{pk}$	ΔH_p (kJ/mol)	$J, \log K_j$	$\Delta_c G$ (kJ/mol)	$\Delta_c H$ (kJ/mol)	$T\Delta_c S$ (kJ/mol)
AC	1	4.65 ± 0.03 (4.62) ^a	-1.68	1	1.97 ± 0.05 (1.97) ^a	-11.2	6.2 ± 0.8 (7.1,8.8) ^a
	2			2	1.48 ± 0.09 (1.41) ^a	-8.4	1.7 ± 0.30 (3.6) ^a
SA	1	5.25 ± 0.01 (5.12) ^b	-2.0	1	3.05 ± 0.046 (2.99) ^c , (2.96) ^b	-17.4	9.5 ± 0.2 (12.4) ^b
	2	3.99 ± 0.01 (4.01) ^b	-4.47	2	1.71 ± 0.12 (1.91, 0.1M) ^c	-9.80	-
PA	1	4.66 ± 0.001 (4.61) ^b	0.61	1	3.06 ± 0.04 (3.5) ^d	-17.5	10.3 ± 0.20 ($U = 11.6$) ^e
	2	2.66 ± 0.003 (2.64)	1.91	2	1.97 ± 0.05 (1.67) ^d	-11.3	-0.9 ± 0.4 ($U = 1.7$) ^e
HMP Glycolate ^f	1	3.73 ± 0.01 (3.75) ^d	-2.12 (-2.07) ^f	1	2.84 ± 0.04 (2.7) ^g	-16.2	-2.1 ± 0.10 (-4.0) ^f
	2			2	1.87 ± 0.06 (2.24) ^g	-10.7	-5.0 ± 0.05 (-5.3) ^f
	3			3	1.69 ± 0.07 (1.58) ^g	-9.7	-5.7 ± 0.6 (-6.5) ^f

^a Ref. [3].

^b Ref. [4].

^c Ref. [14].

^d Ref. [15].

^e Ref. [4] uranyl ion data.

^f Ref. [3] glycolate data.

^g Ref. [22].

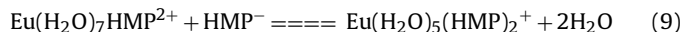
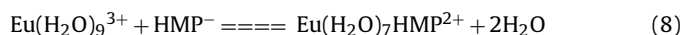
Table 3
Heat of reaction Q_i^r at each injection step (i) during calorimetric titration for all the ligands (concentrations are provided in Table 1).

Injection no. (i)	Volume of titrant (V_i), ml	Q_i^r (mJ)			
		AC	SA	PA	HMP
1	0.01	-8.838	-16.375	4.136	-2.890
2	0.02	-8.721	-17.140	4.035	-3.147
3	0.03	-8.516	-16.946	3.849	-3.126
4	0.04	-8.221	-16.613	3.750	-3.199
5	0.05	-7.315	-16.007	3.694	-3.247
6	0.06	-3.663	-14.914	3.591	-3.261
7	0.07	4.658	-12.412	3.523	-3.409
8	0.08	8.883	-7.376	3.570	-3.511
9	0.09	9.314	-1.227	3.700	-3.684
10	0.10	8.738	2.752	4.068	-3.852
11	0.11	8.224	4.493	4.603	-4.015
12	0.12	7.574	5.160	5.202	-4.182
13	0.13	7.010	5.310	5.877	-4.312
14	0.14	6.547	5.235	6.499	-4.449
15	0.15	6.085	5.068	7.039	-4.544
16	0.16	5.591	4.890	7.582	-4.548
17	0.17	5.160	4.682	7.910	-4.536
18	0.18	4.826	4.375	8.180	-4.558
19	0.19	4.483	4.088	8.371	-4.477
20	0.20	4.250	3.970	8.334	-4.400
21	0.21	4.006	3.750	8.251	-4.230
22	0.22	3.702	3.497	8.067	-4.100
23	0.23	3.526	3.322	7.750	-4.026
24	0.24	3.286	3.075	7.450	-3.858
25	0.25	3.099	2.880	7.037	-3.811
26	0.26	2.881	2.695	6.636	-3.684
27	0.27	2.684	2.596	6.133	-3.568
28	0.28	2.567	2.462	5.762	-3.480
29	0.29	2.432	2.316	5.295	-3.382
30	0.30	2.399	2.105	4.905	-3.086
31	0.31	2.307	1.961	4.575	-3.024
32	0.32	2.109	1.832	4.242	-2.941
33	0.33	2.027	1.785	3.952	-2.828
34	0.34	1.960	1.713	3.758	-2.754
35	0.35	1.748	1.598	3.540	-2.550
36	0.36	1.730	1.489	3.212	-2.518
37	0.37	1.771	1.400	3.029	-2.451
38	0.38	1.567	1.328	2.796	-2.288
39	0.39	1.570	1.248	2.603	-2.270
40	0.40	1.550	1.148	2.540	-2.190
41	0.41	1.524	1.072	2.417	-2.127
42	0.42	1.347	0.730	2.124	-2.163
43	0.43	1.305	0.853	2.017	-2.125
44	0.44		0.672	1.870	-1.983
45	0.45		0.698	1.837	-1.986
46	0.46		0.693	1.672	-1.824
47	0.47		0.643	1.659	-1.715
48	0.48		0.556		-1.643

and SA (Fig. 2 and Table 3), the heat values at initial injections are exothermic with negative Q_i^r and as more ligand is added Q_i^r becomes endothermic. During the initial injections the predominant reaction is protonation of the ligand which is exothermic for AC and SA. On adding more volume of ligand, the complexation reaction dominates resulting in endothermic Q_i^r . In the case of Eu(III)-PA, both protonation and complexation are endothermic which results in endothermic Q_i^r at all the injections. However in case of HMP, protonation as well as complexation reactions are exothermic. Thus Q_i^r at all the titration points are negative.

The four ligands, AC, HMP, SA and PA can be grouped into two classes; the monocarboxylates (AC and HMP) and dicarboxylates (SA and PA). Both the monocarboxylates (AC and HMP) are found to form ML, ML₂ and ML₃ complexes with Eu(III). The data for ML₃ for Eu(III)-AC have not been reported due to its low concentration. For HMP the evidence for the formation of the three complexes was observed in TRFS study [11]. The complexation of Eu(III) by HMP results in expulsion of water molecules, viz., Eqs. (8) and (9). The lifetime data of ⁵D₀ excited state of Eu³⁺ were used to deduce the number of coordinated water molecules (nH_2O). The results clearly

showed the removal of two water molecules for every ligand anion.



and likewise for the formation of ML₃ complex. This shows that HMP acts as a bidentate ligand. Studies on Eu(III)-AC complex showed that AC ion also acts as a bidentate ligand [20,3]. As these interactions are electrostatic in nature, there should be linear correlation between basicity of ligand anion and stability constant. The basicity of ligand anion increases with log K_p , thus log K_1 also increases linearly with log K_p . Rao et al. [9] observed such a correlation in case of U(VI). Fig. 3 shows a plot of log K_1 vs log K_p for Eu(III) carboxylates. Some of the data in the figure have been taken from Choppin et al. [21,22]. The simple monocarboxylates and hydroxy carboxylates fall on two separate straight lines with hydroxy carboxylate having higher log K_1 than simple monocarboxylates. 2-Hydroxy-2-methylpropanoic acid being a stronger acid than acetic acid has weaker conjugate base. Thus the higher stability of Eu(III)-HMP can be explained only on the basis of

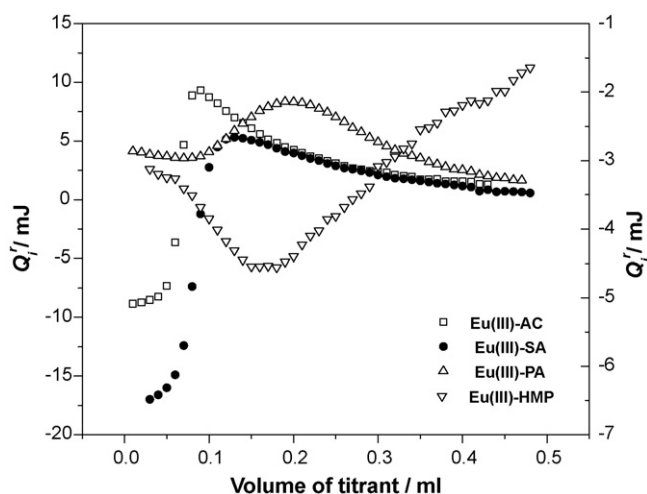


Fig. 2. Integrated calorimetric titration data of Eu(III) solution (2.7 ml of 7.78 mM Eu(III) in 0.012 M HClO₄) by buffered (left y axis) AC, SA, PA and (right y axis) HMP (concentrations are given in Table 1b).

participation of hydroxyl group which increases the interaction of ligand with Eu(III). The increased interaction between HMP and Eu(III) is reflected in its enthalpy of complexation which is found to be exothermic. The enthalpy of complex formation can be expressed as the resultant of enthalpy of dehydration of metal ion ($\Delta H_{\text{metal dehydration}}$) and that of metal ligand bond formation ($\Delta H_{\text{M-L bond formation}}$). As the metal dehydration energy is constant, variation in $\Delta_c H$ are mainly due to $\Delta H_{\text{M-L bond formation}}$

$$\Delta_c H = \Delta H_{\text{metal dehydration}} - \Delta H_{\text{M-L bond formation}} \quad (10)$$

The linear correlation between $\log K_1$ and $\log K_p$ has also been observed in hydroxy carboxylates but their stability constant are higher than monocarboxylates (Fig. 3). The higher stability constants of hydroxy carboxylates than mono carboxylates can be attributed to the chelation through hydroxy group in the former. The shorter U–O_{eq} bond lengths in UO₂²⁺–HMP complexes compared to UO₂–AC obtained in extended X-ray absorption fine structure spectroscopy measurements further corroborate the chelate formation in the case of hydroxy carboxylate [23,24]. The

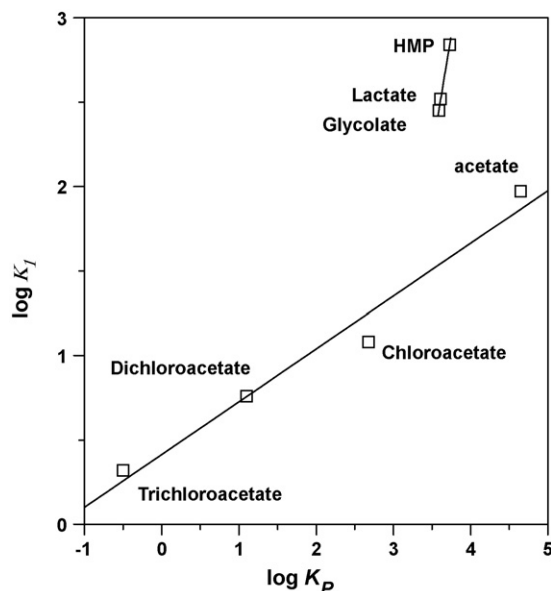
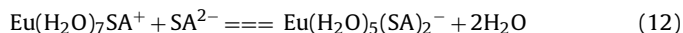
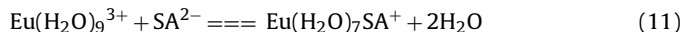


Fig. 3. Plot of $\log K_1$ vs $\log K_p$ for Eu(III) carboxylates.

sharper increase in $\log K_1$ with $\log K_p$ for hydroxy carboxylate complex compared to monocarboxylate could be due to the shorter Eu³⁺–O_{ax} bond distance which leads to large increase in electrostatic interaction with increase in ligand basicity.

Potentiometric data for SA and PA are best fitted assuming ML and ML₂ complexes. The $\log K_1$ for both the ligands is same, while $\log K_2$ is slightly higher for PA than SA. The complexation reaction can be represented as



The evidence for the 7 and 5 coordinated water molecules in ML and ML₂ for SA and PA complexes of Eu(III) was obtained from the TRFS measurements [12]. This shows that both SA and PA behave as bidentate ligands.

Comparison of the $\log K_1$ value in all ligands indicates that dicarboxylates form stronger complexes than monocarboxylates. The $\Delta_c H$ values for the formation of ML are more endothermic for both the dicarboxylates than monocarboxylate. The higher stability of dicarboxylate complexes is mainly due to the $T\Delta_c S$ values.

Higher $T\Delta_c S$ values for dicarboxylates suggest the chelate formation through two carboxylate groups. Due to higher dehydration energy required for metal ion as well as ligand, $\Delta_c H$ becomes more positive compared to monocarboxylates. Other than basicity, chelate ring size also plays an important role in determining thermodynamic parameter of the complex. For example, malonate ion is weaker base ($\log K_{p1} = 5.09$ and $\log K_{p2} = 2.59$) than SA ion ($\log K_{p1} = 5.25$ and $\log K_{p2} = 3.99$) but forms stronger complex due to the formation of more stable six membered ring than Eu(III)–SA. Such correlation of ring size and ligand stability has also been found by Kirishima et al. in case of UO₂²⁺ [4]. In case of Eu(III)–SA and Eu(III)–PA complexes ring size is same. Though PA is weaker base but preorganized cis conformation of two carboxylate groups increases its stability. Similar thermodynamic parameters for Eu(III)–SA and PA suggest compensation in these two opposing factors. The $\Delta_c H_2$ is found to be less than $\Delta_c H_1$ in all the cases, which is due to the reduced charge of interacting species in the ML₂ formation. For Eu(III)–PA there is significant decrease in $\Delta_c H$ from ML to ML₂ (10.3 to –0.9 kJ/mol) whereas decrease in $\Delta_c H$ on successive complexation is less in the case of monocarboxylates (AC and HMP). The large decrease in $\Delta_c H$ was also observed in case of UO₂²⁺–PA [4]. This can be explained on the basis of charge neutralization of metal ion during complexation (ML) which is more for dicarboxylates. Thus, the dehydration energy for ML₂ formation is reduced resulting in reduction of $\Delta_c H$.

The role of substituents on the stability of the complex and the thermodynamic parameters is an important aspect which needs to be studied in detail. Further the structure of the complex ought to be determined to substantiate the inference drawn from potentiometric titration data about the stoichiometry of the complex as was done by Jiang et al. [23], Rao et al. [23,25] and Jensen and Nash [10]. Further experiments on the determination of the thermodynamic parameters at higher temperatures would help in predicting the complexation behavior of Eu(III) by carboxylates under the conditions prevailing in the natural environment in the vicinity of the repository.

4. Conclusion

Complexation of Eu(III) by carboxylates, namely, AC, SA, PA and HMP has been found to be governed by entropy with the reaction enthalpy being endothermic for AC, SA and PA and slightly exothermic for HMP. The dicarboxylate complexes were found to have higher stability than monocarboxylates which is attributed to the predominant role of entropy than enthalpy. Further, the presence

of hydroxyl group in the aliphatic chain close to the carboxylate group results in the increase in the stability of the complex, which appears to be mainly due to enthalpy factor.

Acknowledgement

Authors thank Professor Radha Tomar for her support during the analysis of potentiometric titration data by Hyperquad 2008.

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