

SPECIATION STUDIES OF EUROPIUM (III) WITH (POLY)PHOSPHONATE LIGANDS. THE CASE OF EDTMP

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Abstract

The complex formation equilibrium of ethylenediamine-tetramethylenephosphonic acid (EDTMP, H₈L) with europium (III) has been studied potentiometrically at 25°C and ionic strength of 0.15 M (NaCl). To examine the experimental data, titration curves of ligand in presence of europium (III) were compared with the references curves obtained in its absence. The complex formation constants were determined with the PSEQUAD program. The speciation in the system Eu (III) – EDTMP was calculated and drawn with HySS computer program.

Key words: EDTMP, Eu (III), potentiometry, speciation, Psequad, Hyss

Introduction

The development of Nuclear Magnetic Resonance Imaging techniques as a clinical diagnostic modality has prompted the need for a new class of pharmaceuticals – paramagnetic contrast agents, used to enhance the differences between normal and diseases tissue, or to indicate specific organ functions. Complexes of paramagnetic transition metal and lanthanide ions have been considered as potential contrast agents (Reichert, 1999) and numerous complexes of polyaminopolycarboxylic acid with these metal ions have been studied from this respect (Aime, 1999; Bianchi, 1999).

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In this work are presented the results of some aqueous solution studies concerning the formation, stability and speciation of coordination compounds of Eu (III) with EDTMP.

Experimental

Potentiometric titrations were performed with an OAKTON[®] pH 10 series pH-meter, equipped with a glass electrode OAKTON[®] WD-35801-00. The pH electrode was calibrated using three standard buffer solutions. All calibrations and titrations were carried out under a CO₂-free nitrogen atmosphere to avoid any contact with carbon dioxide, in a glass vessel (25 cm³) thermostatted at 25±0.1°C and an ionic strength of 0.15 mol·dm⁻³ NaCl. CO₂-free solution was used as titrand, which consists from 0.1822 mol·dm⁻³ KOH, to minimise ionic strength change during the titration.

The potentiometric equilibrium studies were made on solutions of mixtures ligand + Eu(III), with the M:L ratios 1:1, 1:2 and 1:4 respectively. The pH data were obtained after addition of 0.050 cm³ increments of standardised KOH solution with a burette Radelkis OP-930/1.

At low values of pH, in the presence of europium ions, in the solution there is solid phase. This phase disappeared at pH over 5. For calculus of overall stability constants, has to take in consideration the pH values for clear solutions. At pH = 5 - 8, the equilibrium's were slow to attain and about 5 min were required for each point of the titration.

A stock solution of 0.0203 mol·dm⁻³ Eu³⁺ in 2·10⁻² mol·dm⁻³ HCl was prepared from europium triacetate and a standardised HCl solution. The titrant solution was prepared from KOH and it was standardised with potassium hydrogen iodide. Eu³⁺ solution was standardised by complexometric titrations with EDTA using hexamethylenetetramine as buffer and xylenol orange as an indicator (Shetty, 1976).

The purity of ligand was confirmed by titration with a standardised ZnSO₄ solution, in presence of Eriochrom black T, at buffered value of pH = 10. The overall stability constants of the various europium complexes formed in aqueous solution were determined from the titration data with the Fortran computer program PSEQUAD (Zekany,

1985). Species distribution diagrams and pM values were computed from the overall formation constants with HySS computer program (Alderighi, 1999).

The pK_w values for the aqueous system, defined as $-\log [H^+][OH^-]$ at the ionic strength employed, was 13.76 at 25°C (Harned, 1958).

Results and Discussions

All the reactant concentrations used in these studies, along with the pH ranges on which the calculations are based, are reported in Table 1. The measurements made at acidic pH, where the solid complexes of Eu (III) were separated, were removed from final calculations. Such measurements are indicated by the pH values in parentheses in Table 1.

Table 1. Summary of the titration data used for calculating formation constants

System	C_{Eu} (mmol·dm ⁻³)	C_L (mmol·dm ⁻³)	C_H (mmol·dm ⁻³)	pH range used (investigated)	n
Eu (III) – edtmp	4.060	4.188	37.504	5.21 – 11.58	69
	2.030	4.188	35.504	5.98 – 11.63	70
	1.015	4.188	34.504	6.40 – 11.60	65

n – represents the number of experimental observations in each titration

The titration curves of the ligand, in the absence or in the presence of different concentrations of europium ions, indicate the formation of ferric chelates containing hydrogen ions in addition to the metal. At higher pH the both acidic chelates and normal chelate go over to the “hydroxo” chelate.

The stability constants of the various species formed in the aqueous solution were obtained from the experimental data of titrations of solution with different ligand : europium ions ratios, using the PSEQUAD program. The initial computation was obtained in the form of overall stability constants:

$$\beta_{pqr} = [M_p L_q H_r] [M]^{-p} [L]^{-q} [H]^{-r} \quad (1)$$

where M, L, and H represent metal, ligand and hydrogen ions, respectively, and species concentrations, [], are expressed in units of mol·dm⁻³. Hydroxy species are represented as $M_p L_q H_{-r}$ and not as

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$M_pL_q(OH)_r$. The symbols $(OH)_r$ and H_{-r} are related through the ionisation constant K_w (where $K_w = [H^+][OH^-]$). Hence:

$$\beta_{pq-r} = \frac{[\text{hydroxy species}]}{[M]^p[L]^q[H]^{-r}} = \beta'_{pqr} \cdot K_w^r \quad (2)$$

where $\beta'_{pqr} = \frac{[\text{hydroxy species}]}{[M]^p[L]^q[OH]^r} = \frac{[\text{hydroxy species}]}{[M]^p[L]^q K_w^r [H]^{-r}} \quad (3)$

In table 2 there are the values of overall formation constants of Eu (III) – EDTMP complexes.

Table 2. The overall formation constants of Eu (III) – EDTMP complexes (25°C, I = 0.15 M (NaCl))

Complex	Species pqr	log β_{pqr}
EuL	1 1 0	12.43(2)
EuLH	1 1 1	18.08(2)
EuLH ₂	1 1 2	23.88(10)
EuLH ₋₁	1 1 -1	5.08(1)

Witt and his co-workers reported the formation and protonation constants of EDTMP complexes with yttrium (1998) and samarium (1996) ions. Their values agree with our data. The values of K_{pqr} , defined as $K_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$ and the values of β'_{pqr} there are in

table 3.

Table 3. Formation constants of Eu (III) – EDTMP complexes (log K_{pqr}) (25°C, I = 0.15 M (NaCl))

Equilibrium quotient	log K_{pqr}
$[EuL]/[Eu][L]$	12.43
$[EuLH]/[Eu][HL]$	5.94
$[EuLH_2]/[Eu][H_2L]$	2.19
$[EuLH_{-1}]/[Eu][L][OH]$	18.84

As can be observed from table 3 the formation constant of the normal chelate of Eu (III) with EDTMP ($\log K_{110} = 12.43$) is much smaller than those of EDTA chelate ($\log K_{110} = 17.3$) (Mazor, 1966). This indicates that one of the nitrogen atoms of EDTMP is not coordinating (Sawada, 1987). Because $\log K_{110} = 12.43 > \log K_{111} = 5.94$, this suggest a very strong Eu — N bond, which in protonation complex cannot be ruptured (Sawada, 2000). As a consequence, the protonation of the EuL chelate occurs on the free oxygen atoms of the phosphonate groups of the complex.

The speciation diagrams (figure 1) show that the EuLH₁ species exist in great percentage in the pH range over 9, and a pH < 6 there are not aqueous soluble species of europium chelates.

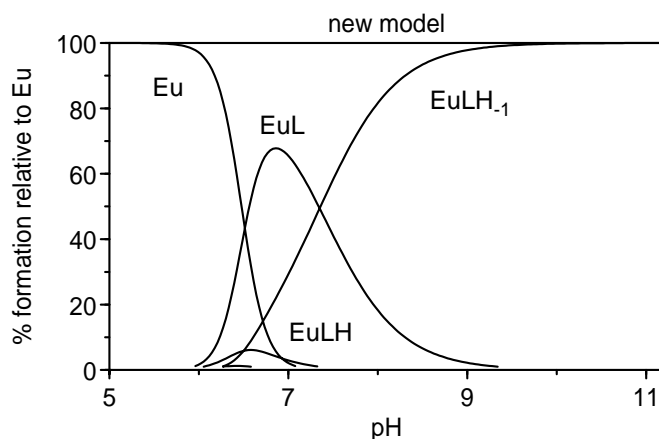


Fig. 1. Speciation diagrams of the Eu (III)–EDTMP chelates, calculated for $C_L = 0.004188 \text{ mol dm}^{-3}$, $C_{Eu} = 0.0005 \text{ mol dm}^{-3}$, at 25°C and $I = 0.15 \text{ M}$

The fact that the first protonation constant of the complex ($\log K_{111} = 5.94$) is smaller than second protonation constant of the ligand ($\log K_{012} = 9.364$) indicates the first protonation occurs on the free oxygen atoms of the phosphonate groups of the complex (Yang, 1998). It could be observed that the second protonation constant of the complex ($\log K_{112} = 2.19$) is smaller than third protonation constant of the ligand ($\log K_{013} = 7.504$) also. That means that the second protonation of the Eu (III)–EDTMP complexes occur on the free oxygen atoms of the phosphonate groups of the complex, too.

Conclusions

Were calculated the overall formation constants of EDTMP chelates with europium ion at 25°C and an ionic strength of 0.15 M (NaCl). The values are almost similar with the samarium chelates ones. At physiological pH there are two soluble species: EuL and EuLH₋₁.

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