

Electrochemical Reactions of Europium in H₂O-H₃PO₄-DTPA System

B. BELQAT*, K. EL KACEMI and S. BELCADI

*Laboratoire d'Electrochimie et Chimie Analytique, Dep. Chimie, Fac. Sciences
Rabat BP1014, Morocco*

E-mail: Bouchrabelqat@hotmail.com

The reduction of Eu(III) ions in phosphoric acid with or without diethylenetriamine-pentaacetic acid (DTPA) was studied by electrochemical analyses. Electrochemical reactions involved complexation and solvation processes of europium ions with DTPA species in phosphoric acid. The diffusion coefficient of Eu(III) species was determined in diffusion-flow media. The effect of the europium concentration and the solvent on the complexation reactions was discussed. In addition to electrochemical informations on Eu-H₃PO₄-DTPA system in solution, spectrophotometric investigation confirms the formation of complexing species.

Key Words: Phosphoric acid, Europium, Diethylenetriamine Pentaacetic acid, Electrochemical, Complexation.

INTRODUCTION

The europium species were used in various areas such as in incandescence lamps, in the tube revetment of television and in various other applications¹⁻⁶. Several ores contain rare earths such as Morocco phosphate⁷, which produce phosphoric acid by sulfuric acid treatment. The europium contents around 20–40% are resumed in phosphoric acid and the rest in the phosphogypse as insoluble forms⁸⁻¹⁰. Consequently, the europium ion recovery necessitates a precise knowledge of its redox state and their behaviour in phosphoric acid. Some workers have approached the electrochemical aspect of europium in different media such as perchloric acid and glycine¹¹⁻¹³. The addition of the multidentals such as diethylenetriamine pentaacetic acid (DTPA) ligand in phosphoric acid solution containing Eu³⁺ ions can favour the europium complexation and therefore minimize its loss in the phosphogypse. The knowledge of stability constants for europium chelates gives a good indication on its extraction process. DTPA species presents a higher stability constant ($\log K_{BA} = 22.91$) than other ligands such as EDTA ($\log K_{BA} = 17.35$) and HEDTA ($\log K_{BA} = 15.15$) and may form more complexes with europium ions¹⁴. The current study using electrochemical and UV-visible spectroscopy demonstrates some interaction reaction (complexation and solvating) between the europium ions and DTPA species in phosphoric acid.

EXPERIMENTAL

The phosphoric acid used (Riedel De Haen pure for analysis) was taken at different concentrations varying from 0.1 to 14 M. The diethylenetriamine

pentaacetic acid C₁₄H₂₃N₂O₁₀ (DTPA) (Labos for analyses) and Eu₂O₃ (Merck products for analysis) were introduced in the solution by a complete dissolution in phosphoric acid solution. Electrochemical techniques involve the classic and impulse polarographies (Polaroprocasseur POL150 Polarographic to analyze) and potentiostatic coulometry. A cell in glass containing the studied solution was used, in which the work electrode was mercury and the auxiliary electrode was platinum with Ag/AgCl (0.1 M H₃PO₄) electrode reference. To avoid the chloride diffusion between the reference electrode and the solution cell, the Ag/AgCl electrode was connected to work cell by a capillary containing a phosphoric acid (0.1 M), diving in solution containing ferricinium species. The potential junction between the two phosphoric acid media was corrected for all measurements described elsewhere¹⁵ During all experimental setup, bubbling of nitrogen was maintained in the solution to avoid the presence of dissolved oxygen.

Spectrophotometric study was performed with a double beam absorption spectrophotometer (Varian, Series 634).

RESULTS AND DISCUSSION

Eu(III) in H₂O-H₃PO₄: Polarograms of Eu³⁺ ions in H₃PO₄ taken at different concentrations are reported in Fig 1. In calculating the potentials $E_{1/2}$, $E_{1/2(\text{marked})}$ and $(E_{3/4}-E_{1/4})$ given in Table-1, a reversible electrochemical reduction of Eu³⁺ ions in phosphoric acid was obtained. A half wave potential $E_{1/2(\text{marked})}$ displaces to most negative values when the phosphoric concentration increases and the diffusion current is proportional to the europium concentration (Fig. 2).

The analysis of the reduction wave shows that the values of $E_p(\text{marked})$ varies straight line with $\log(I_d - I)/I$ where the transferred electron number equals to 1 provided also by coulometry method. The potential values of $E_{1/2(\text{marked})} = -0.666$ V/ Ag/AgCl (1 M H₃PO₄) and $E_{1/2(\text{marked})} = -0.647$ V/ Ag/AgCl (5.5 M H₃PO₄) when $\log(I_d - I)/I = 00$ (Fig.3).

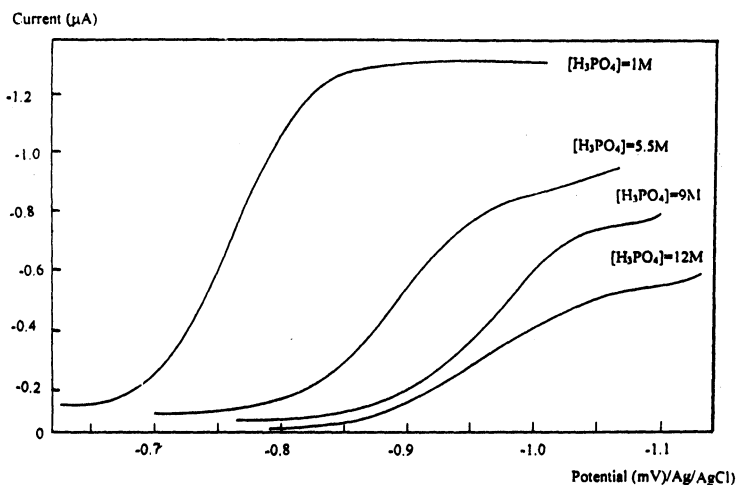
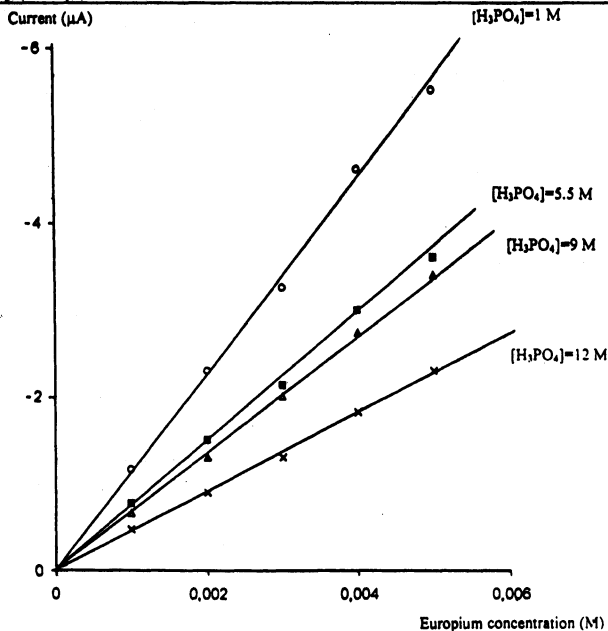
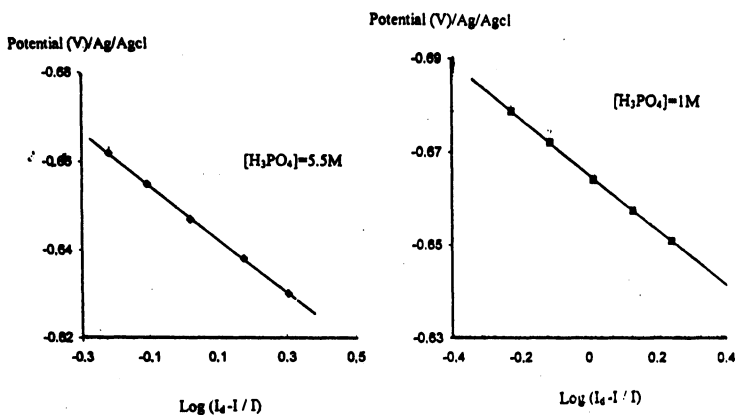


Fig. 1. Polarograms of Eu(III) ions in H₃PO₄ solution ($C_{\text{Eu(III)}} = 10^{-3}$ M; $C_{\text{H}_3\text{PO}_4} = 1.0$ M; 5.5 M; 9.0 M; 12.0 M).

TABLE-1

 $E_{1/2}$, $E_{1/2}$ (MARKED) AND $(E_{3/4}-E_{1/4})$ VALUES vs. H_3PO_4 CONCENTRATION

$[H_3PO_4]$ (M)	1.0	5.5
$E_{1/2}$ (V)/Ag/AgCl	-0.756	-0.894
$E_{1/2}$ marked (V)/Ag/AgCl	-0.666	-0.649
$(E_{3/4} - E_{1/4}) \pm 5$ (mV)	59	65

Fig. 2. Diffusion current I_d versus europium concentration at different phosphoric concentrations.Fig. 3. Dependence of the potential peak as function of $\log(I_d - I)/I$ at 1.0 M and 5.5 M H_3PO_4 .

The diffusion coefficients of Eu(III) ions according to phosphoric acid concentration were calculated from the Ilkovic equation¹⁶: $I_d = 607 \text{ nm}^{2/3} t^{1/6} D^{1/2}$,

while the viscosities of phosphoric acid at different concentrations are given in literature (Table-2). The low diffusion coefficient of Eu(III) species in concentrated H₃PO₄ should be related to the high medium viscosity as described by several workers^{17, 18}

The diffusion coefficients of Eu(III) ions according to phosphoric acid concentration were calculated from the Ilkovic equation¹⁶: $I_d = 607 \text{ nm}^{2/3} i^{1/6} D^{1/2}$, while the viscosities of phosphoric acid at different concentrations are given in literature (Table-2). The low diffusion coefficient of Eu(III) species in concentrated H₃PO₄ should be related to the high medium viscosity as described by several workers^{17, 18}.

TABLE-2
DIFFUSION COEFFICIENT AND VISCOSITY VALUES OF Eu³⁺ IONS
IN H₃PO₄ MEDIA

[H ₃ PO ₄][M]	D · 10 ⁶ (cm ² s ⁻¹)	η (centipoises) (Ref. 16)
1.0	0.98	1.2
5.0	0.34	3.9
9.0	0.22	10.6
11.5	0.11	20.2

Eu(III) in H₂O-H₃PO₄-DTPA system: Fig. 4 shows the impulse polarograms obtained in 1 M H₃PO₄ and 10⁻³ M Eu(III) ions with or without 6 × 10⁻³ M DTPA

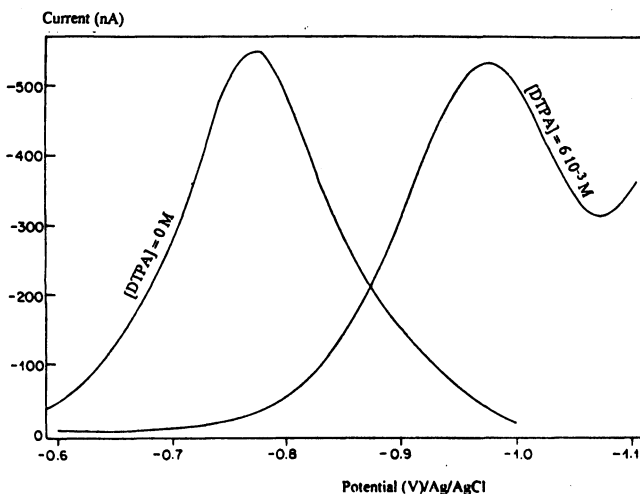


Fig. 4. Impulse polarograms of 10⁻³ M Eu(III) ions in 1 M H₃PO₄ with or without DTPA species. In the absence of DTPA, $E_{p(\text{marked})} = -0.673 \text{ V/Ag/AgCl}$, which is similar to previous value of $E_{1/2}$ using classic polarography ($E_{1/2(\text{marked})} = -0.666 \text{ V/Ag/AgCl}$), whereas the reduction peak of the Eu(III) ions displaces to most negative values according to the DTPA concentration. Using the slope line values of $\Delta E_p = (E_p(C_{\text{DTPA}} \neq 0)) - E_p(C_{\text{DTPA}} = 0)$ values as a function of DTPA concentration ($C_{\text{Eu(III)}} = 10^{-3} \text{ M}$) (Fig. 5), the Eu(III) coordination numbers calcu-

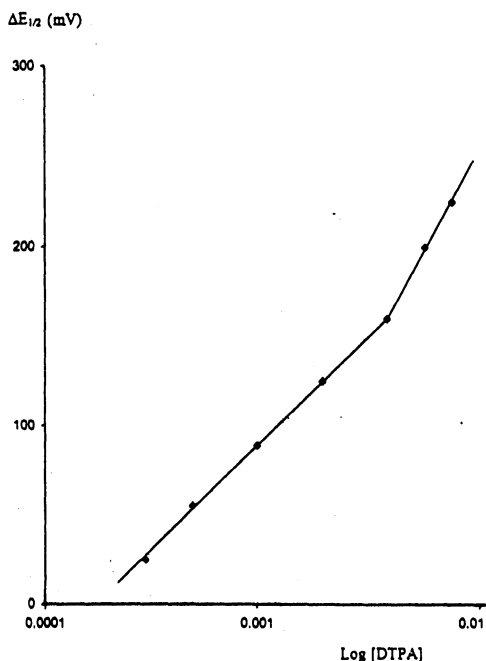


Fig. 5. Dependence of the values of ΔE_p as a function $\log[\text{DTPA}]$ at 1 M H_3PO_4

lated were respectively 4, 7 and 9 indicating three environments present in solution in our operation conditions. This provides that one Eu^{3+} ion was bonded either with 4 DTPA, 7 DTPA or 9 DTPA according to the DTPA concentration. Moreover, DTPA is a multidentate ligand and Eu^{3+} ion is able to accommodate as much as four DTPA molecules in its coordinate sites, which is in relation with the used DTPA amount. However, this complexation is also influenced by phosphoric acid medium, because the europium ion can form a complex with H_3PO_4 acid.

The addition of DTPA with different concentrations ranged from 3 M to 14.8 M H_3PO_4 ; the reduction peak of $\text{Eu}(\text{III})$ to $\text{Eu}(\text{II})$ ions was observed without displacement in mode impulse polarography. This is due only to the $\text{Eu}(\text{III})$ ion solvating by the H_3PO_4 acid and by the DTPA species.

In order to explain better, some differences of the europium behaviour in H_3PO_4 with or without DTPA species, we have used $R_0(\text{H})$ values in $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}$ (Table-3), given by Louis *et al.*^{18, 19} and we have calculated the potential peak via $R_0(\text{H})$ in H_3PO_4 -Eu-DTPA system (Fig. 6). The dependence of the potential E_p (marked) according to $R_0(\text{H})$ shows two segment lines, which proves the existence of two phenomena such as complexation and solvation processes that govern the electrochemical behaviour of europium ions in H_3PO_4 acid. From 0.1 M to 3 M H_3PO_4 , the reduction peak of $\text{Eu}(\text{III})/\text{Eu}(\text{II})$ system displaces to most negative values.

However, in the presence of the DTPA species, the electrochemical change was observed. The potential ΔE_p increases to most positive values when the H_3PO_4 concentration increases. Indeed, it has been demonstrated that the $\text{Eu}(\text{III})$ ions give a complex with phosphate groups such as $\text{Eu}(\text{HPO}_4)^+$ or $\text{Eu}(\text{H}_2\text{PO}_4)^{2+}$ complexes. The apparent normal potential of the $\text{Eu}(\text{III})/\text{Eu}(\text{II})$ system in H_3PO_4 decreases and

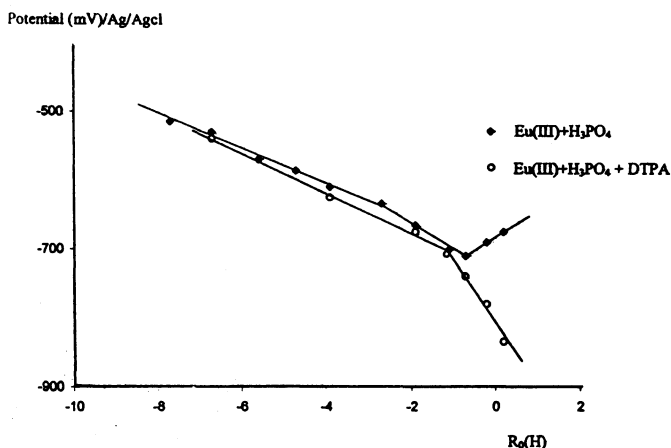


Fig. 6. Reduction potential peak E_p of Eu(III) ions vs. $R_0(H)$ of H₃PO₄ with and without DTPA ligands.

the Eu(II) becomes more reducing. This suitably intervenes a complexation phenomenon of Eu(III) ions. In concentrated values of H₃PO₄ superior to 3 M H₃PO₄, the potential shift displaces to most positive values which is related to the solvating phenomenon by H₂O molecules, when the phosphoric acid concentration increases whereas that of water decreases, the solvating process decreases and the electrochemical reactivity of Eu(III) ion increases. After, the reduction of Eu(III) becomes easy provided by the displacement of the reduction peak to less cathodic potentials. In H₃PO₄ with DTPA, the Eu(III) ion behaviour changes with $R_0(H)$ is different such as in H₃PO₄, but it is due to the different acidity effect on the complexation process. In addition, the Eu³⁺ ion should be complexed by both phosphate and DTPA species. The same results¹⁵ are obtained in Fe³⁺-H₃PO₄.

TABLE-3
R₀(H) ACIDITY VALUES AS A FUNCTION OF H₃PO₄ CONCENTRATION

[H ₃ PO ₄]	1.0	2.0	5.5	8.0	11.5	14.0
R ₀ (H)	+0.2	-0.2	-1.9	-3.2	-6.1	-8.9

The most suitable range of wavelengths for spectrophotometric measurements of Eu³⁺ ions in 1 M H₃PO₄ with or without DTPA shows the greatest difference of absorption spectra between the two solutions. The typical spectral curves are reported in Fig. 7. This shows the formation of Eu³⁺ ions in H₃PO₄ with or without DTPA species. The DTPA species being an multidentate ligands have been formed also very stable chelate complexes with alkaline earth ions and with others triply charged metal ions such as Sm(III) ions^{20, 21}. It is seen that ΔE_p for Eu-H₃PO₄-DTPA system varies with species concentration contained in solution. So, mixture complexes can be formed between the three species in solution as shown in UV- visible study.

Conclusion

The Eu(III)-DTPA system should be presented in stable form only in dilute phosphoric acid. Electrochemical and UV-visible data have demonstrated that the europium behavior changes with H₃PO₄ acidity and the used techniques are

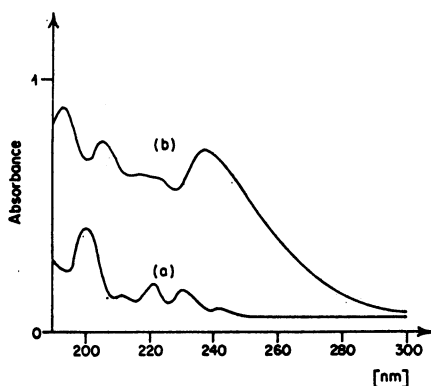


Fig. 7. Typical UV-visible spectra of europium species in 1 M H_3PO_4 without DTPA (a), and with DTPA species (b). $C_{\text{Eu(III)}} = 10^{-3}$ M.

considerably advantageous over other chemical methods of complex used formation. Consequently, the extraction of europium ions from phosphoric acid depends also on their concentration and the complexing effect.

REFERENCES

1. D. Binham and M. Dobroba, *J. Inorg. Biochem.*, **59**, 39 (1996).
2. X.Y. Ci and Y. Chen, *Chem. Journal of Chinese Universities (Chinese)*, **16** (1995).
3. X.Y. Yang, *Talanta*, **41**, 1807 (1994).
4. M. Tereda, T. Nakai and K.A. Mikami, *Inorg. Chim. Acta*, **222**, 377 (1994).
5. H. Ohno and H. Yoshihara, *Solid State Ionics*, **80**, 251 (1995).
6. B. Piriou, D. Fahmi, J. Dexpere, R. Loisean, A. Taitai and J.L. Lacout, *J. Luminescence*, **39**, 97 (1987).
7. A. Laghzizil, N. Elherch, O. Britel, A. Bouhaouss, M. Ferhat, *J. Fluorine Chem.*, **101**, 169 (2000).
8. J.C. Elliot, *Studies of Inorganic Chemistry*, p. 18 (1998).
9. J.O. Nriagu and P.B. Moore, *Phosphate Minerals*, Springer-Verlag (1984).
10. P. Becher, *Phosphates and Phosphoric Acid*, Marcel-Dekker, New York, Vol. 3 (1983).
11. L.M. Anderson and J.J. Macero, *J. Phys. Chem.*, **58**, 1577 (1963).
12. H.B. Silber, R.L. Campbelle, N. Nguyen, T. Parker and S.P. Sibley, *J. Alloys Compounds*, **225**, 291 (1995).
13. B. Timer, M. Shuruyters Rehbach and J.H. Shyters, *J. Electroanal. Chem.*, **14**, 18 (1967).
14. R. Harder and S. Chaberek, *J. Inorg. Nucl. Chem.*, **11**, 197 (1959).
15. B. Belqat, A. Laghzizil, A. Bouhaouss, K. Elkacimi and S. Belcadi, *J. Fluorine Chem.*, **105**, 1 (2000).
16. J.R. Van Vaser, *Phosphorous and Its compounds*, Interscience, New-York, p. 1, (1958).
17. Y.P. Galaktionov and K.V. Astakhov, *Russian J. Inorg. Chem.*, **8**, 724 (1963).
18. C. Louis and J. Bessiere, *Analytical Letters*, **13**, 937 (1980).
19. J. Bessiere, N. Tahani and C. Louis, *J. Chem. Engg., Data* **39**, 38 (1994).
20. S. I. Stenstrom, *Hydrometallurgy*, **18**, 1 (1987).
21. T.T. Tijioe, P. Weij, J.A. Wesselingh, G.M. Van Rosrnalen, *Solvent Extraction and Ion-exchange*, **6**, 505 (1988).