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pH-metric Studies and Electrochemical Behavior of Eu(III)-7-carboxymethoxy-4-methylcoumarin with 5'-GMP

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The interaction of Eu(III)-7-carboxymethoxy-4-methylcoumarin(CMMC) with guanosine-5′-momophosphate (5'-GMP) has been investigated using electron analytical, fluorescence, and potentiometric methods in the ethanol-water mixture solvent (0.15 volume fraction). The formation of the different binary, ternary, and quaternary complexes is confirmed by the corresponding pH-potentiometric curves. SUPERQUAD computer program has been used for the refinement of all the calculated constants in our present study. Electroanalytical techniques have been used to confirm the formation of different binary and ternary complexes under investigation. The binding constant of the ternary complex Eu(III)-CMMC-5'-GMP calculated by fluorescence technique was found to be 1.8 x 10^7 with 1:1 molar ratio. DNA cleavage properties of the CMMC, gibberellic acid, and their europium complexes were tested by gel electrophoresis.

Keywords: Potentiometry; Eu(III)-7-carboxymethoxy-4-methylcoumarin (CMMC); 5'-GMP binding properties; Voltammetry; Fluorescence spectroscopy.

1. INTRODUCTION

Guanine nucleotides play an important role in many biological processes related to signal transduction molecule, blood pressure [1], normal cellular, purine metabolism in hearts, and cardiac activities [2-5]. Guanosine-5′-monophosphate (5'-GMP) is a fundamental part of the synthesis of nucleic acids and metabolic processes [6, 7]. 5'-GMP is synthesized from xanthine monophosphate

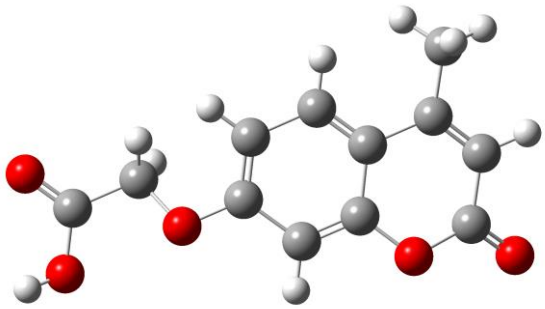
and is the starting material for the synthesis of other guanosine derivatives. It is very important to detect and determine GMP in biology and medicine. There are many techniques to detect 5'-GMP such as capillary electrophoresis [8], Fluorescence, UV spectrophotometry [9-11], High-performance liquid chromatography (HPLC) [12, 13], and high performance anion-exchange chromatographic methods [14]. Also, pH titration provides additional information regarding the binding sites on the 5'-GMP that is formed at different pH values. 5'-GMP can coordinate different lanthanide ions and lanthanide complexes in different binding modes [15].

Coumarin derivatives and their lanthanide complexes are interesting owing to their many biological activities such as antioxidant activity, anti-tumor [16], anti-inflammatory, and anticoagulant [17-23]. The lanthanide complexes have recently attracted much attention as fluorescence and electro probes for nucleotides and nucleic acids [24-30]. Our current measurements aim to study the interaction of Eu(III) ions with CMMC, and guanosine-5′-monophosphate (5′-GMP) by pH-potentiometric, electroanalytical, and fluorescence techniques. The DNA cleavage efficiency of the CMMC, gibberellic acid (GA) as hormone plant, and their europium complexes was tested agarose gel electrophoresis.

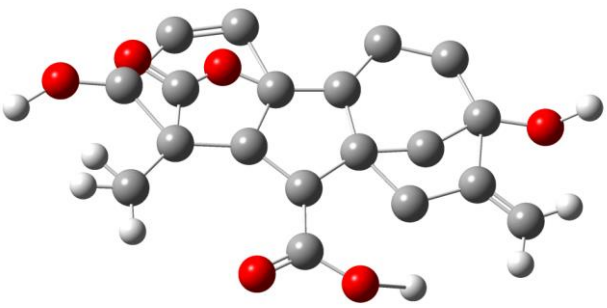
2. EXPERIMENTAL

2.1. Materials.

$Eu(NO_3)_3 \cdot 6H_2O$ and guanosine 5`-monohosphates (5`-GMP), gibberellic acid (GA) were of the Sigma Chemical Co. products. 7-carboxymethoxy–4-methylcoumarin (CMMC) was synthesized according to the literature [31, 32]. CMMC was recrystallized from ethanol (Mp 199-201) ^{0}C, lit.204-206 ^{0}C [31]. Confirmation of the structure of CMMC ($C_{12}H_{10}O_5$) has been carried out using elemental and Infrared (IR) analysis. Carbon (C) and Hydrogen (H) analysis; (calc.) C, 61.54; H, 4.3; found: C, 61.9; H, 4.9 and IR (KBr, cm^{-1}) 3424, 3045, 2925, 1734, 1606. Structures of 7-carboxymethoxy–4-methylcoumarin (CMMC) and gibberellic acid (GA) are shown in Figure 1.



A



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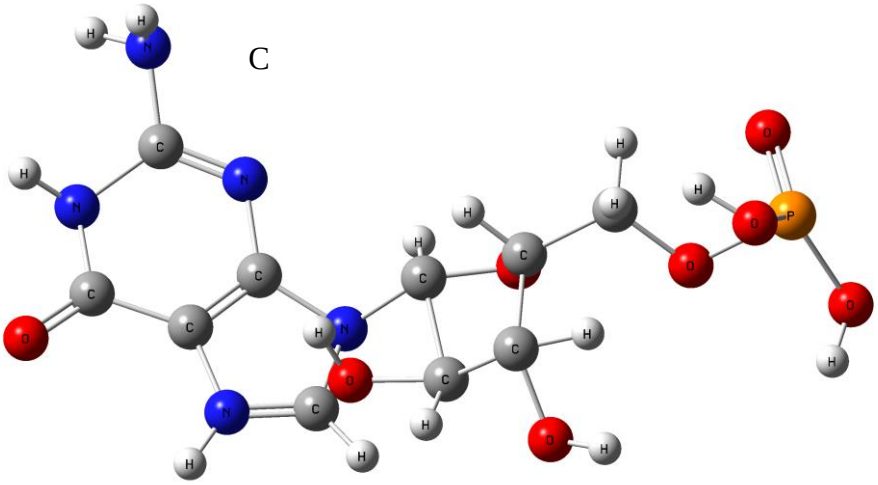

Figure 1. Structure of 7-carboxy methoxy-4-methylcoumarin (CMMC)(A), gibberellic acid (B), and guanosine 5`-monohosphates (5`-GMP).

Complexometric titration with EDTA [33] has been used to check the concentration of the metal ions in stock solutions. 0.1 mol dm^{-3} KNO_3 and the alcoholic solution of p-toluenesulfonate (Merck AG) were used to adjust the ionic strength of the solutions in potentiometric and electrochemical measurements, respectively.

2.2. Apparatus.

Voltammetry measurements were carried out using a 270 Electrochemistry System (EG&G, USA) in which platinum wire and saturated calomel electrodes (SCE) were used as counter and a reference electrodes. A glassy carbon electrode was used as a working electrode. Elementar vario and Bruker Alpha with KBr discs were used for elemental and IR analysis, respectively. A Jasco 6300 spectrofluorotometer was included in fluorescence measurements. pH measurements were carried out on (pH-220 L) pH- meter.

2.3. Procedure

The procedures for potentiometric measurements, electrode calibrations, and determination of dissociation constants were used as reported in our previous paper [34].

For the stability constant determinations the following schemes were used:

(a) 2.86 $x10^{-3}$ mol. dm^{-3} HNO_3 + $5x10^{-4}$ mol dm^{-3} CMMC;

(b) 2.86 $x10^{-3}$ mol. dm^{-3} HNO_3 + $5x10^{-4}$ mol dm^{-3} nucleotide (5′-GMP);

(c) solution (a) + $5x10^{-4}$ mol dm^{-3} Eu(III);

(d) solution (b) + $5x10^{-4}$ mol dm^{-3} Eu(III); and

(e) $2.86x10^{-3}$ mol.dm^{-3} HNO_3 + $5x10^{-4}$ mol dm^{-3} CMMC + $5x10^{-4}$ mol dm^{-3} nucleotide (5′-GMP) + 5 $x10^{-4}$ mol dm^{-3} Eu(III).

All the calculated formation constants of the systems under investigation have been refined using the SUPERQUAD [34, 35] computer program. The stability constant can be represented by

$$K_{M(P)(Z)} = \frac{[M_p(P)_q(Z)_r]}{[M_pP_q][Z]^r} \quad (1)$$

The overall complexation reaction involving protonation is

$$pM + qP + rZ + sH \rightleftharpoons M_p(P)_q(Z)_r(H)_s \quad (2)$$

$$\beta_{pqrs} = \frac{M_p(P)_q(Z)_r(H)_s}{[M]^p[P]^q[Z]^r[H]^s} \quad (3)$$

in which P = deprotonated nucleotide guanosine-5′-monophosphate, Z = CMMC ligand, M = Eu(III) ions. Hydrolysis side reactions for Eu(III) ions have been considered during refinements.

Cyclic voltammetry, square wave voltammetry, and differential pulse voltammetry are collected using the methods and conditions described elsewhere [33]. The following solutions

(a) 5 x 10^{-4} mol dm^{-3} Eu(III),
(b) 5 x 10^{-4} mol dm^{-3} Eu(III) + 5 x 10^{-4} mol dm^{-3} CMMC,
(c) 5 x 10^{-4} mol dm^{-3} Eu(III) + 5 x 10^{-4} mol dm^{-3} 5′-GMP,
(d) 5 x 10^{-4} mol dm^{-3} Eu(III) + 5 x 10^{-4} mol dm^{-3} CMMC + 5 x 10^{-4} mol dm^{-3} 5′-GMP.

2.4. DNA Cleavage Activity

The CMMC, GA, and their metal complexes are studied for their DNA cleavage activity by the agarose gel electrophoresis method against DNA of fish sperm. Tested samples (0.25 mg/mL) were prepared in dimethyl sulfoxide (DMSO). The test samples were incubated with the DNA of fish sperm for 2h at 37^{o}C. The mixtures of DNA samples with the analyte (1:1) were loaded into agarose electrophoresis chamber (1g agarose dissolved in 100ml of tris-borate EDTA (TBE) buffer with 5µ of ethidium bromide) for 30 minutes at 80V. The gel was visualized by gel documentation (BioRad) by using image lab software [35].

3. RESULTS AND DISCUSSION

3.1. pH-potentiometric measurements

Potentiometric equilibrium measurements for the interaction between Eu(III), CMMC and 5′-GMP have been carried out in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} KNO_3. Representative titration curves are shown in Figures 2 and 3 for different complex systems under investigation. The acid dissociation constants for 7-carboxymethoxy-4-methylcoumarin (CMMC) are 3.90 $\pm$ 0.02 and 10.20 $\pm$ 0.02 referred to the deprotonation constant of the carboxylate

group and oxygen of coumarin ring. The obtained values agree well with previous studies on coumarin derivative [36]. The dissociation constant of nucleotide molecule 5′-GMP is 9.50± 0.02 referred to the deprotonation of N1H and the values agree with those found in the literature [37].

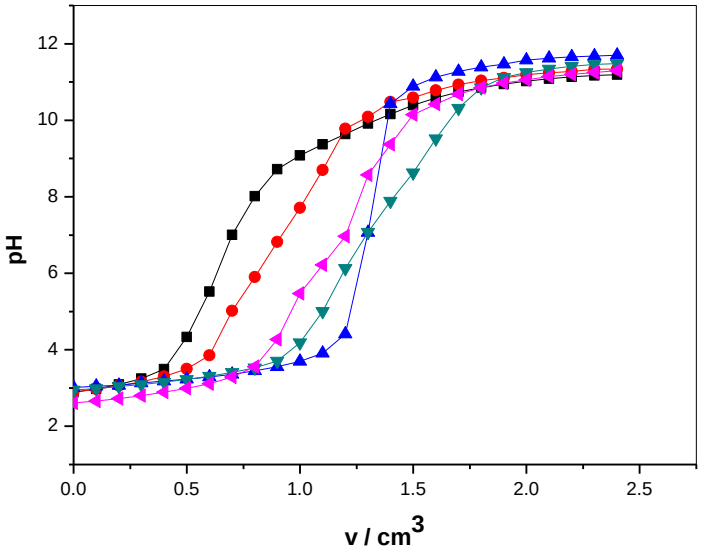

Figure 2. pH against volume of 0.022 mol dm^{-3} KOH for Eu(III)+ 5′-GMP + CMMC system in 15%v/v ethanol-water mixture, I=0.1 mol dm^{-3} KNO_3 at 25°C. (a) ■ 2.86 x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} 5′- GMP. (b) ● 2.86x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} 5′- GMP + 5x10^{-4} mol dm^{-3} Eu(III). (c) ▲ 2.86 x10^{-3} mol dm^{-3} HNO_3 5x10^{-4} mol dm^{-3} CMMC. (d) ▼ 2.86 x10^{-3} mol dm^{-3} HNO_3+ 5x10^{-4} mol dm^{-3} CMMC+ 5x10^{-4} mol dm^{-3} Eu(III). (e) ◄ 2.86 x10^{-3} mol dm^{-3} HNO_3+5x10^{-4} mol dm^{-3} 5′-GMP + 5x10^{-4} mol dm^{-3} CMMC + 5x10^{-4} mol dm^{-3} Eu(III).

Table 1. Formation constant comparisons for the binary complexes in 1:1 and 1:2 ratios in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} KNO_3 at 25°C.

Complex species	Log K1	Log K2	Reference
Eu(III)(CMMC)	7.84± 0.02	8.55± 0.02	This work
Eu(III)(5′-GMP)	4.66± 0.03	4.5±0.03	This work
	5.26± 0.04	-	49
	5.25	5.7	48
Cu(II)(5′-GMP)	3.3	-	50
Cd(II)(5′-GMP)	2.98	-	51
Al(III)(5′-GMP)	3.49 ± 0.02	-	52
Tl(I)(5′-GMP)	2.98	-	53

The stability constant comparisons for Eu(III)-CMMC and Eu(III)-5′-GMP in 1:1 and 1:2 molar ratio are given in Table 1. The formation constant of the Eu(III)-(CMMC) complex is 8.55 ± 0.02 indicating the binding between Eu(III) ions and the carboxylate group of 7-carboxymethoxy-4-

methylcoumarin ligand(CMMC). The equilibrium constants of the interaction of different metal and lanthanide ions with nucleotides in solution have been extensively studied by various techniques such as pH-metric [37-40], spectrophotometric titration [41], NMR [42-45], and calorimetry [46-48]. For purine nucleoside 5`-monophosphates, the metal ion is bound to (N7) and hydrogen bonding with phosphate group via water molecules of the metal coordination [39, 48]. The formation constants of Eu(III) with 5′-GMP in 1:1 and 1:2 molar ratio are an inconsistency with that previously reported in the literature [37, 48].

Figure 2 shows the titration curves for the formation of the Eu(III)-5′-GMP-CMMC ternary complex with 1:1:1 molar ratio which can be represented by the following equations

$$Eu(III) + 5'\text{- GMP} \rightleftharpoons Eu\ (III)\ \text{-}5'\text{-}\ GMP \quad (4)$$

$$Eu(III)\ \text{-}5'\text{-}\ GMP + CMMC \rightleftharpoons Eu(III)\ \text{-}\ 5'\text{-}\ GMP\text{-}\ CMMC \quad (5)$$

where the complex is formed with the formation constant (log K) equals 7.08± 0.02.

Titration curves for the formation of Eu(III)-5′-GMP-CMMC(1:2:1) and Eu(III)-5′-GMP-CMMC(1:1:2) are depicted in Figure 3. The calculated formation constants as given in Table 2 are 3.47± 0.02 and 9.01± 0.02, respectively. The formation of Eu(III)-5′-GMP-CMMC in (1:1:2) occurs via the mechanism:

$$Eu\ (III)(\ 5'\text{-}GMP)(CMMC) + CMMC \rightleftharpoons Eu(III)\text{-}5'\text{-}GMP\text{-}\ (CMMC)_2 \quad (6)$$

The formed quaternary complex has a formation constant of 9.01± 0.02. The formation of Eu(III)-5′-GMP-CMMC in 1:2:1 takes place via the mechanism

$$Eu\ (III)\ \text{-}5'\text{-}\ GMP\text{-}\ CMMC + 5'\text{-}\ GMP \rightleftharpoons Eu(III) - (5'\text{-}GMP)_2(CMMC) \quad (7)$$

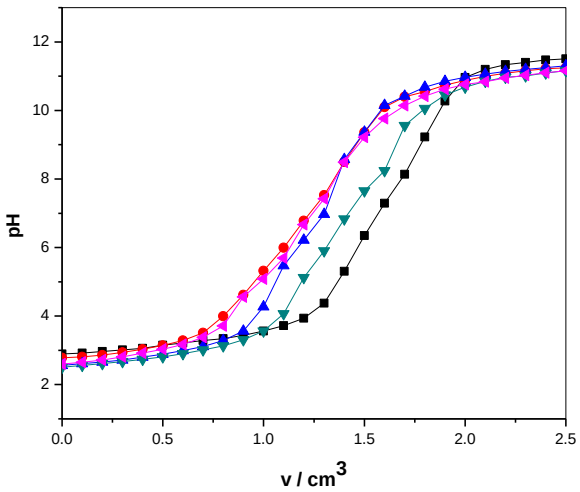

Figure 3. pH against volume of 0.022 mol dm^{-3} KOH for Eu(III) + 5′-GMP+CMMC system in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} KNO_3 and at 25°C. (a) ■ 2.86x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} Eu(III)+ 1x10^{-3} mol dm^{-3} CMMC. (b) ● 2.86x10^{-3} mol dm^{-3} HNO_3+ 5x10^{-4} mol dm^{-3} Eu(III) + 1x10^{-3} mol dm^{-3} 5′-GMP. (c)▲2.86x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} Eu(III) + 5x10^{-4} mol dm^{-3} 5′-GMP+ 5x10^{-4} mol dm^{-3} CMMC. (d) ▼ 2.86x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} Eu(III) + 5x10^{-4} mo dm^{-3} 5′-GMP+ 1x10^{-3} mol dm^{-3} CMMC. (e) ◄ 2.86x10^{-3} mol dm^{-3} HNO_3 + 5x10^{-4} mol dm^{-3} Eu(III) +1x10^{-3} mol dm^{-3} 5′-GMP+ 5x10^{-4} mol dm^{-3} CMMC.

The quaternary system of Eu(III)-5′-GMP-$(CMMC)_2$ gives higher stability than Eu(III)–$(5'-GMP)_2$(CMMC). The latter acquires low formation constant equals 3.47± 0.02 which can be attributed to the steric hindrance for the including of two nucleotide molecules in this system. This finding is agreed with the literature [37]. Representative distribution curves for the systems under investigation are given in Figure 4.The monoprotonated ternary complex, Eu(III)-5′-GMP-CMMC, starts to form at pH~3 reaching its maximum concentration at pH~6.5.

Table 2. Formation constants of the quaternary complex species formed in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} KNO_3 and at 25°C.

Complexes species	Log K	Log β
Eu(III)(5′-GMP)($CMMC)_2$	9.01±0.03	16.09±0.03
Eu(III)$(5'-GMP)_2$(CMMC)	3.47±0.02	10.55±0.02

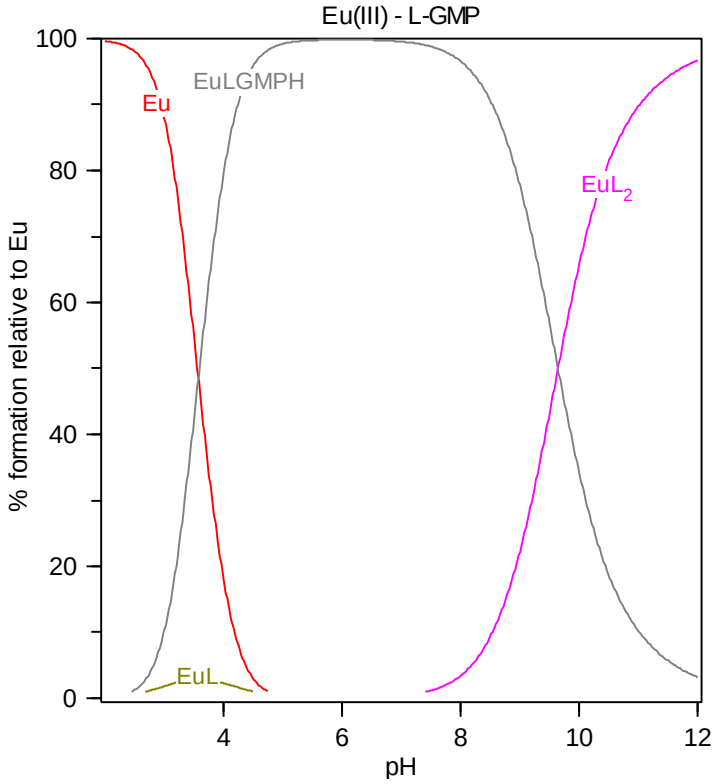

Figure 4. Distrebution curves for protonated ternary system Eu(III)-CMMC–GMP and Eu(III)-$(CMMC)_2$ binary system under investigation, L=CMMC.

3.2. Electrochemical studies

In the present study electrochemical methods including differential pulse voltammetry (DPV), cyclic voltammetry (CV), and square wave voltammetry (SWV) carried out on the glassy carbon

electrode confirmed the formation of Eu(III)-CMMC-5′-GMP in solution as shown in Figures 5 to 10. This observation agrees will with the potentiometric results. CV studies confirmed the reversibility of the electrochemical reactions for the ternary systems under investigation. More than 80 mV as peak separation between the anodic and cathodic peaks indicates the quasireversible nature of the electrochemical reduction of the free Eu(III) ions as well as both the binary and ternary complexes formed in solution at the glassy carbon electrode.

3.2.1. Electrochemical Studies on the Interaction of Eu(III) with CMMC.

The cyclic voltammograms for the free ligand (7-caboxymethoxy-4-methylcoumrin) as shown in Figure 5 using glassy carbon working electrode at I = 0.1 mol dm^{-3} p-toluenesulfonate and at 25 ^{o}C. The free ligand doesn't exhibit reduction or oxidation peak within the studied potential range -0.30 to -0.90 V. Figure 5 shows the interaction of Eu(III) with the ligand in the molar ratio of Eu(III)CMMC (1:2). The Eu(III)-CMMC in 1:2 ratio has a considerable decrease in the cathodic current which could be attributed to the decrease in the concentration of Eu(III) ions in the bulk solution due to the higher affinity of complexation with two molecules of the ligand.

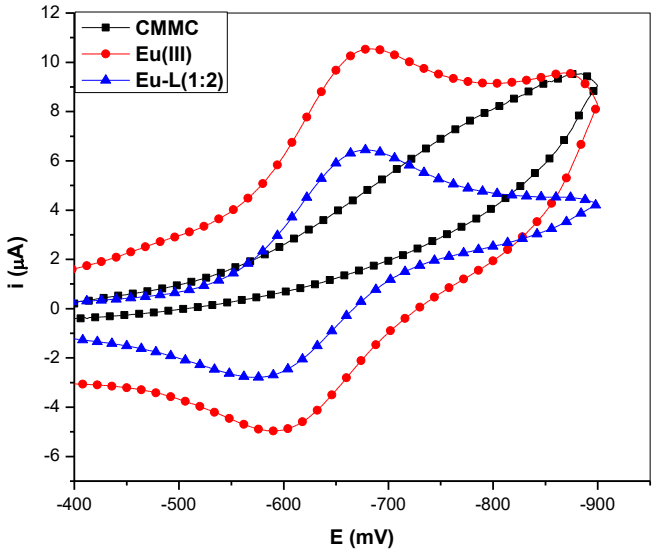

Figure 5. Cyclic voltammograms for the free ligand (2-(4-methyl-2-oxo-2H-chromen-7-yloxy) acetic acid) CMMC, Eu(III), and Eu(III)–CMMC (L) binary complex in 0.15 volume fraction ethanol-water mixture solvent, I=0.1 mol dm^{-3} p-toluenesulfonate,ν = 100 mVs^{-1}, and at 25.0 ^{o}C., L=CMMC.

The differential pulse voltammograms (Figure 6) are confirmed the interaction between Eu(III) ions and CMMC. The reduction of Eu(III) ions in solution show a cathodic peak (E_p) at -0.630 V using scan rate 100 $mV{\cdot}s^{-1}$ which is corresponding to Eu(III)/Eu(II) redox system. This peak can be assigned to the reduction of Eu(III) to Eu(II) via a one electron transfer process. Generally, the

addition of CMMC to Eu(III) solution results in a shift of the cathodic peak to a more negative potential indicating the formation of the binary complexes in solution.

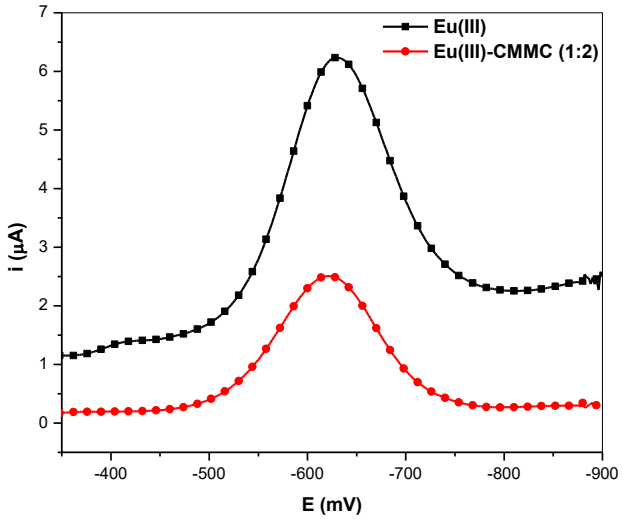

Figure 6. Differential pulse voltammograms for the Eu(III) and Eu(III)–CMMC binary complexes in 0.15 volume fraction ethanol-water mixture solvent, I= 0.1 mol dm^{-3} p-toluenesulfonate, ν = 15 mVs^{-1} and at 25.0 ^{o}C

The square wave voltammetry for the formation of Eu(III) and Eu(III)-CMMC has been investigated as displayed in Figure 7. The Eu(III)-CMMC complex shows the maximum wave at the potential of -0.696 mV which is shifted to more negative potential with increasing CMMC concentration, indicating a considerable interaction between the Eu(III) metal ion and CMMC under experimental conditions.

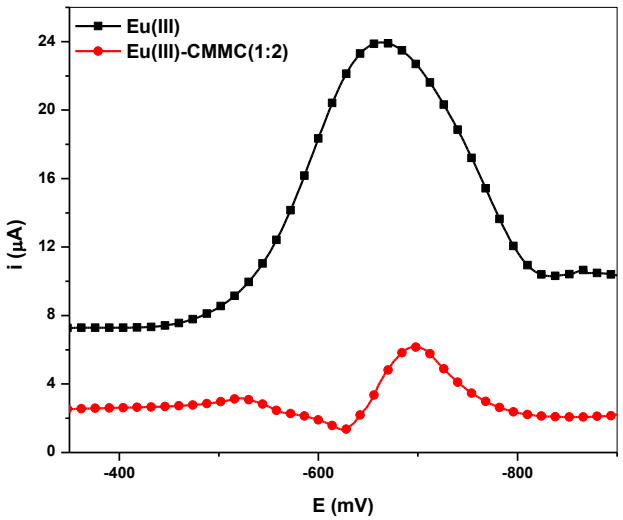

Figure 7. Square wave voltammograms for the Eu(III) and Eu(III)-CMMC binary complexes in 0.15 volume fraction ethanol-water mixture solvent, I=0.1 mol dm^{-3} p-toluenesulfonate, f = 40 Hz, and at 25.0 ^{o}C

3.2.2. Electrochemical Investigation of the Interaction of Eu(III)-CMMC with 5'-GMP.

To the author's knowledge, no data for the ternary and quaternary complexes of lanthanide coumarin derivatives with nucleotide monophosphates are available in the literature for comparison. The electrochemical properties of 5`-GMP have been previously investigated by Goyal et.al [54, 55] and other authors [56, 57]. The cyclic voltgramms of 5`-GMP at a pyrolytic graphite electrode (PGE) within the electrode potential range of -0.30 to 1.20 V is displayed one well defined oxidation peak and three cathodic peaks which were dependent on pH and shift to more negative with increasing pH value [58]. The 5`-GMP doesn't exhibit oxidation or reduction peak within the investigated potential range -0.35 to -0.90 V which corresponds to the electrochemical active range of Eu(III) metal ion. The three voltammograms for Eu(III), Eu(III)-5-GMP(1:1) and Eu(III)-5′-GMP-CMMC (1:1:1) are shown in Figure 8. The cyclic voltammograms for the reaction of the aquated lanthanide metal ion $[Eu(H_2O)_9]^{3+}$ with 5'-GMP is clearly observed that the coordination of the nucleotide molecule to the lanthanide metal ion is accompanied by a shift in the reduction potential to more negative which may be attributed to the formation of more stable complex than the aquated one. The voltammogram for the ternary complex in1:1:1 ratio is shifted towards more negative potential with a decrease in the reduction current than that for Eu(III)-5′-GMP(1:1). Thus, the mechanism of formation of the ternary complex may be represented as equations 5 and 4.

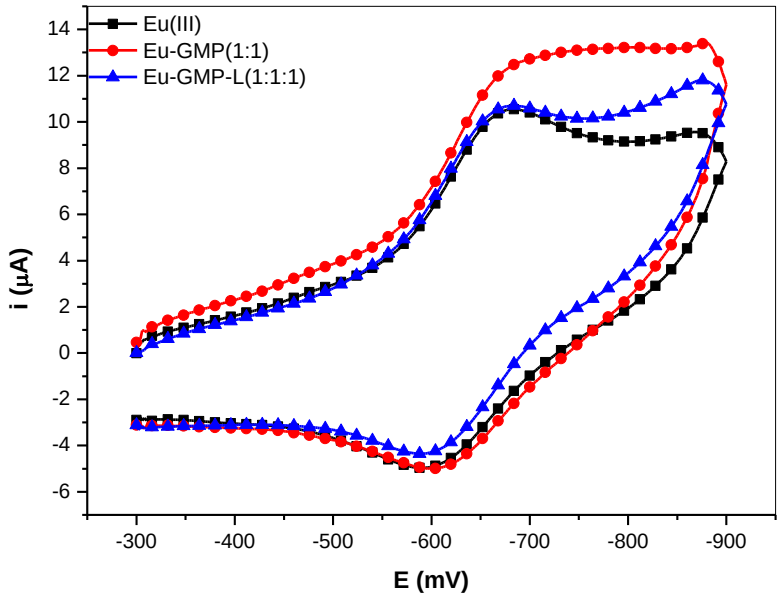

Figure 8. Cyclic voltammograms for the Eu (III) + 5'-GMP + CMMC (1:1:1) system in comparison to Eu(III) + 5'-GMP (1:1), in 0.15 volume fraction ethanol-water mixture solvent, I=0.1 mol dm^{-3} p- toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^{o}C., L=CMMC.

In contrary as depicted in Figure 9 where the three voltammograms for Eu(III), Eu(III)-CMMC and Eu(III)-5′-GMP-CMMC are collected, there is no appreciable change in cathodic potential or current which mean that the following mechanism is not favored for the formation of the ternary complex.

$$Eu(III) + CMMC \rightleftharpoons Eu(III)\text{-}CMMC \quad (8)$$

$$Eu(III)\text{-}CMMC + 5'\text{-}GMP \rightleftharpoons Eu(III)\text{-}CMMC\text{-}5'\text{-}GMP \quad (9)$$

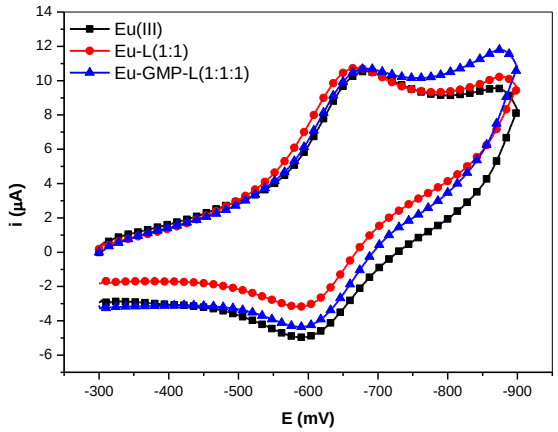

Figure 9. Cyclic voltammograms for the Eu(III) + 5'-GMP + CMMC (1:1:1) system in comparison to Eu (III) + CMMC (1:1) in 0.15 volume fraction ethanol- water mixture solvent , I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^{o}C., L=CMMC.

3.2.3. Electrochemical parameters

The ratio of the anodic and cathodic peak currents shows that the kinetics of the oxidation and reduction of the Eu(III) binary and the ternary system is not reversible but nevertheless quasi-reversible. The correlation between the cathodic and anodic peak currents (ip_c and ip_a) and the square root of scan rate $\nu^{1/2}$ are depicted in Figures 10 and 11 which reveals that the electrochemical processes are controlled by the diffusion mechanism.

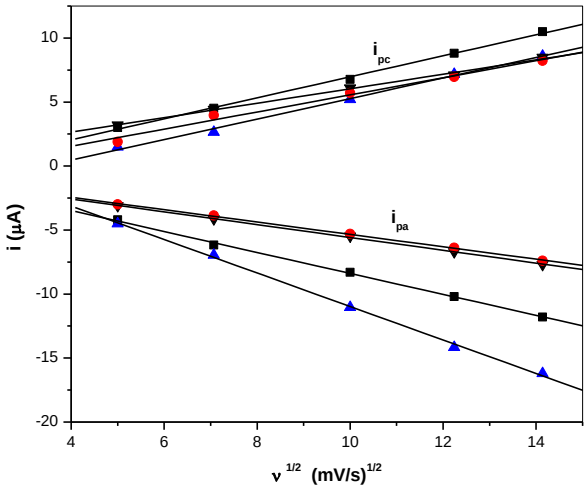

Figure 10. Correlation between cathodic peak current (i_{pc}), anodic peak current (i_{pa}) with square root of scan rate ($\nu^{1/2}$) for Eu(III)-CMMC (■ 1:1and 1:2) and for Eu(III)-5'-GMP (▲ 1:1, and ▼1:2) binary complex in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^{o}C, $C_{Eu(III)} = 5x10^{-4}$ mol dm^{-3}.

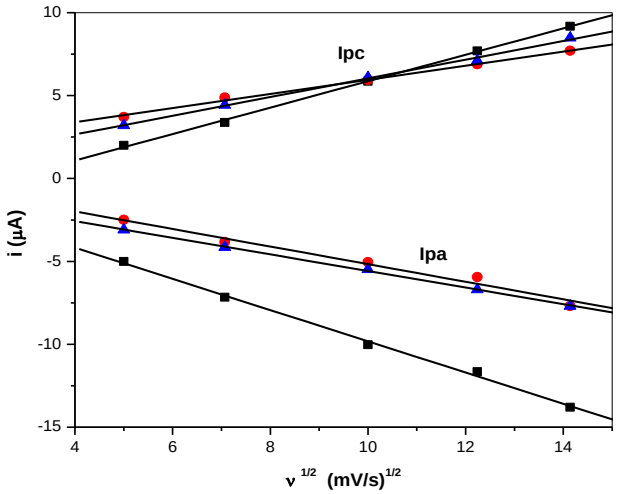

Figure 11. Correlation between cathodic peak current (ipc), anodic peak current (ipa) with square root of scan rate ($\nu^{1/2}$) for Eu(III)-5'-GMP-CMMC ternary complex (■ 1:1:1and ● 1:2:1) and ▲ 1:1:2) in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 °C., $C_{Eu(III)}$ = 5 x10^{-4} mol dm^{-3}.

Also, the correlation between the (E_{pc}) and log scan rate (logν) are plotted as shown in Figures 12 and 13. The obtained straight lines are of slopes ranging from 0.011 to 0.027 which confirm the quasi reversible behavior for the studied systems.

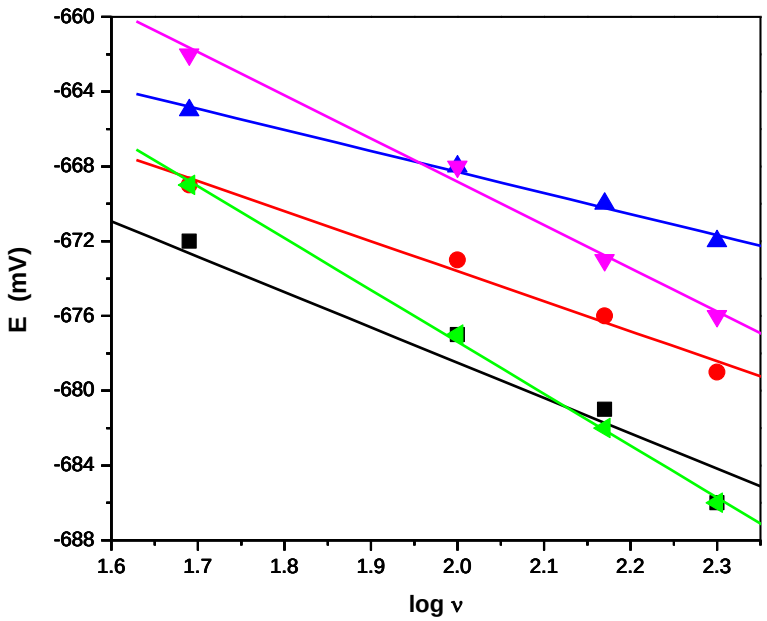

Figure 12. Correlation between cathodic peak potential (Ep_c) and log ν for ■ Eu (III) free metal ion, 1:0.5,▲ 1:1,▼ 1:2, and◄ 1:3 Eu(III)-CMMC in 0.15 volume fraction ethanol-water mixture solvent , I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 °C

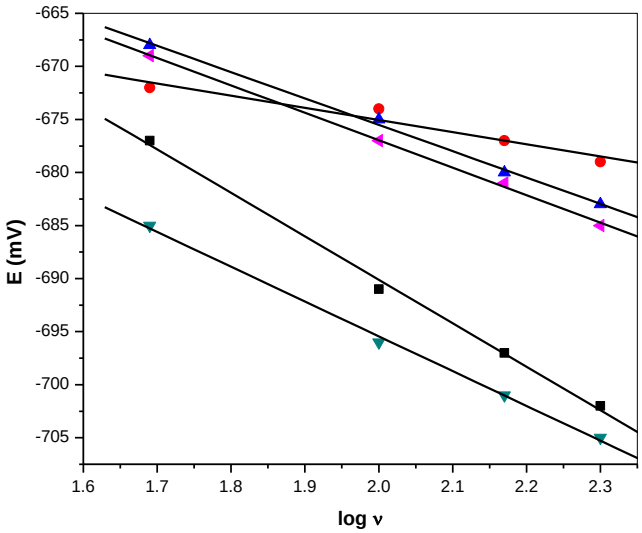

Figure 13. Correlation between cathodic peak potential (Ep_c) and log ν for Eu(III)-5'-GMP (■ 1:1, 1:2) and Eu(III)-5'-GMP-CMMC (▲ 1:1:1, ▼ 1:2:1, and ◀ 1:1:2) in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^oC.

Table 4. Voltammetric data for Eu (III) + CMMC, Eu (III) + 5'-GMP binary and Eu (III) + 5'-GMP + CMMC ternary complexes in different metal: ligand ratios in 0.15 Volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, and at 25 ^oC.

System	E_{pc} mv	E_{pa} mv	$E_{p/2}$ mv	E^o mV	ip_a/ip_c	ΔE mV	α	$D_{ox}\ 10^{-7}$ $cm^2.s^{-1}$	$D_{red}\ .\ 10^{-7}$ $cm^2.s^{-1}$	$K_s\ .\ 10^{-6}$ $cm.s^{-1}$
Eu(III)	-684	-590	-619	637	1.53	94	0.73	12.95	5.47	1.62
Eu-CMMC (1:0.5)	-678	-582	-602	630	1.20	96	0.62	9.48	6.55	0.604
Eu-CMMC (1:1)	-668	-586	-596	627	1.19	82	0.66	10.19	7.09	0.6
Eu–CMMC (1:2)	-678	-574	-607	626	0.94	104	0.67	4.1	4.61	0.279
Eu-CMMC (1:3)	-674	-576	-599	625	1.105	98	0.63	8.46	6.93	0.56
Eu-5'-GMP (1:1)	-691	-598	-635	644	2.12	93	0.68	17.4	3.89	0.546
Eu-5'-GMP (1:2)	-674	-588	-606	631	0.9	86	0.70	3.74	4.19	0.276
Eu-5'-GMP (1:3)	-693	-607	-626	650	1.25	86	0.71	3.04	1.97	0.159
Eu-5'-GMP-CMMC (1:1:1)	-674	-589	-618	631	1.71	85	0.85	14.76	4.94	0.655
Eu-5'-GMP-CMMC (1:2:1)	-696	-580	-617	638	0.85	116	0.60	3.65	5.08	0.27
Eu-5'-GMP-CMMC (1:1:2)	-677	-587	-605	632	0.89	90	0.66	4.91	5.35	0.336

Randles Sivick equation [59] can be used for calculation of diffusion coefficients for different species during the oxidation reduction reaction

$$i_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} \nu^{1/2} C \quad (10)$$

where 2.69×10^{-5} is a collection of constants at 25 ^oC, i_p, n, A, D, ν and C are the peak current, the number of electrons transferred, the electrode area (cm^2), the diffusion coefficient ($cm^2\ s^{-1}$), the scan rate ($V\ s^{-1}$), and the concentration of species, respectively. The value of D_{red} of Eu(III)-CMMC (1:1) is higher than that for the free metal ion Eu(III) and Eu(III)-5′-GMP(1:1) as indicated in Table 4. The diffusion coefficient D_{red} for Eu(III)-5′-GMP -CMMV(1:1:1) is lower than that of Eu(III)-CMMC (1:1). The diffusion coefficient D_{ox} for Eu(II)-CMMC doesn't changed greatly compared to free metal ion, while for Eu(II)-5′-GMP the D_{ox} is higher than that of Eu(II) ion and Eu(II)-CMMC binary complex. The ternary complex Eu(II)-5′-GMP-CMMC in 1:1:1 ratio acquires higher D_{ox} value than the corresponding Eu(II)-CMMC binary.

The standard rate constant for the electron transfer can be represented by the separation of the peak potentials, ΔE_p. Values of ΔE_p calculated during our extensive analysis for the different voltammograms were used for the calculation of transfer parameter, Ψ, by the aid of the working curve described by Nicholson [60]. Then standard heterogeneous charge-transfer rate constant (*K*s) for the electron-transfer process has been calculated by the following equation:

$$\Psi = \frac{(D_O / D_R)^{(\frac{\alpha}{2})} K_S}{D_O \pi \nu (\frac{nF}{RT})^{1/2}} \quad (11)$$

In which the diffusion coefficients for oxidized and reduced species are represented by D_O and D_R, respectively. Equation (19) was used to calculate the transfer coefficient (α) [61]

$$\alpha = \frac{1.857\, R\, T}{nF\left[E_p - E_{p/2}\right]} \quad (12)$$

where E_p is the peak potential (V) and $E_{p/2}$ is the half-peak potential, (F) is Faraday's constant, (R) is the gas constant($J\ mol^{-1}\ K^{-1}$), and (T) is the temperature (K). Electrochemical characteristics and kinetic parameters of the systems studied are listed in Table 4.The standard rate constant *K*s of Eu(III)-CMMC (1:1) doesn't change appreciably compared to Eu(III)-5'-GMP-CMMC ternary complex in 1:1:1 ratio. Upon forming the ternary complex the rate constant for 1:1:1 species is higher than that of Eu(III)-5′-GMP complex in 1:1.

For the quaternary complex Eu(III)-$(5'\text{-GMP})_2$-MMC (1:2:1), The proposed mechanism is postulated as in Equations 7, where the ternary complex in 1:1:1 is formed when a molecule of the nucleotide will attack this complex forming the quaternary one. The other proposed mechanism is

$$\text{Eu(III)-}(5'\text{-GMP})_2 + \text{CMMC} \rightleftharpoons \text{Eu(III)-}(5'\text{-GMP})_2\text{-CMMC (1:2:1)} \quad (13)$$

In the latter mechanism, the binary complex of metal: nucleotide in 1:2 ratios reacts with CMMC to form the quaternary complex. The cyclic voltammograms for the 1:2:1 quaternary complex compared to the binary complex Eu(III)-$(5'\text{-GMP})_2$(1:2) and the ternary complex Eu(II)-5′-GMP-L(1:1:1) displayed in figure (14A) don't acquire appreciable change in reduction or oxidation potentials and current which means that mechanism (13) is not the favorable one.

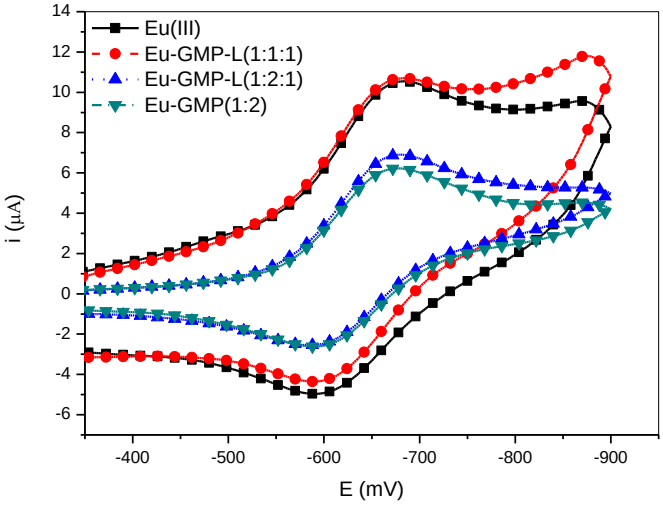

Figure 14. A Cyclic voltammograms for the Eu (III) + 5'-GMP+CMMC (1:2:1) system in comparison to Eu (III) +5'-GMP (1:2) & Eu (III) + 5'-GMP+CMMC (1:1:1) system, in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^{o}C., L=CMMC.

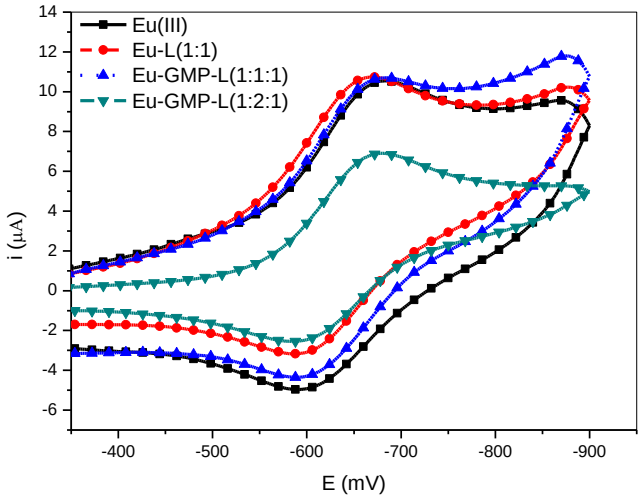

Figure 14. B Cyclic voltammograms for the Eu (III) + 5'-GMP + CMMC (1:2:1) system in comparison to Eu(III)+CMMC(1:1) & Eu(III)+5'-GMP+CMMC (1:1:1) system, in 0.15 volume fraction ethanol-water mixture solvent, I = 0.1 mol dm^{-3} p-toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^{o}C., L=CMMC.

The decrease in cathodic current for the voltammogram of Eu(III)-5′-GMP-CMMC upon interacting with 5′-GMP forming Eu(III)-(5′-GMP)$_2$-CMMC such decrease in cathodic current may be a good indication of the mechanism (7). Inspecting also the voltammograms in Figure (14B) to compare the curves for Eu(III)-CMMC(1:1), Eu(III)-5′-GMP-CMMC (1:1:1) and the quaternary species Eu(III)-5′-GMP-CMMC (1:2:1) no definite mechanism could be proposed. Figure 15 displays the cyclic voltammograms for the quaternary complex species Eu(III)-5'-GMP-(CMMC)$_2$(1:1:2) ratio in comparison to Eu(III)-5'-GMP(1:1) and the ternary complex Eu(III)-5'-GMP-CMMC(1:1:1), while

the volammograms for the quaternary complex (Figure 15b) is compared with the binary one Eu(III)-CMMC (1:2) and the ternary complex species (1:1:1).The data reveals that the proposed mechanism of formation of the quaternary one may tack place via Equation 6. Where the ternary complex is formed at first then the second molecule of ligand (CMMC) will attack the ternary complex forming the quaternary one. On the other hand, the second proposed mechanism (Eq.14) is not favored.

$$\text{Eu(III)-CMMC (1:2)} + 5'\text{-GMP} \leftrightarrow \text{Eu(III)}(5'\text{-GMP})(\text{CMMC})_2 \quad (14)$$

The diffusion coefficient of the formed quaternary species (D_{red}) is higher than the corresponding values for the ternary complex species Eu(III)-5'-GMP–CMMC(1:1:1), the binary Eu(III)-CMMC(1:2), or Eu(III) 5'-GMP (1:2) as shown in the table 4.

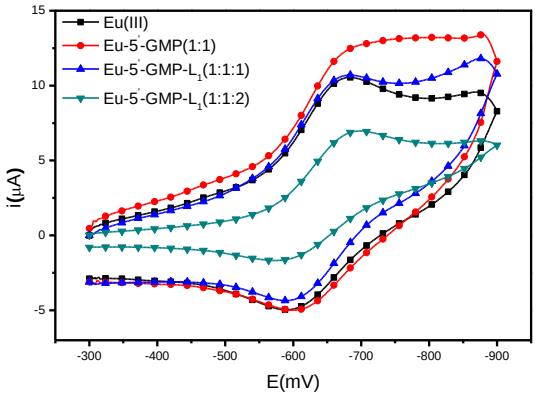

Figure 15. A Cyclic voltammograms for the Eu(III) + 5'-GMP + CMMC (1:1:2) system in comparison to Eu (III) + 5'-GMP (1:1) & Eu(III) + 5'-GMP + CMMC (1:1:1) system, in 15% v/v ethanol-water mixture, I=0.1 mol dm^{-3} p- toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^oC.

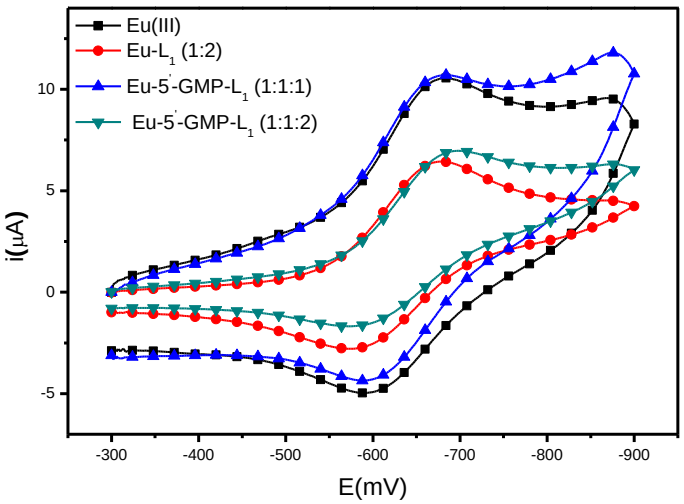

Figure 15. B Cyclic voltammograms for the Eu(III) + 5'-GMP + CMMC (1:1:2) system in comparison to Eu(III) + CMMC (1:2) & Eu(III) + 5'-GMP + CMMC (1:1:1) system, in 15% v/v ethanol-water mixture, I=0.1 mol dm^{-3} p- toluenesulfonate, ν = 100 mVs^{-1}, and at 25.0 ^oC., L=CMMC.

3.3. Comparison the stability constants between binary, ternary, quaternary complexes

According to Sigel [62], The stability constant of ternary complex Eu(III)-5'-GMP-CMMC (1:1:1) in comparison to Eu(III)-5'-GMP and Eu(III)-CMMC (1:1) binary complexes, one may consider the following equation:

$$\Delta \log K_{M} = \log \frac{Eu(III)-5'-GMP}{Eu(III)-5'-GMP-CMMCn} - \log \frac{Eu(III)}{Eu(III)-CMMCn} \quad (15)$$

$n = 1$ *or* 2

The Δ log KM value for Eu(III)-5'-GMP-CMMC (1:1:1) is a negative value. Whereas, the negative values showed that the ternary complexes are less stable than binary complexes, because of having the steric hindrance between various groups present in nucleotide monophosphate and coumarin moiety. The positive value of the quaternary complex Eu(III)-5'-GMP-CMMC (1:1:2) is more stable than both binary Eu(III)-CMMC (1: 2) and ternary Eu(III)-5'-GMP-CMMC (1:1:1) complexes [37,63].

3.4. Fluoresce spectra of the interaction of Eu(III)-CMMC with 5′- GMP

The fluorescence spectrum of Eu(III)-(CMMC) complex displays the characteristic emission bands of Eu(III) ion and maximum at 383 nm for ligand nucleus. The emission band of Eu(III)-$(CMMC)_2$ complex centered at 615 nm ($^5D_0 \rightarrow {}^7F_2$) is higher than that at 591 nm ($^5D_0 \rightarrow {}^7F_1$) and 645 nm ($^5D_0 \rightarrow {}^7F_3$), indicating that the Eu(III) ion is in a center of symmetric coordination site [24].

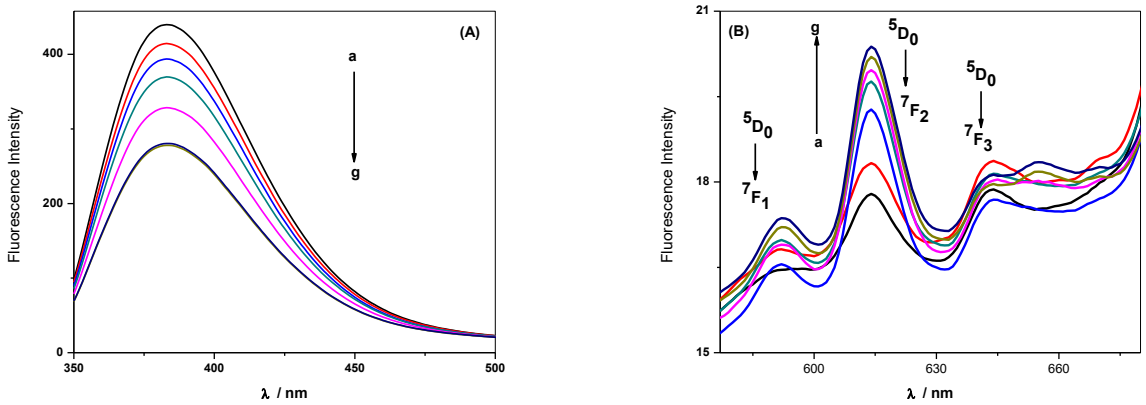

Figure 16. Effect of addition of 5'-GMP on emission spectra of Eu(III)-(CMC) complex in ethanol. (A): 383 nm; (B): 616 nm. 5'-GMP (x 10^{-6} M), a=0.0; b=1; c=2; d=4; e=6 f= 8, and g=10.

Azab et al [37] investigated the luminescence of Eu(III)-5`-GMP binary complex. The spectrum of this binary complex did not show a characteristic emission bands for Eu(III) ion under experimental conditions (depicted only the stray light of the excitation wavelength), indicating there is no pronounce energy transfer from the excited triplet state of 5`-GMP molecule to the $^5D_0$ excited

states of Eu(III) ions. Addition 5'-GMP for the Eu(III)-(CMMC) solution results in quenching the fluorescence intensity at 383 nm and enhance the emission at 616 nm as shown in Figure 16. As previously reported by various authors [64, 65], guanosine monophosphate nucleotide enhances the lanthanide ion emission whereas the other nucleotides do not. The above result means that the combination of 5′-GMP with Eu(III)-CMMC complex decreases the energy gap between the excited triplet state of CMMC and $^5D_0$ excited states of Eu(III) and prompts the probability of energy transfer from CMMC to Eu(III) ion.

The change in the fluorescence intensity can be employed to calculate the binding constant between Eu(III)-(CMMC) and 5'-GMP using the following relationship [66]

$$\frac{1}{\Delta F} = \alpha + \frac{\alpha}{\mathrm{K}\quad [DNA]} \quad , \; \alpha = \frac{1}{F_0(F_0 - F_l)} \tag{16}$$

where ΔF is the fluorescence intensity difference in the absence (F_0) and presence of DNA (F), respectively. F_l is the limiting intensity of fluorescence and α is $1/F_0(F_0 - F_l)$. A plot of $1/\Delta F$ versus 1/[GMP] according to Eq.16 should give a straight line (R = 0.988) with stoichiometry of the formed complex 1:1 (Figure 17). The binding constants of 5'-GMP with Eu(III)-(CMMC) complex were found to be 1.8 x 10^7 ± 0.75 M^{-1}.

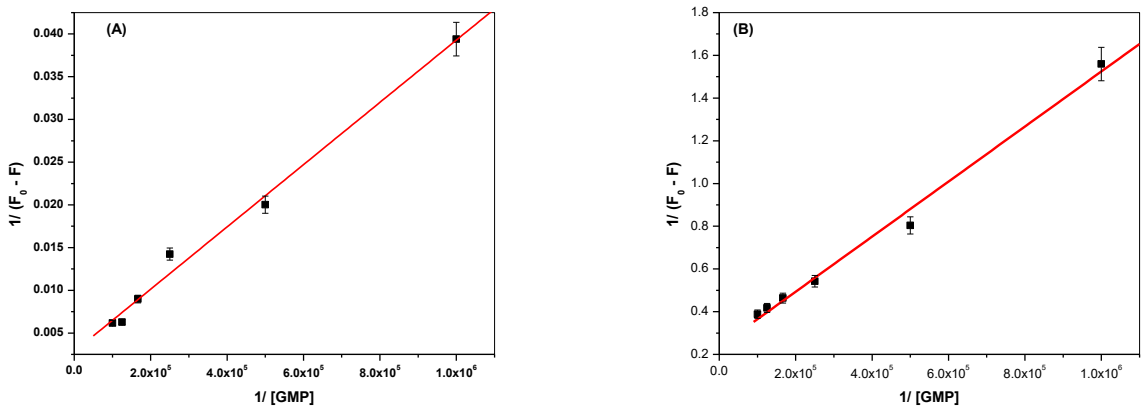

Figure 17. Double reciprocal plots for Eu(III)-(CMC) complex with 5'-GMP in ethanol. (A): 383 nm; (B): 616 nm.

3.5. DNA cleavage activity

The gel electrophoresis is shown in Figure 18 reveals that the control experiment (Lane 2) did not show any apparent cleavage of DNA. The disappearance of bands was observed in the Eu(III)-CMMC (lane 4) and Eu(III)-CMMC-GA (lane 5) complexes indicate the complete DNA cleavage activity. In the case of the parent ligand CMMC (lane 6) and GA (lane 3) a decrease in the intensity of bands was observed compared to the control. This is probably due to the partial cleavage of the DNA. From the above experiment, the Eu(III)-CMMC and Eu(III)-CMMC-GA complexes inhibit the growth of the pathogenic organism by cleaving the genome [67, 26].

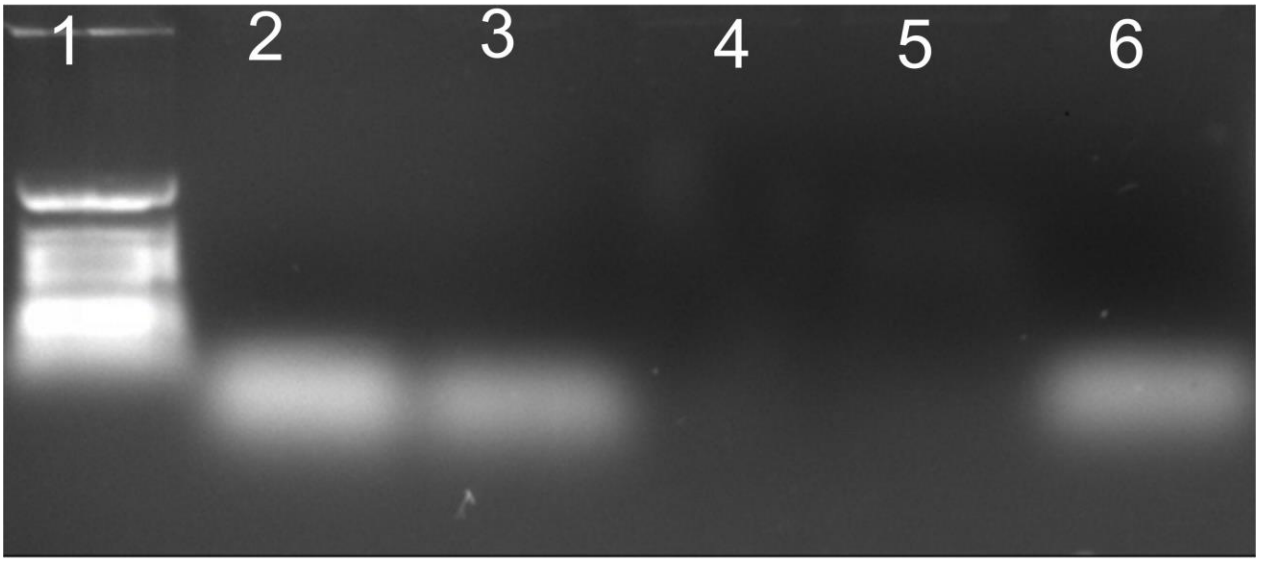

Figure 18. Gel electrophoresis diagram showing the cleavage of DNA. Lane 1: standard; lane 2: DNA; lane 3: DNA + GA; lane 4: DNA + Eu(III)-CMMC; lane 5: DNA + Eu(III)-CMMC-GA complex; lane 6: DNA + CMMC.

4. CONCLUSION

In this part, the interaction of Eu(III)-CMMC with 5'-GMP was carried out using pH-metric method, fluorescence spectroscopy, cyclic voltammetry (CV), differential pulse voltammetry(DPV) and square wave voltammetry (SWV) on the surface of glassy carbon electrode (GCE). Cyclic voltammograms showed that the mechanism of formation of ternary complex Eu (III)-(CMMC)-(5'-GMP) in 1:1:1 can be postulated to occur via the stepwise mechanism which is in parallel with the result obtained from potentiometric measurements. DNA cleavage studies of Eu(III)-CMMC-GA complex showed more efficiently in comparison to the parent ligands.

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