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Research Article

Bioelectrochemical and Pharmacological Study of Co-Coumarin Complex

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Abstract

Polarography is widely used to determine diverse organic and inorganic depolarizers present at micro- to ultra-micro levels. Accordingly, experimental sets were prepared by maintaining the overall concentrations of metal ion and supporting electrolyte (ammonium tartrate) constant at 1.0 mM and 1.0 M, respectively. Coumarin and its complexes showed well-defined cathodic reduction waves at pH 8.2 ± 0.02 in a 0.2 M ammonium tartrate medium. The plots of i_d vs $\sqrt{h_{corr}}$ showed a linear relationship and passed through the origin in all cases, indicating that the electrode reduction process was diffusion-controlled. Polarographic measurements showed that increasing the ligand concentration shifted the half-wave potential to more negative values. The plot of change in half wave potential with logarithm of change in ligand concentration yielded a straight line, demonstrating the formation of a single complex species for the Co(II)-coumarin system. A comparison between the infrared spectra of the free drug and its Co(II) complex showed the disappearance of the carbonyl (C=O) band at 1725 cm^{-1}. Additionally, the sharp -OH band observed at 3570 cm^{-1} in free coumarin shifted to 3600 cm^{-1} in the Co(II)-coumarin complex. The anticoagulant activity of the normal control and the respective test drug samples was evaluated, and the results are presented in the respective tables. The mean prothrombin times obtained for coumarin and its complexes are illustrated clearly in this research article. Polarography is widely utilized for the determination of diverse organic and inorganic depolarizers present at micro- to ultra-trace levels in analytical samples.

Keywords

Coumarin, Metal Complex, Ammonium Tartrate, Polarography, In-Vitro Study, Pharmacology

1. Introduction

Over the past decade, interest in the metabolic roles of essential trace elements in humans has grown substantially. [1, 2]. This has been driven largely by the clinical recognition of trace element deficiencies, arising from nutritional deficits as well as underlying pathologies and the discovery that certain inherited disorders stem from inborn errors of trace element metabolism [3-5].

Coordination compounds are of particular importance in the chemistry of transition and inner transition elements [6]. In

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these elements, the tendency of complex formation is developed due to the availability of partially filled 'd' and 'f' orbitals. The lanthanides, [7, 8]. Commonly known as 'rare earths', [9] have incompletely filled orbitals and have been placed together in the third group of the periodic table [10, 11].

Polarography is widely utilized for the determination of diverse organic and inorganic depolarizers present at micro- to ultra-trace levels in analytical samples [12, 13]. For a current voltage curve, [14, 15] if the specific rate of the electrochemical reaction is very high, so that the current is controlled essentially by diffusion process, [16, 17]. the calculation of the shape of the current-voltage curves is relatively very easy and such process is termed as the reversible electrode process [18-21]. In the last decades, the technique has found increasing application as a means of identifying the stoichiometry and formation constants of coordination compounds. [22-26] Literature also reports the use of polarography for the analysis of coumarins, [27-30].

2. Experimental

All chemicals used were of analytical grade (HiMedia/BDH/CDH). Cobalt(II) was introduced as its sulfate salt ($CoSO_4$). Double-distilled water was used to prepare all aqueous solutions. Stock solutions of ammonium tartrate (1.0 M) and coumarin (0.01 M) were prepared in double-distilled water and ethanol, respectively. The experimental sets maintained constant metal ion and supporting electrolyte concentrations of 1.0 mM and 1.0 M, respectively, at pH 8.2 ± 0.02. Dilute hydrochloric acid and sodium hydroxide were employed for pH adjustment. Authentic coumarin was obtained from CDH Laboratories and prepared as a stock solution in a methanol-water mixture (2: 3, v/v). Test solutions were prepared in the polarographic cell by combining 1.0 mL of the coumarin stock solution with 10.0 mL of ammonium tartrate supporting electrolyte, followed by dilution to 50.0 mL with distilled water. The pH was subsequently maintained at 8.2 ± 0.1 by titration with dilute sodium hydroxide or hydrochloric acid.

3. Results and Discussion

Coumarin and its complexes displayed sharp cathodic reduction waves at pH 8.2 ± 0.02 in 0.2 M ammonium tartrate. Linear relationships between i_d vs $\sqrt{h_{corr}}$ passing through the origin confirmed that the reduction proceeds via a diffusion-controlled mechanism.

Ligand Concentration Effect

Polarographic analysis revealed that increasing the ligand concentration systematically shifted the half-wave potential to more negative values. Plots of $E_{1/2}$ vs log Cx were linear, demonstrating the formation of a single complex species for both Co(II)-coumarin). Lingane treatment of the observed polarographic data in case of Co(II)-Coumarin system, revealed the stoichiometry and formation constants of the complex formed. The results have been tabulated. (Table 1 and Table 2).

Table 1. *Formation Constant of Coumarin complexes.*

Complex	Stoichiometry	Formation Constant log β_1
Co-(II)-Coumarin	1: 1	5.25

Table 2. *Polarographic parameters of the Co(II)-coumarin complex system.*

Concentration of ligand (M)	log Cx	$E_{1/2}$
0.0000	-	-1.20
0.0005	-3.301	-1.204
0.0010	-3.000	-1.22
0.0020	-2.698	-1.227
0.0030	-2.522	-1.242
0.0040	-2.397	-1.252

Co(II)=1.0 mM, 0.2 M Ammonium tartrate pH = 8.2±0.02

log β_1= 5.25

Polarograms of Co(II)-Coumarin complex.

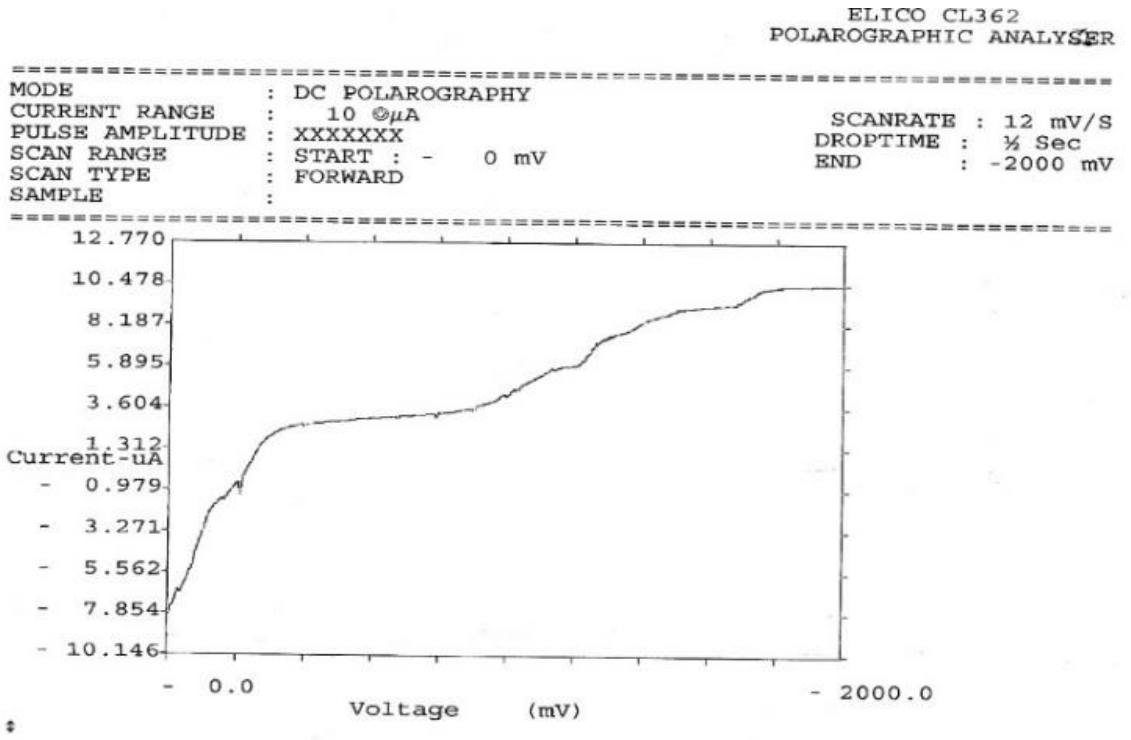


Figure 1. *Direct current Polarogram of Co(II)-Coumarin complex in ammonium tartrate (0.2M) pH 8.2±0.1.*

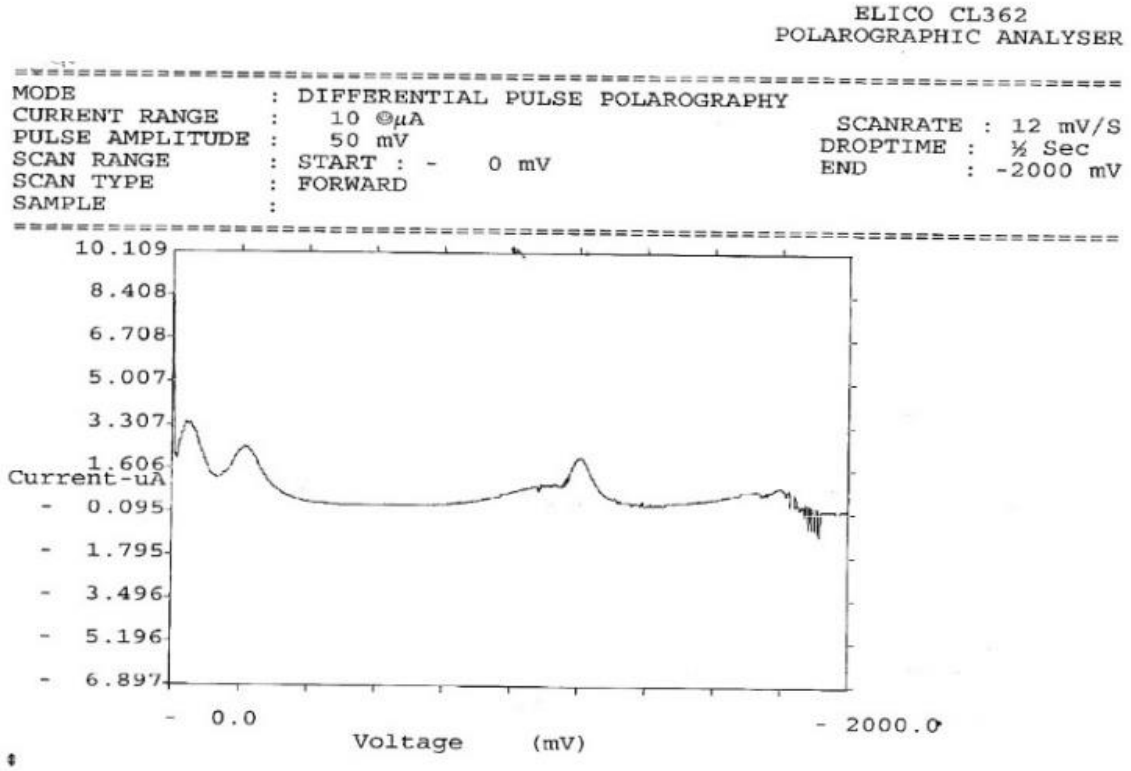


Figure 2. *Differential pulse Polarogram of Co(II)-Coumarin and complex in ammonium tartrate (0.2M) pH 8.2±0.1.*

Plot of $E_{1/2}$ vs log Cx.

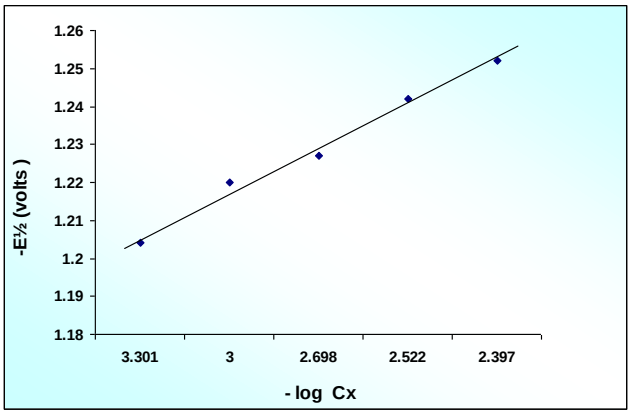


Figure 3. *Co(II)-Coumarin Complex.*

Infrared Spectral Studies on the Co(II)-Coumarin Complex:

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A comparison between the infrared spectra of the free drug and its Co(II) complex showed the disappearance of the carbonyl (C=O) band at 1725 cm^{-1}. Additionally, the sharp -OH band observed at 3570 cm^{-1} in free coumarin shifted to 3600 cm^{-1} in the Co(II)-coumarin complex. These spectral modifications confirm the direct coordination of both the \text{C=O} and -OH moieties to the Co(II) centre. Based on the polarographic and IR spectroscopic results, we propose a tentative structure for the 1: 1 Co(II)-coumarin complex below.

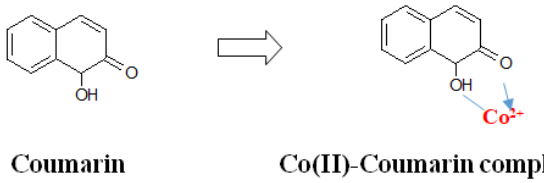


Figure 4. *A tentative structure for the 1:1 Co(II)-coumarin complex*

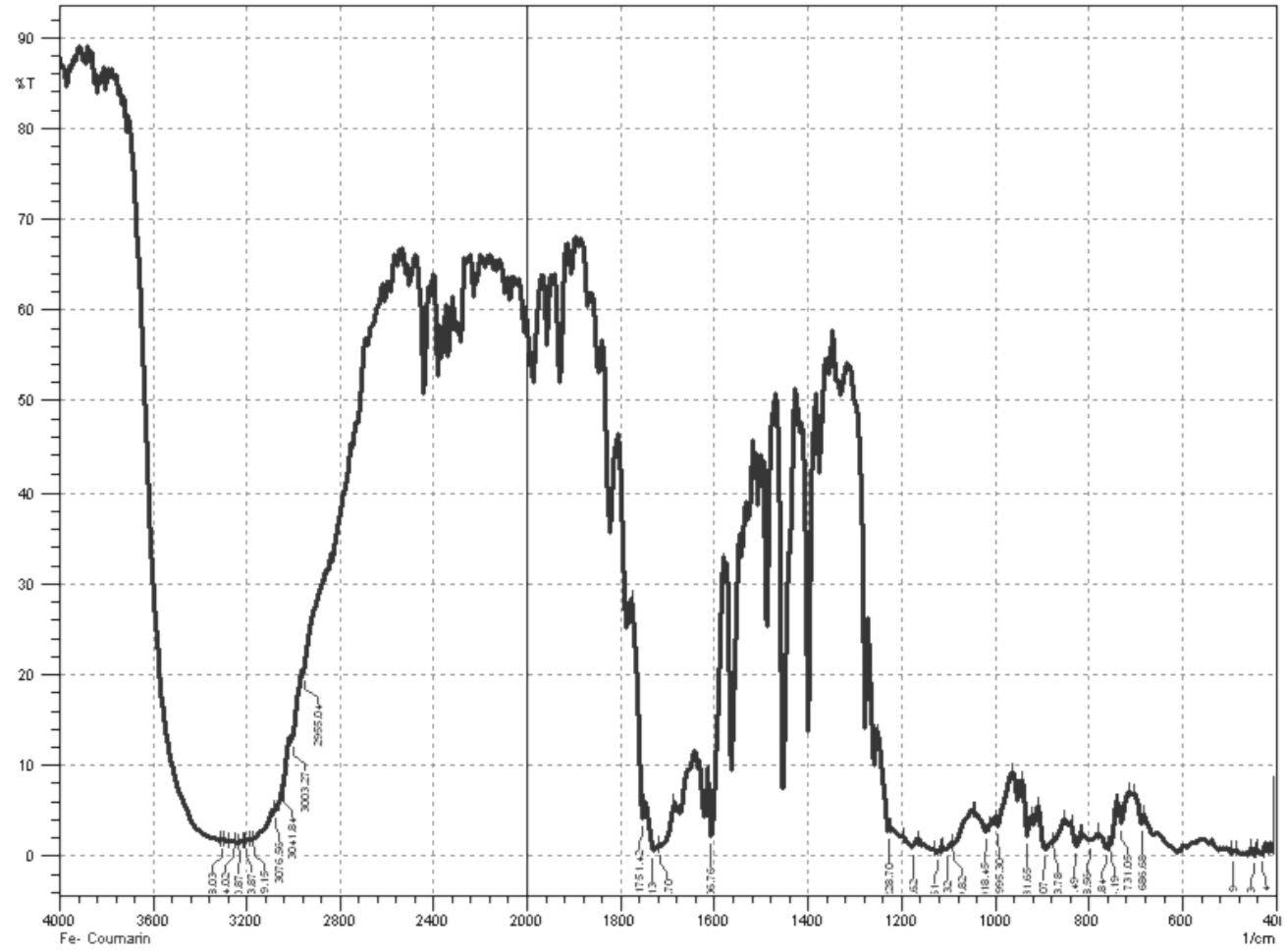


Figure 5. *IR Spectra of Co- Coumarin complex.*

Pharmacological Experiments (Prothrombin Time Assessment)

In Vivo Anticoagulant Activity in Albino Mice: We evaluated the in vivo anticoagulant activity of coumarin and its metal complexes in albino mice. The anticoagulant activity of the normal control and the respective test drug samples was evaluated, and the results are presented in the respective tables. The mean prothrombin times obtained for coumarin and its complexes are illustrated in the corresponding bar diagram. The bar diagram clearly indicates that the mean prothrombin time increased from 11.94 s in the animal's blood plasma without drug administration to 20.74 s following treatment with coumarin. Notably, the coumarin complex exhibited a greater anticoagulant effect, extending the mean prothrombin time to 22.81 s.

Table 3. *Normal anticoagulation action without any drug in Albino Mice.*

S. No.	Body weight of animal	Plasma Prothrombin Time in sec.			Average P. T. Sec.
	Grams	a	b	c	(a+b+c)/3
1.	42.20	11.92	11.96	11.99	11.95
2.	35.32	11.22	11.65	11.86	11.57
3.	40.28	11.90	11.92	11.95	11.92
4.	42.36	11.98	11.99	11.96	11.97
5.	Mean average P. T.				11.85

Table 4. *In Vivo Anticoagulation Action of Coumarin in Albino mice.*

S. No.	Body Weight of Animal	Dose administered	Plasma Prothrombin Time in sec.			Average P. T. Sec.
	Grams	mL	a	b	c	(a+b+c)/3
1.	48.44	0.48	20.52	20.66	20.78	20.65
2.	45.52	0.45	20.92	20.75	20.88	20.85
3.	42.12	0.42	20.75	20.72	20.75	20.75
4.	40.11	0.40	20.70	20.72	20.72	20.72
5.	Mean average P. T.					20.74

Table 5. *In Vivo Anticoagulation Action of Co(II) Coumarin Complex in Albino mice.*

S. No.	Body Weight of Animal	Dose administered	Plasma Prothrombin Time in sec.			Average P. T. Sec.
	Grams	mL	a	b	c	(a+b+c)/3
1.	46.44	0.46	22.82	22.86	23.88	22.85
2.	45.52	0.45	22.72	22.75	23.78	23.74
3.	44.12	0.44	22.85	22.82	22.85	22.85
4.	42.11	0.42	22.80	22.83	22.83	22.83
5.	Mean average P. T.					22.81

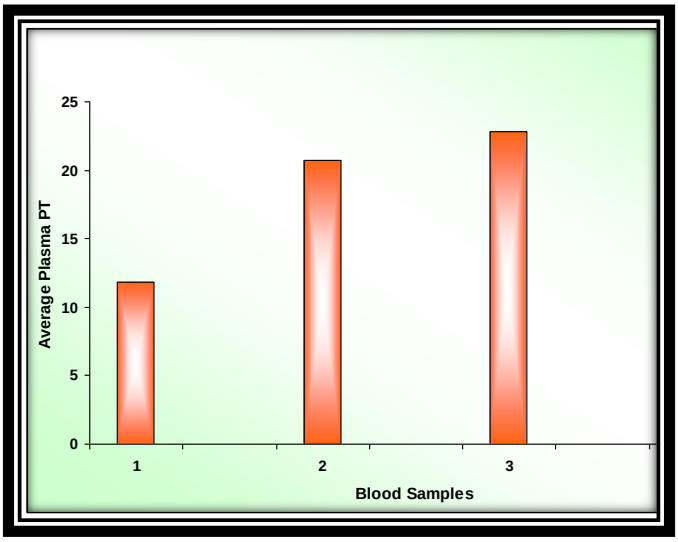


Figure 6. Blood Samples.

1= Normal blood plasma (control), 2= Coumarin-treated blood plasma, 3= Co-coumarin-treated blood plasma.

4. Conclusion

The obtained analytical results demonstrate the stoichiometric formation of coumarin complexes in a 1: 1 ratio in each case. Pharmacological screening further confirmed that these modified derivatives possess superior anticoagulant efficacy relative to free coumarin.

Based on these findings, the proposed electroanalytical methods prove both accurate and precise for trace-level analysis of coumarin and its derivatives. The simplicity and efficiency of the method make it attractive for quality-assurance workflows in pharmaceutical manufacturing. Furthermore, We also encourage pharmacological researchers to investigate these modified complexes further as their enhanced anticoagulant properties make them promising candidates to supersede conventional coumarin.

Abbreviations

DPP	Differential Pulse Polarography
DCP	Direct Current Polarography

Author Contributions

Rakesh Choure: Conceptualization, Resources
Neelam Choure: Data curation, Methodology
SK Abdus Samim: Writing – review & editing

Conflicts of Interest

The authors declare no conflicts of interest.

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