

Binding of Tris (1, 10-Phenanthroline) Ruthenium(II) Cation with Polyphenols in Aqueous Medium

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ABSTRACT: The binding of polyphenols (gallic acid and quercetin) with $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) complex in aqueous medium at pH 12.5 has been studied by absorption spectral techniques. The complex shows a ligand centred (LC) absorption peak at 262 nm and a metal to ligand charge transfer (MLCT) absorption peak at 445 nm in aqueous medium. The $[\text{Ru}(\text{phen})_3]^{2+}$ complex shows an emission maximum at 593 nm. The binding constant (K_b) for this reaction is determined from the Benesi-Hildebrand plot using absorption intensity data. The K_b of gallic acid with $[\text{Ru}(\text{phen})_3]^{2+}$ complex at 262 and 445 nm is 3.40×10^3 and $1.05 \times 10^2 \text{ M}^{-1}$ whereas for quercetin is 1.50×10^4 and $4.73 \times 10^3 \text{ M}^{-1}$ respectively. Structural effect seems to play a vital role on the binding of the gallic acid and quercetin with the complex.

KEYWORDS: $[\text{Ru}(\text{phen})_3]^{2+}$ complex; Gallic acid; Quercetin; Benesi-Hildebrand equation; Binding constant

I. INTRODUCTION

Polyphenols have considerable interest in the field of food chemistry, pharmacy and medicine due to a wide range of favourable biological effects including antioxidant properties. The antioxidant property of polyphenols is mainly due to their redox properties. They act as reducing agents, hydrogen donors, singlet oxygen quenchers and metal chelators [1]. The antioxidant activity of polyphenols depends on the number of hydroxyl groups that are strengthened by steric hindrance [2]. In addition to antioxidant and free-radical scavenger properties, polyphenols have numerous other biological activities, such as antihistamine activity, as well as anti-inflammatory, protecting against cardiovascular diseases and anticancer activity [3]. Polyphenols with gallol group (gallic acid) or catechol group (quercetin) are generally the most potent antioxidants, primarily because of their large iron-binding stability constant and have different activities, depending on the metal ion [4].

Gallic acid (3,4,5-trihydroxybenzoic acid) is a basic structural unit of hydrolyzable tannins widely distributed in the plant kingdom especially in tanniferous plants. Gallic acid is a strong chelating agent and forms stable complexes with iron [5]. The degree of chelation increases as the pH increases. The pK_a values of gallic acid are 4 (carboxylic acid), 8.7, 11.4 and > 13 (phenolic-OH groups). Thus, under the two pH conditions (9 and 11), the carboxylic acid as well as a phenolic-OH of the semiquinone will be ionized [6]. Quercetin (3,3',4',5,7-pentahydroxy flavone) is particularly interesting because it is one of the most biologically active and common dietary flavonols. Quercetin has two different pharmacophores, the catechol group in ring B and the three hydroxyl groups in rings A and C, of which the catechol moiety is the most reactive one where deprotonation occurs easily [7]. The pK_{a1} and pK_{a2} values of quercetin are 5.87 and 8.48 [8].

Ruthenium(II) complexes have particularly drawn significant interest, since they are able to catalyse reduction and oxidation processes under visible light irradiation enclosing a broad range of substrates. These privileges could be utilized for applications including, the photocatalytic decomposition of water and the implementation in photovoltaic devices. The light sensitizing feature of ruthenium coordination compounds has been further used as luminescent

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chemosensors as well as for the production of singlet molecular oxygen [9]. Based on the literature survey, the present study concentrates on the binding studies of gallic acid and quercetin on $[\text{Ru}(\text{phen})_3]^{2+}$ (phen = 1,10-phenanthroline) complex in aqueous medium at pH 12.5. The binding constant (K_b) for this reaction is determined from the Benesi-Hildebrand plot using absorption intensity data.

II. MATERIALS AND METHODS

$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, 1,10-phenanthroline and polyphenols (gallic acid and quercetin) were procured from Sigma-Aldrich. HPLC grade solvents were used for the synthesis of the complex. The binding studies were carried out with double-distilled deionized water. The complex, $[\text{Ru}(\text{phen})_3] \text{Cl}_2$ was synthesized according to the procedure previously described [10]. Sample solutions of the $[\text{Ru}(\text{phen})_3]^{2+}$ complex, gallic acid and quercetin were freshly prepared for each measurement. The absorption spectral measurements were carried out using SHIMADZU UV-1800 spectrophotometer. The emission intensity measurements were carried out and the emission spectra were recorded using JASCO FP-6300 spectrofluorometer.

The binding of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with various concentrations of gallic acid and quercetin (2.3×10^{-5} - 3.5×10^{-4} M) in aqueous medium at pH 12.5 has been studied by absorption spectral technique. Phenolate ions of gallic acid and quercetin for the binding studies were prepared by mixing the corresponding phenolic derivatives with NaOH and the pH of the solution was maintained at 12.5. The binding constant (K_b) of the $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin was determined from the Benesi-Hildebrand equation using absorption intensity data.

$$1/\Delta A = 1/K_b \Delta \epsilon [\text{H}] + 1/\Delta \epsilon [\text{G}]$$

where ΔA is the change in absorption of the complex with different concentrations ($[\text{G}]$) of polyphenols. The plots of $1/\Delta A$ versus $1/[\text{G}]$ give a straight line, K_b can be obtained from the ratio of Y-intercept to the slope of the straight line.

III. RESULTS AND DISCUSSION

The structure of the complex, gallic acid and quercetin used in the present study are shown in Fig. 1. The complex shows a ligand centred (LC) absorption peak of high energy at 262 nm and a metal to ligand charge transfer (MLCT) peak at 445 nm in aqueous medium at pH 12.5 (Fig. 2). The emission maximum of $[\text{Ru}(\text{phen})_3]^{2+}$ complex occur at 593 nm.

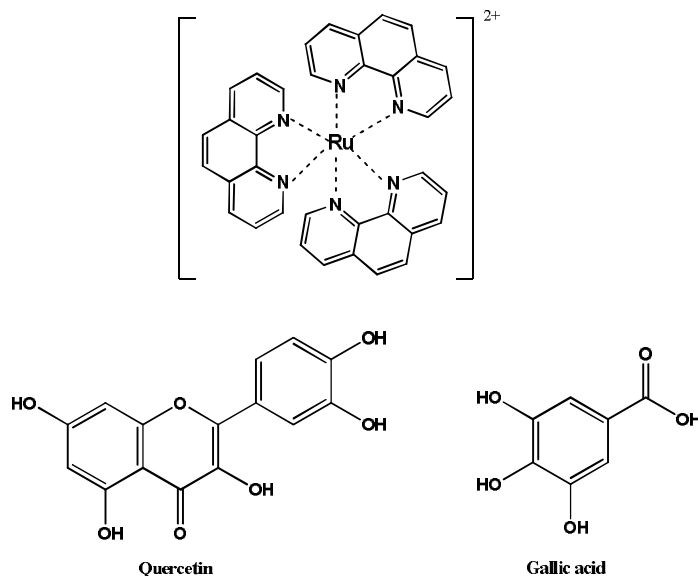


Fig. 1 Structure of $[\text{Ru}(\text{phen})_3]^{2+}$ complex and gallic acid

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The absorption spectral studies of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with the incremental addition of gallic acid and quercetin show a steady increase in the LC and MLCT absorption maximum, indicates the formation of ground state complex. Absorption spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with incremental addition of gallic acid in aqueous medium at pH 12.5 is shown in **Fig. 3**. Addition of gallic acid to the $[\text{Ru}(\text{phen})_3]^{2+}$ complex increases the absorbance at 262 and 445 nm, indicates the ground state binding of the acid to the complex. Gallic acid and quercetin has a weak absorption near the MLCT absorption of the complex, hence gallic acid and quercetin binds with the LC and MLCT absorption peaks of $[\text{Ru}(\text{phen})_3]^{2+}$ complex in the ground state [11]. The absorption spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin show a hypsochromic shift of 5 to 10 nm, which may be due to the formation of ground state complex. The K_b of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin in aqueous medium is calculated from Benesi-Hildebrand plot and the result is tabulated in **Table 1**. Benesi-Hildebrand plot on MLCT absorption of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with incremental addition of quercetin in aqueous medium at pH 12.5 is shown in **Fig. 4**. The plot of $1/\Delta A$ versus $1/[\text{Quercetin}]$ give a straight line, K_b of quercetin with $[\text{Ru}(\text{phen})_3]^{2+}$ complex can be obtained from the ratio of Y-intercept to the slope of the straight line.

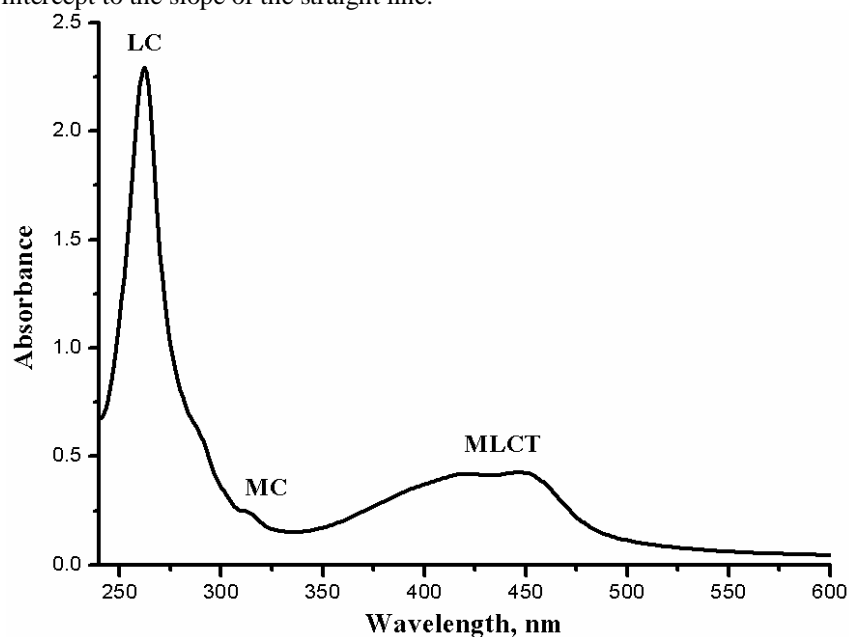


Fig. 2 Absorption spectrum of $[\text{Ru}(\text{phen})_3]^{2+}$ complex in aqueous medium

The ground-state interactions between polyphenols and the phenanthroline rings of $[\text{Ru}(\text{phen})_3]^{2+}$ complex are hydrophobic or π - stacking in nature [12]. To the extent that π - π stacking interactions exist between the ligands of Ru(II) complex and the quencher, the binding becomes stronger. The binding takes place in the LC and in the MLCT absorption maximum of the complex in the ground state. The K_b calculated for gallic acid and quercetin from the LC and MLCT absorption data shows that quercetin undergoes strong binding with the $[\text{Ru}(\text{phen})_3]^{2+}$ complexes than that of gallic acid.

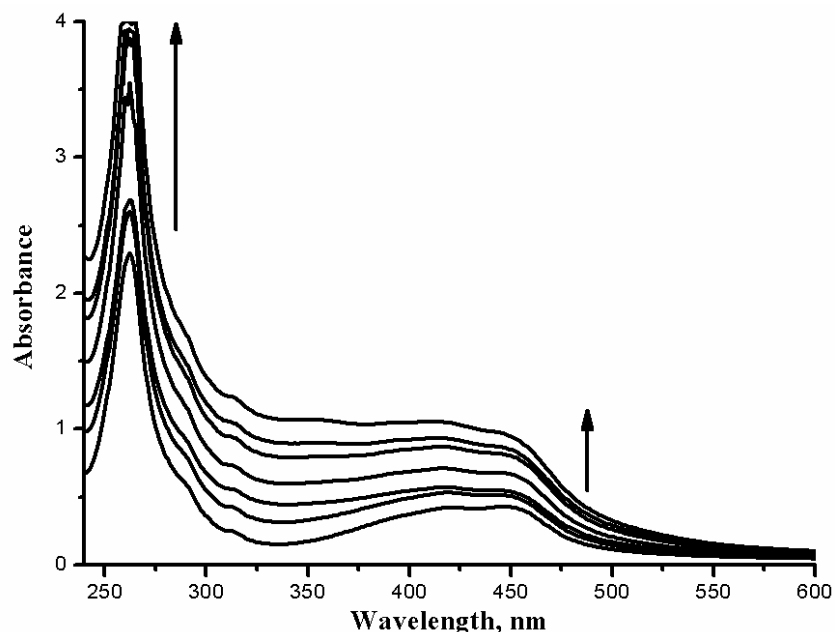


Fig. 3 Absorption spectra of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with incremental addition of gallic acid in aqueous medium at pH 12.5

The K_b of gallic acid with $[\text{Ru}(\text{phen})_3]^{2+}$ complex at 262 and 445 nm is 3.40×10^3 and $1.05 \times 10^2 \text{ M}^{-1}$ whereas for quercetin is 1.50×10^4 and $4.73 \times 10^3 \text{ M}^{-1}$ respectively. Gallic acid consists of three phenolic–OH groups, in alkaline medium especially above pH 9 the three phenolic–OH groups of gallic acid are 8.7, 11.4 and > 13. Quercetin has two different pharmacophores, the catechol group in ring B and the three hydroxyl groups in rings A and C, of which the catechol moiety is the most reactive one where deprotonation occurs easily [11]. The pK_a values of quercetin are 5.87 and 8.48. The binding process is highly sensitive to the pH of the medium. The K_b value is largely pH dependent at $\text{pH} > pK_a$ whereas the K_b value is little sensitive to the change of pH of the medium at $\text{pH} < pK_a$.

Table 1 Binding constant, K_b (M^{-1}) at LC and MLCT absorption maximum of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin in aqueous medium at pH 12.5

Polyphenol	Binding constant, K_b (M^{-1})	
	LC (262 nm)	MLCT (445 nm)
Gallic acid	3.40×10^3	1.05×10^2
Quercetin	1.50×10^4	4.73×10^3

Gallic acid consists of 3 phenolic–OH groups and at pH 12.5 all the phenolic–OH are converted into phenolate ions whereas quercetin consist of 4 phenolic–OH groups. The binding constant depends on the number of phenolic–OH groups. As the number of phenolic–OH groups increases the binding constant also increases. Hence quercetin shows a higher binding constant than gallic acid with $[\text{Ru}(\text{phen})_3]^{2+}$ complex. Thus the binding constant depends on the substituent present in the polyphenols.

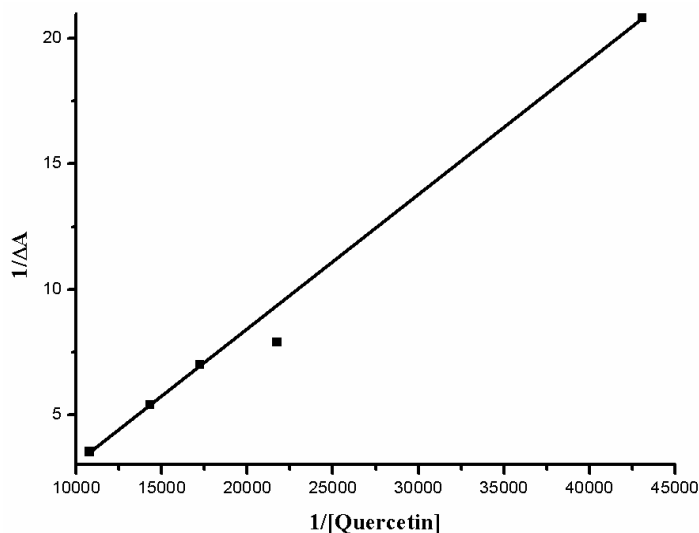


Fig. 4 Benesi-Hildebrand plot on MLCT absorption of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with incremental addition of quercetin in aqueous medium at pH 12.5

The binding constant varies with pH of the medium. As the pH of the solution increases more and more phenolic–OH groups are converted into phenolate ions, these phenolate ions bind with the complex in the ground state. The ground state binding of $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin are in good agreement with that of the reported values of binding of $[\text{Ru}(\text{bpy})_3]^{2+}$ complex with gallic acid and quercetin in aqueous medium at pH 11. Quercetin shows a higher binding constant than that of gallic acid with $[\text{Ru}(\text{bpy})_3]^{2+}$ complex in aqueous medium at pH 11 [13]. The K_b of MLCT absorption on $[\text{Ru}(\text{phen})_3]^{2+}$ complex with quercetin ($4.73 \times 10^3 \text{ M}^{-1}$) in aqueous medium at pH 12.5 is in close agreement with the K_b of quercetin-Pd(II) complex ($4.38 \times 10^3 \text{ M}^{-1}$) with DNA [14]. Therefore, the present investigation deals with the binding of antioxidants with $[\text{Ru}(\text{phen})_3]^{2+}$ complex in aqueous medium at pH 12.5. The binding constant depends on the nature of substituents present in the antioxidants.

IV. CONCLUSION

The binding of gallic acid and quercetin with $[\text{Ru}(\text{phen})_3]^{2+}$ complex in aqueous medium at pH 12.5 has been studied by absorption spectral techniques. The K_b of the $[\text{Ru}(\text{phen})_3]^{2+}$ complex with gallic acid and quercetin are determined from the Benesi-Hildebrand plots. The K_b of gallic acid with $[\text{Ru}(\text{phen})_3]^{2+}$ complex at 262 and 445 nm is 3.40×10^3 and $1.05 \times 10^2 \text{ M}^{-1}$ whereas for quercetin is 1.50×10^4 and $4.73 \times 10^3 \text{ M}^{-1}$ respectively. The binding constant depends on the number of phenolic–OH groups. As the number of phenolic–OH groups increases the binding constant also increases. Quercetin shows higher binding constant than gallic acid due to the presence of more number of phenolic–OH groups. Thus, the nature of the substituents present in the antioxidants play a vital role on the binding of $[\text{Ru}(\text{phen})_3]^{2+}$ complex in the ground state. This study confirms the structural effects on the binding of biologically important phenolate ions with $[\text{Ru}(\text{phen})_3]^{2+}$ complex in the ground state.

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