Binding of Tris (2,2'-Bipyridyl)Ruthenium(II) Cation with Antioxidants in Aqueous Acetonitrile

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Abstract

The binding of antioxidants (gallic acid and quercetin) with $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'- bipyridine) complex in 50 % aqueous acetonitrile at pH 11 has been studied by absorption spectral techniques. The complex shows absorption and emission maximum at 450 and 614 nm and it shows a lifetime of 740 ns in aqueous medium. The excited state reduction potential of the complex ($E^0_{Ru}{}^{2+*/+}$) *vs* Ag/Ag^+ is 0.74 V. The binding constant (K_b) for these reactions are determined from the Benesi-Hildebrand equation using absorption intensity data. The K_b of gallic acid and quercetin with $[Ru(bpy)_3]^{2+}$ complex is 1.8×10^3 M^{-1} and 2.5×10^4 M^{-1} respectively. Structural effect seems to play a vital role on the binding of the antioxidants with the complex.

Keywords: Antioxidants; Benesi-Hildebrand equation; binding constant; structural effects

Introduction

Phenolic acids and flavonoids constitute one of the most common and widespread group of substances in flowering plants, occurring in all vegetative organs and fruits. They are considered secondary metabolites involved in the chemical defence of plants against predators and in plant-plant interferences. Several thousand plant polyphenols are known, encompassing a wide variety of molecules that contain at least one aromatic ring with one or more hydroxyl groups in addition to other substituents. 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].

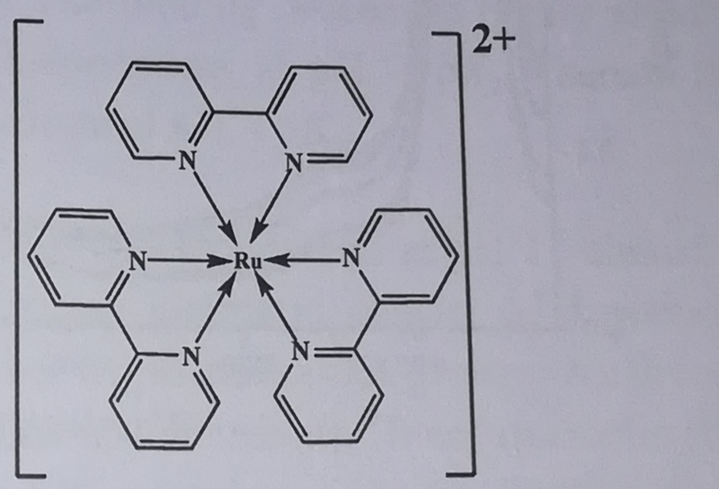
Ruthenium(II)-polypyridine complexes have particularly drawn significant interest, since they are able to catalyze reduction and oxidation processes under visible light irradiation enclosing a broad range of substrates. These privileges could be utilized for applications including, the photocatalytic decomposition of water and the implementation in photovoltaic devices. The light sensitizing feature of ruthenium coordination compounds has been further used as luminescent chemosensors as well as for the production of singlet molecular oxygen [4].

Polyphenols with gallol or catechol groups are generally the most potent antioxidants, primarily because of the large iron-binding stability constants for these groups. Polyphenols containing catechol (quercetin) and gallol (gallic acid) groups have very different activities, depending on the metal ion [5,6]. Based on the literature survey, the present study concentrates on the binding studies of gallic acid and quercetin on $[Ru(bpy)_3]^{2+}$ (bpy = 2,2'- bipyridine) complex in 50 % aqueous acetonitrile at pH 11.

Experimental Section

The complex, $[Ru(bpy)_3]\ Cl_2$ was synthesized according to the procedure previously described [7]. Then the complex was treated with sodium tetrafluoroborate to get the $BF4^-$ salt $[Ru(bpy)_3](BF_4)_2$. Sample solutions of the $[Ru(bpy)_3]^{2+}$ complex and polyphenols were freshly prepared for each measurement. The absorption spectral measurements were carried out using SYSTRONICS 2203 double beam spectrophotometer. Emission intensity measurements were carried out and the emission spectra were recorded using ELICO SL 174 spectrofluorometer. Excited state lifetime of the complex was made with laser flash photolysis technique using an Applied Photophysics SP-Quanta Ray GCR-2(10) Nd:YAG laser as the excitation source. The redox potential of the $[Ru(bpy)_3]^{2+}$ complex in aqueous medium was determined by cyclic voltammetric technique using CH1604C electrochemical analyzer.

The structure of the complex and the polyphenols used in the present study was shown in **Fig. 1**. Phenolate ions of the gallic acid and quercetin for the binding studies were prepared by mixing the corresponding polyphenols with NaOH and the pH of the solution was maintained at 11 to confirm that the quencher was present as phenolate ions. The binding of $[Ru(bpy)_3]^{2+}$ complex with various concentrations (2×10^{-5} - 1.4×10^{-4} M) of antioxidants in 50 % aqueous acetonitrile at pH 11 has been studied by absorption spectral technique.



Gallic acid Quercetin

Fig.1 Structure of complex and polyphenols

The binding constant (K_b) of the $[Ru(bpy)_3]^{2+}$ complex with gallic acid and quercetin were determined from the Benesi-Hildebrand equation using absorption intensity data [8].

$$1/\Delta A = I/K_b\, \Delta\varepsilon\, [H] + 1/\Delta\varepsilon\, [G]$$

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

Results and Discussion

The absorption and emission maximum of $[Ru(bpy)_3]^{2+}$ complex are at 450 and 614 nm and it shows a life time at 740 ns in aqueous acetonitrile. The ground state and excited state redox potentials *vs* Ag/Ag^+ of the $[Ru(bpy)_3]^{2+}$ complex in this medium is –1.36 and 0.74 V respectively.

The absorption spectral studies of $[Ru(bpy)_3]^{2+}$ complex with the incremental addition of gallic acid and quercetin ($2 \times 10^{-5} - 1.4 \times 10^{-4}$ M) shows a slight increase in the metal-ligand charge transfer (MLCT) absorption maximum, indicates the formation of ground state complex (**Fig. 2**). Gallic acid and quercetin have weak absorption at 454 and 426 nm [9]. Gallic acid and quercetin bind with the $[Ru(bpy)_3]^{2+}$ complex in aqueous medium at pH 11 since, gallic acid and quercetin have weak absorption close to the region where Ru(II) complex have strong MLCT absorption. The absorption spectra of $[Ru(bpy)_3]^{2+}$ complex with the antioxidants, gallic acid and quercetin shows a hypsochromic shift of 2 to 3 nm, which may be due to the formation of ground state complex. The binding constant (K_b) of $[Ru(bpy)_3]^{2+}$ complex with gallic acid and quercetin in aqueous acetonitrile calculated from Benesi-Hildebrand plot (**Fig. 3**) at pH 11 is shown in **Table 1**.

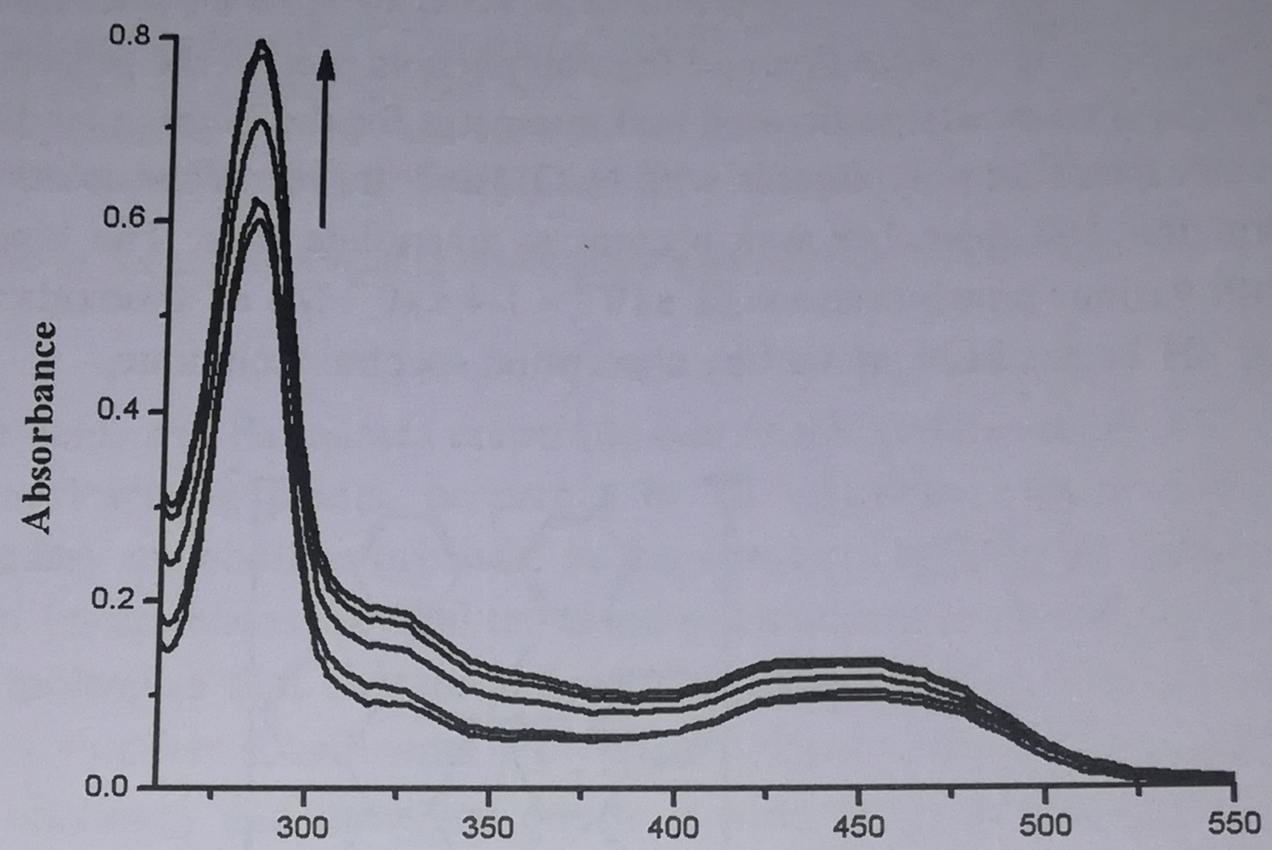


Fig.2 Absorption spectrum of $[Ru(bpy)_3]^{2+}$ with incremental addition of quercetin in 50 % aqueous acetonitrile at pH 11

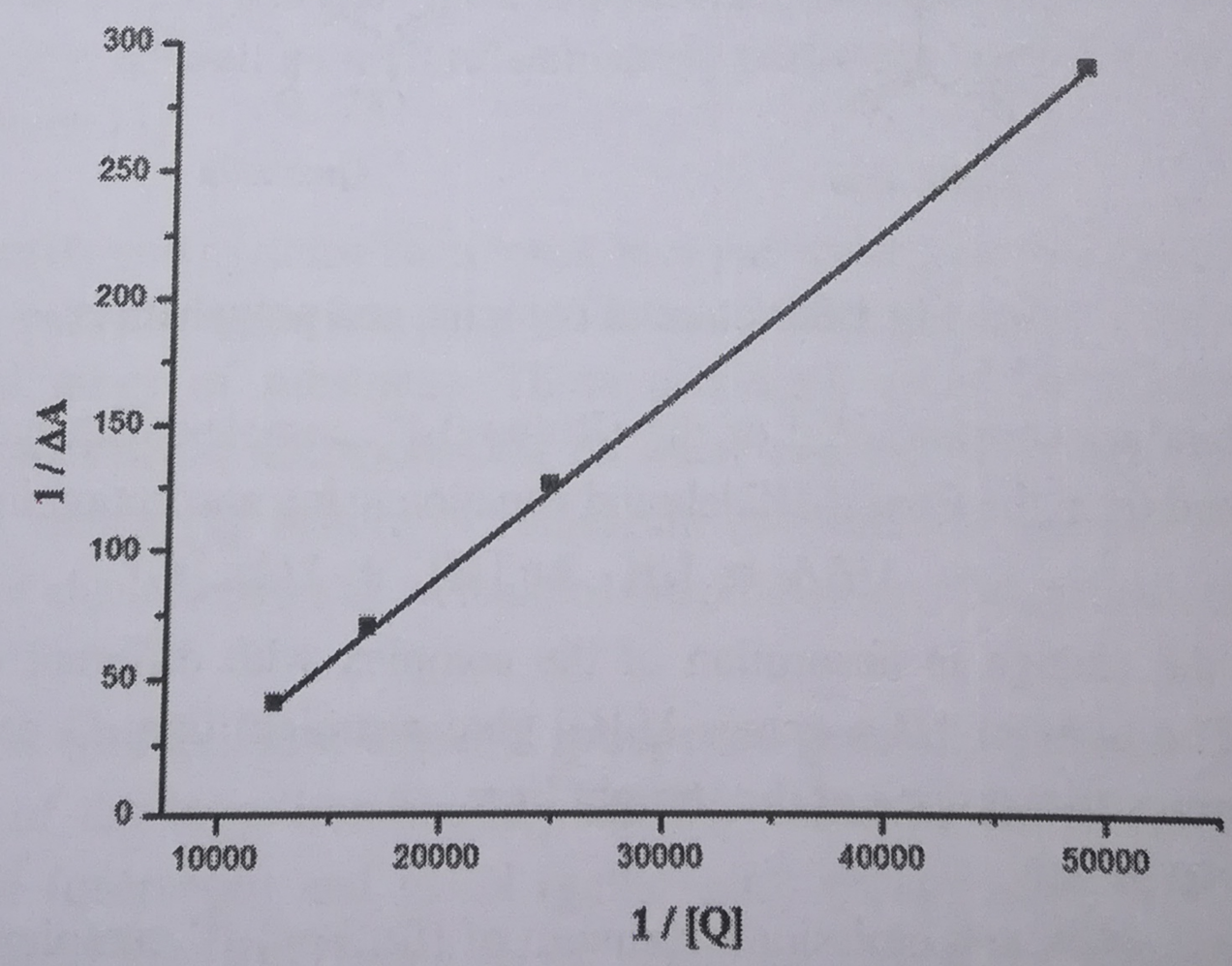


Fig.3 Benesi-Hildebrand plot of $[Ru(bpy)_3]^{2+}$ with incremental addition of gallic acid in 50 % aqueous acetonitrile at pH 11

Table 1 Binding constant, K_b (M^{-1}) for gallic acid and quercetin with $Ru(bpy)_3]^{2+}$ in 50% aqueous acetonitrile at pH 11

Polyphenol	Binding constant, K_b (M^{-1})
Gallic acid	1.8×10^3
Quercetin	2.5×10^4

The ground-state interactions between polyphenols and the bipyridyl rings of $[Ru(bpy)_3]^{2+}$ complex are hydrophobic or π-stacking in nature [10]. To the extent that π - π stacking interactions exist between the ligands of Ru(II)- complexes and the quencher, the binding becomes stronger. The K_b calculated for gallic acid and quercetin from the absorption spectral data shows that quercetin undergoes strong binding with the $[Ru(bpy)_3]^{2+}$ complex than that of gallic acid. Gallic acid consist of three phenolic–OH groups, in alkaline medium especially above pH 9, the three phenolic–OH groups get ionized. The pK_a values for 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. 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 pH > pK_a whereas the K_b value is little sensitive to the change of pH of the medium at pH < pK_a.

Gallic acid consist of 3 phenolic–OH groups and at pH 11 almost 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 $[Ru(bpy)_3]^{2+}$ complex. Thus the binding constant depends on the substituent present in the polyphenols.

Conclusion

The binding of gallic acid and quercetin with $[Ru(bpy)_3]^{2+}$ complex in 50 % aqueous acetonitrile at pH 11 has been studied by absorption spectral techniques. The binding constant (K_b) of the $[Ru(bpy)_3]^{2+}$ complex with gallic acid and quercetin are determined from the Benesi-Hildebrand plot. The K_b of gallic acid and quercetin with $[Ru(bpy)_3]^{2+}$ complex are 1.8×10^3 M^{-1} and 2.5×10^4 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 that of gallic acid due to the presence of more number of phenolic–OH groups. This study confirms the structural effects on the binding of biologically important phenolate ions with $[Ru(bpy)_3]^{2+}$ complex.

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