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Luminescence quenching of $[Os(bpy)_3]^{2+}$ by Mn^{7+}, Cr^{6+} and Ce^{4+} ions in acidic aqueous solution

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ABSTRACT

Luminescence quenching of $[Os(bpy)_3]^{2+}$ by Mn^{7+}, Cr^{6+} and Ce^{4+} ions in acidic aqueous media are studied. Ground state interactions between $[Os(bpy)_3]^{2+}$ and these ions show ground state association with stoichiometric ratios in accordance with the electron transfer process. Positive deviation is observed from the linear Stern–Volmer relationship which with the ground state association is in support of static quenching mechanism. Benesi-HildEbrand equation was used to evaluate the association constant which were found to be $5\times10^3\ M^{-1}$, $6.6\times10^4\ M^{-1}$ and be $1.1\times10^5\ M^{-1}$ for association of $[Os(bpy)_3]^{2+}$ with Ce^{4+}, Cr^{6+} and Mn^{7+}, respectively, based on luminescence intensity measurements. Different models for static luminescence quenching were employed to discuss the results.

1. Introduction

Luminescence quenching phenomenon of $d\pi^6$ transition metals Ru(II) and Os(II) complexes has been widely studied with a wide range of quenchers in different solvents. Polypyridyl complexes of $d\pi^6$ transition metals Ru(II) and Os(II) have low-lying metal to ligand charge transfer (MLCT) excited states which have properties which make them attractive candidates for studies involving electron or energy transfer processes. The excited states are long lived, luminescent, and relatively photochemically stable [1–7]. Since the emitting state of these metal complexes have both very strong reducing and moderately strong oxidizing properties, electron transfer can occur rapidly to substrates that are either oxidizing or reducing. An evidence that the emitting state is acting as an electron donor (oxidative quenching) requires the use of a substrate to which energy transfer cannot readily occur and which accepts electrons to give a reduced product that is not rapidly oxidized back by the oxidized donor [8]. Similar situation holds true for reductive quenching where the oxidized product is not reduced back by the reduced acceptor [8].

Studies on luminescence quenching on osmium(II) complexes are very rare compared with their analogue ruthenium complexes despite the fact that the reduction potential of osmium complexes are much lower than their analogue ruthenium complexes and much shorter excited state lifetime [1–20].

Luminescence quenching normally is a dynamic process whose second-order rate constant usually is determined from either stationary (I_0/I) or dynamic (τ_0/τ) linear dependence on the quencher concentration, Q. Quenching of charged excited donors by charged acceptors may lead to static quenching by ground-state association of donor and acceptor. Static quenching is easily recognized in Stern–Volmer plots as the dependence of (I_0/I) on the quencher concentration is not linear and deviating upward and their values are higher than the corresponding (τ_0/τ) values. Some authors try to fit the observed stationary quenching curves by a quadratic equation and they determined the association constant from the regression parameters of the quadratic equation by introducing the quenching constant from dynamic quenching experiments into the formulas [11]. Static versus dynamic fluorescence quenching of some aromatic hydrocarbons by a variety of quenchers is a topic of current interest [21–34].

In the present paper, we report on the luminescence quenching of tris(2,2′-bipyridyl) osmium(II) complex ion by a number of inorganic ion salts with different oxidation potentials, namely Mn^{7+}, Cr^{6+} and Ce^{4+} ions in acidic aqueous solution in order to assess the influence of ground state association on the quenching process. Effect of pH on both ground state interaction and the luminescence quenching process is also reported.

2. Experimental

The absorption spectra were recorded on an Agilent diode array 8453 spectrophotometer. Steady state fluorescence measurements

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were obtained using a Shimadzu 5301 spectrofluorophotometer. Luminescence decay measurements was carried out using nitrogen laser strobe fluorescence lifetime system from Photon Technology International, Inc. Steady state luminescence measurements were collected at wavelength of excitation were all samples absorb the same, i.e., at the longest isosbestic point in each system.

$[Os(bpy)_3]^{2+}$ was synthesized as in literature [12]. $KMnO_4$, K_2CrO_4 and $(NH_4)_2[Ce(NO_3)_6]$ were all of the highest purity obtained from Aldrich were used as the source of Mn^{7+}, Cr^{6+} and Ce^{4+}, respectively. ^1H NMR spectra were recorded in D_2O on a Bruker Avance 400 MHz spectrometer. Chemical shifts have been expressed in parts per million (ppm) relative to HDO signal as a reference at 4.80 ppm. The effect of the pH on the redox reaction between $[Os(bpy)_3]^{2+}$ and metal cations was studied in the 2.0–12.0 range using H_2SO_4 and NaOH. Phosphate buffer of pH 2.6 was used in all studies.

3. Results and discussion

The absorption spectrum of $[Os(bpy)_3]^{2+}$ in aqueous solution is shown in Fig. 1. It has been established that the visible region absorption spectrum of $[Os(bpy)_3]^{2+}$ is dominated by the intense spin-allowed $d(t_{2g})\rightarrow\pi^*$ metal to ligand charge transfer (MLCT) transition in the range from 400 to 550 nm resulting in the formation of the first excited singlet metal to ligand charge transfer state (^{1}MLCT). The absorption spectrum also show two strong bands with several shoulders in the uv region at λ_{max} of ~250 nm and ~290 nm that are assigned as the $\pi\rightarrow\pi^*$ transitions of the ligand. In addition, transitions that are formally spin forbidden exhibit enhanced intensity due to the high degree of spin orbit coupling in case of osmium (3381 cm^{-1} [35]). These transitions to ^{3}MLCT appear as broad structureless bands at wavelengths above 550 nm.

It has been found that the ground state absorption spectrum of $[Os(bpy)_3]^{2+}$ hardly shows any pH dependence over the range 2–12. Addition of 5 μM of Mn^{7+}, Cr^{6+} or Ce^{4+} ion salts to the $[Os(bpy)_3]^{2+}$ complex ion solution did not make any spectral changes on the absorption spectrum of $[Os(bpy)_3]^{2+}$ complex ion as the pH decreased from 12.0 to 7. At pH values <7, there was a sudden depletion of the metal to ligand charge transfer bands of $[Os(bpy)_3]^{2+}$ complex ion across the visible region and for the band centered at 290 nm with concomitant increase in the absorbance at 246 nm and 315 nm bands. The effect of pH on the absorption band is shown in Fig. 2 at different wavelengths for the interaction of $[Os(bpy)_3]^{2+}$ with 5 μM Mn^{7+}. It shows that the effect of pH is pronounced at values of $pH<5$ for the interaction of $[Os(bpy)_3]^{2+}$ with Mn^{7+}, similar results were obtained for the interaction of $[Os(bpy)_3]^{2+}$ with Cr^{6+} or Ce^{4+} ions. Therefore, values of pH of 2–3 were used to study the interaction of $[Os(bpy)_3]^{2+}$ with Mn^{7+}, Cr^{6+} or Ce^{4+} ion salts. Results in Fig. 2 can be explained in terms of an efficient redox reaction between $[Os(bpy)_3]^{2+}$ and Mn^{7+}, Cr^{6+} or Ce^{4+} ion salts, as redox potential of Mn^{7+}, Cr^{6+}, and Ce^{4+} is known to be pH dependent and are getting higher as the pH is getting lower; for example the redox potential of Mn^{7+} increases from 0.60 to 1.68 upon changing from alkaline to acidic medium.

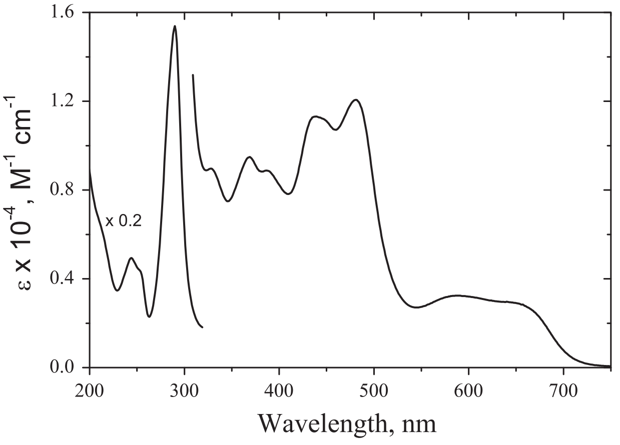

Fig. 1. The absorption spectrum of 2.6×10^{-5} M of $[Os(bpy)_3]^{2+}$ in aqueous solution, pH 6.

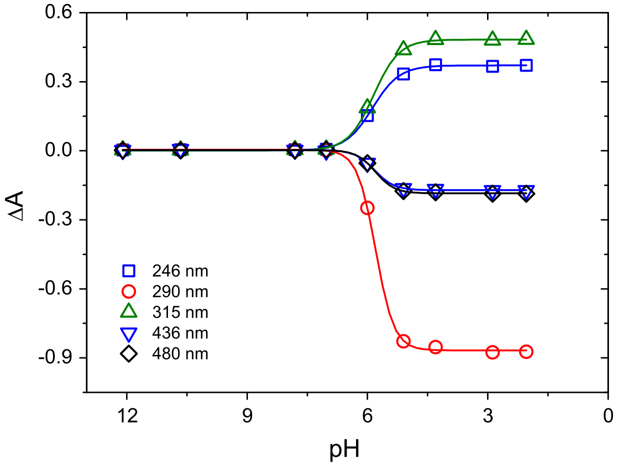

Fig. 2. Effect of pH on the absorbance changes at 246 nm, 290 nm, 315 nm, 436 nm and 480 nm upon the addition of 5 μM Mn^{7+} to $[Os(bpy)_3]^{2+}$ sample solution.

Fig. 3A–C shows the absorption spectra of $[Os(bpy)_3]^{2+}$ in the absence and presence of different concentrations of Mn^{7+}, Cr^{6+} or Ce^{4+} ion salts versus water at pH 2.5 ± 0.5. It has been observed that the metal to ligand charge transfer bands in the visible region as well as the band at 290 nm decrease with concomitant increase of the band intensity at 240 nm and 315 nm with the appearance of three isosbestic points at 273 nm, 299 nm and 348 nm in case of Mn^{7+}, 273 nm, 299 nm and 363 nm in case of Cr^{6+} and 273 nm, 299 nm and 356 nm in case of Ce^{4+}.

In order to identify the stoichiometry of the reaction between $[Os(bpy)_3]^{2+}$ complex ion and Mn^{7+}, Cr^{6+} and Ce^{4+} ions, the method of the molar ratio method was employed. Fig. 4 shows the absorbance change as a function of the molar ratio between M^{n+} and $[Os(bpy)_3]^{2+}$ complex ion (represented as $[Os]^{2+}$ in the Figure). It has been found that the intersection point was obtained at a molar ratio value of 0.2 Mn^{7+} to $[Os(bpy)_3]^{2+}$ complex ion, which corresponds to a stoichiometry of 1 Mn^{7+} to 5 $[Os(bpy)_3]^{2+}$, about 0.34 Cr^{6+} to $[Os(bpy)_3]^{2+}$ which corresponds to a stoichiometry of 1 Cr^{6+} to 3 $[Os(bpy)_3]^{2+}$ and 1 Ce^{4+} to $[Os(bpy)_3]^{2+}$ which corresponds to a stoichiometry of 1 Ce^{4+} to 1 $[Os(bpy)_3]^{2+}$. Therefore, it can be concluded that each mole of Mn^{7+}, Cr^{6+} and Ce^{4+} brings about changes in the absorption of 5 mol, 3 mol and 1 mol of $[Os(bpy)_3]^{2+}$, respectively.

The plot of absorbance changes at any of the wavelengths indicated by the arrows in Fig. 3, shows that the absorption changes is linear up to the stoichiometric limit. Such linear dependence together with the use of very small concentrations of the Mn^{7+}, Cr^{6+} or Ce^{4+} ion to cause changes in the absorption spectrum point to the possibility of using such method for colorimetric determination of these ions with very low detection limits.

The absorption spectral changes indicate the formation of ground state association between $[Os(bpy)_3]^{2+}$ and different ion salts. The association constant, K_A, can be determined according to the Benesi–Hildbrand relation [36] for a 1:1 complex by:

$$\frac{1}{A-A_0}=\frac{1}{\Delta\varepsilon}+\frac{1}{\Delta\varepsilon K_A[Q]} \qquad (1)$$