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Short communication

Spectrophotometric determination of the formation constants of calcium(II) complexes with 2,2'-bipyridyl and 1,10-phenanthroline in acetonitrile

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Abstract

The oxygen-evolving complex (OEC), which consists of a calcium-manganese cluster, is the reaction center of the Photosystem II. At this catalytic site, the water-splitting reaction in dioxygen and hydronium ions occurs. In order to partially reproduce the water splitting process, several studies have reported the synthesis of functional model complexes. Nevertheless, there is a small amount of reports, concerning the spectral behavior of calcium complexes or the calcium role in the cluster. In this work, in order to explore the absorption spectrum of calcium species in acetonitrile, an equilibrium study of the calcium complexes with 2,2'-bipyridyl or 1,10-phenanthroline, was carried out. The formation constants and the calculated electronic spectrum of each complex was obtained by a modified method of continuous variations consisting in a correlation of the experimental spectrophotometric data with the HypSpec software. The values of the formation constants for the calcium(II) complexes with 2,2'-bipyridyl and 1,10-phenanthroline, are $\text{Log } \beta_{110} = 4.39 \pm 0.02$ and $\text{Log } \beta_{110} = 5.94 \pm 0.05$, respectively.

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Keywords: Artificial photosynthesis; Calcium complexes; Equilibrium

1. Introduction

The most important reaction for living beings is possibly the reaction of photosynthesis [1,2]. In this process, CO₂ is used to produce carbohydrates, which serve as an energy source for several organisms [3]. The reaction of photosynthesis takes place at the structures named Photosystem I and Photosystem II [4,5] in plants, algae and cyanobacteria [1,2,6,7]. In Photosystem II we find the oxygen-evolving complex which consists of a tetranuclear cluster of manganese, calcium, and chloride ions

[8]. This structure represents the active site of the splitting water reaction [9,10]. In this process, sunlight is used to split water into dioxygen and hydronium ions [1,2]. Several research groups describe in detail the structure of the oxygen-evolving complex of the thermophilic cyanobacterium: *Thermosynechococcus vulcanus*, evidencing that the cluster calcium-manganese may have the empirical formula: CaMn₄O₅(H₂O)₄ [11].

There is growing interest in the production of molecular hydrogen as a form of environmentally-friendly renewable technology [12]. Inspired by the process of photosynthesis, in recent years, several research groups have proposed an innovative approach to dihydrogen production; this technology is known as artificial photosynthesis [7,13]. Currently, this approximation represents one of the most promising ways to generate dihydrogen and promote the storing of solar energy [14]. Several research groups have focused on the synthesis of a metal complex as a reaction center for charge separation and as

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a catalyst in oxidation-reduction reactions [15], or species for absorbing light [14]. The mechanism of oxidation of water by photosystem II is not fully understood [2,16–18], some mechanistic pathways from theoretical investigations and inorganic modeling of the complex, have been proposed [9]. On the other hand, the calcium ion is involved in a wide range of different activities in biological systems [15], several authors have proposed its possible roles in the oxygen-evolving complex [19]. However, its role remains controversial, it is believed to have functional and structural purposes [20]. Some of the possible aspects in which calcium could be involved in the water splitting reaction: is the dehydrogenation of the Mn-OH_xO cluster, electronic stabilization of oxo-species, regulate high oxidation states and possibly intervenes in the access of water molecules to the active site of the cluster [21]. Finally, it is possible that calcium ions might help to stabilize the oxidation states of manganese at high temperatures [22]. Nevertheless, as far as we know, the use of calcium complexes has not been considered in artificial photosystems.

The production of green hydrogen from sustainable energy sources is an actively developing technology [23]. Energy production through the direct conversion of solar energy into chemical energy remains a challenge today [3]. Several factors have limited the study of the coordination chemistry of calcium complexes, such as its solubility in several solvents. Information regarding the structures and binding sites of calcium complexes are difficult to obtain using techniques other than X-ray crystallography [24]. In this work, we report the formation constants and their speciation, of the complexes generated with Calcium(II), 2,2'-bipyridyl (Bpy) or 1,10-phenanthroline(Phen) in acetonitrile solution. The purpose of the present work was to obtain and explore the individual electronic spectrum of the complexes of Calcium(II) with 2,2'-bipyridyl (Bpy) and 1,10-phenanthroline(Phen).

2. Experimental

2.1. General

In the determination of the formation constants, the acetonitrile (CH₃CN) HPLC grade, is used as a solvent (Tecsiquim, Mexico), Calcium nitrate tetrahydrate, Ca(NO₃)₂·4H₂O, 2,2'-Bipyridyl (C₅H₄N)₂ and 1,10-Phenanthroline (C₁₂H₈N₂) (Sigma-Aldrich) were of analytical grade and used without further purification. All spectral measurements were made on a Cary 50 UV-Vis Spectroscopy System, at 298 K (RT) using a quartz cell with 1 cm of path length and 3 mL volume. For all the experiments, the observed spectral region was from 200 nm to 350 nm. For the determination of formation constants, the spectrophotometric data were fitted with the program HypSpec [25]. Distribution diagrams of species were calculated using the software Hyperquad Simulation and Speciation (HySS) [26].

2.2. Calcium(II)-2,2'-bipyridyl equilibrium studies

Experiments were performed using two different stock solutions of 2,2'-bipyridyl (358 and 250.8 μM). Ca(NO₃)₂·4H₂O

was used to prepare Calcium stock solutions (237.2 and 166.1 μM). In each experiment, the final concentration of Calcium(II) was set constant at 23.72 μM and 16.6 μM, in where the 2,2'-bipyridyl concentrations were varied from 3.58 μM to 53.76 μM and 2.51 μM to 40.1 μM, respectively. A total of 29 spectra were used for the refinement in the HypSpec software, using the modified continuous variations method [27].

2.3. Calcium(II)-1,10-phenanthroline equilibrium studies

Experiments were performed using two different stock solutions of 1,10-phenanthroline (280 and 120 μM). Ca(NO₃)₂·4H₂O was used to prepare ionic calcium stock solutions (237.4 μM and 101.7 μM). In both experiments, the final Calcium(II) concentration was set constant at 23.72 and 10.17 μM and the 1,10-phenanthroline concentrations were varied from 2.8 to 56.0 μM and from 1.2 μM to 24.0 μM, respectively. A total of 38 spectra were used for the refinement in the HypSpec software, as described above.

3. Results and discussion

The calcium complexes reported here, are insoluble in several solvents, such as water, methanol or ethanol. Considering the low donor number or donicity of solvents [28,29], acetonitrile was used instead of the solvents above mentioned. The low donor number of acetonitrile (14.1), against the methanol (19.0) or ethanol (18.5), allows the preparation of solutions at very low concentration, avoiding precipitation of the complexes [28]. Also, ionic strength was not used because it can cause an early precipitation of the complexes; this consideration decreases the ionic solvation sphere and interferes with the stability of the complexes. Finally, the formation constants in this study cannot be regarded as true equilibrium constants and can only be used when they are compared with similar systems using the same method and solvent.

3.1. Formation constants of the calcium(II)-2,2'-bipyridyl and calcium(II)-1,10-phenanthroline complexes

The equilibrium constants for the complexes: Calcium(II)-2,2'-bipyridyl and Calcium(II)-1,10-phenanthroline, have been reported under several conditions and methods. A brief review of these systems is presented in Table 1. Nevertheless, as far as we know, the formation constants of the calcium(II)-2,2'-bipyridyl complexes, have not been reported before in the absence of ionic strength and acetonitrile as solvent. Also, to our knowledge, the electronic spectrum of the calcium complexes with 2,2'-bipyridyl or -1,10-phenanthroline has not been calculated in any other work.

In solution, the formation constants of the system of Calcium(II)-2,2'-bipyridyl has been reported in several solvents and methods: using spectrophotometry as a titration method, ethanol (95%) as solvent, murexide as an indicator, and tetraethylammonium perchlorate (TEAP) 0.05 M as ionic strength [31]; using a titration fluorometric method in acetone and ethanol as solvents, in the absence of ionic strength [32]; using a glass electrode, KCl as ionic strength at 0.20 M [33];

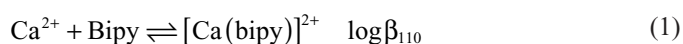
Table 1
Stability constants of the complexes: Ca(II)-2,2'-bipyridyl and Ca(II)-1,10-phenanthroline in acetonitrile, under different experimental and method conditions reported in the literature.

Method*	Dissolvent	Ionic strength	T(K)	Log β_{110}	Log β_{120}	Log β_{130}	Ref.
2,2'-Bipyridyl							
EV*		0.25 KCl*	298	-0.05	-	-	[30]
SP*	Ethanol	0.9 M N(C ₂ H ₅) ₄ ClO*	298	1.97	-	-	[31]
FL*	Acetonitrile	1.0 M N(C ₂ H ₅) ₄ ClO	298	2.71	4.81	5.81	[32]
FL	Acetone	1.0 M N(C ₂ H ₅) ₄ ClO	298	2.0	4.66	-	[32]
FL	Methanol	1.0 M N(C ₂ H ₅) ₄ ClO	298	1.66	2.56	-	[32]
EV	Methanol	0.20 M KCl	298	4.36	-	-	[33]
1,10-Phenanthroline							
SP	Ethanol	0.9 M N(C ₂ H ₅) ₄ ClO	298	2.69	-	-	[31]
FL	Acetonitrile	1.0 M N(C ₂ H ₅) ₄ ClO	298	4.11	7.78	9.72	[32]
FL	Acetone	1.0 M N(C ₂ H ₅) ₄ ClO	298	3.93	5.5	-	[32]
FL	Methanol	1.0 M N(C ₂ H ₅) ₄ ClO	298	2.11	3.32	-	-
EV		0.25 KCl	298	2.20	-	-	[30]
EV		0.1 M KNO ₃ *	308	4.1	-	-	[34]
VP*		0.1 NaClO ₄ *	298	1.1	-	-	[35]

* Abbreviations of the methods are: SP = Spectrophotometric; EV = Glass electrode; FL = Fluorimetry; VP = Potentiometric titration. Abbreviations of the solvents are: KCl = Potassium chloride; N(C₂H₅)₄ClO = Tetrabutylammonium perchlorate; KNO₃ = Potassium nitrate; NaClO₄ = Sodium perchlorate.

using a glass electrode, and potassium chloride to maintain the ionic strength of 0.25 [30]. These systems are reviewed in Table 1, in which a general behavior can be observed, if the ionic strength is maintained constant, the stability constant increases as the donor number of the solvent, decreases.

The electronic spectra for the Calcium-2,2'-bipyridyl system, in acetonitrile, are shown in Fig. 1(a) and (b). For this system a maximum of 236 nm and the other at 281 nm appears at low concentrations of 2, 2'-bipyridyl, as the concentration increases, a hyperchromic effect appears at both wavelengths. The determination of the formation constants corresponds to an equilibrium between Ca²⁺ and 2, 2'-bipyridyl, is performed by processing all spectra obtained from two experiments at different concentrations of calcium stock solutions and different concentration ranges of 2, 2'-bipyridyl. In each experiment, both collections of data are processed simultaneously. This method involves the correlation between the metal and ligand concentration used, the spectrum obtained and a proposal of species that absorb light in the system. The absorbance values observed in different wavelengths were measured at 25 °C. In this system, only an additional species to Ca²⁺ and 2, 2'-bipyridyl was obtained. The determination of the formation constant was achieved using the model:

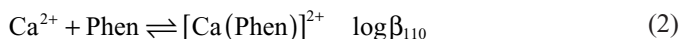


In Fig. 2(a) we show the calculated electronic spectrum of [Ca(bipy)]²⁺ in acetonitrile, also the spectrum of ionic calcium and 2,2'-bipyridyl unbound. It can be observed that the maximum peaks of unbound ligands are maintained in the complex. The calculated electronic spectrum of the [Ca(bipy)]²⁺ shows two absorption maximums at 236 nm and 281 nm, with a molar extinction coefficient $\epsilon = 23641$ and $\epsilon = 28535 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively.

On the other hand, the formation constants of the Calcium-1,10-phenanthroline system have been reported before, under several methods and conditions: spectrophotometry as

method and ethanol (95%) as solvent at an ionic strength of 0.05 M [31]; glass electrode method and 0.1 M of KNO₃ as ionic strength [34]; 0.1 M of NaClO₄ as ionic strength and using a method of potentiometry and spectrophotometry [35]. A review of the systems mentioned above is also presented in Table 1.

In Fig. 3(a) and (b), we show the electronic spectra for the calcium(II)-1,10-phenanthroline system at two different concentrations in acetonitrile. For this system, at low levels of 1,10-phenanthroline, a maximum absorption peak appears at 229 nm and another at 264 nm, as the concentration of ligands increases, a hyperchromic effect is observed at both wavelengths. The determination of the formation constants correspond to an equilibrium between Ca²⁺ and 1,10-phenanthroline, the refinement process was performed as describe above. The observed absorbance values at different wavelengths were recorded at 298 K, considering that just a colored species was found, the determination of the formation constant was performed using the following model:



In Table 2 we report the logarithmic values of the formation constants and a description of the experimental parameters, using the format of Tuck suggested by IUPAC [36]. In Fig. 4(a), we show the calculated electronic spectrum of the [Ca(Phen)]²⁺ in acetonitrile, this spectrum shows an absorption maximum at 229 nm and another at 264 nm, with a molar extinction coefficient of $\epsilon = 66190$ and $\epsilon = 40487 \text{ L mol}^{-1} \text{ cm}^{-1}$, respectively. In Fig. 4(a), we also show the electronic spectrum of 1,10-phenanthroline and ionic calcium, in which Ca²⁺ is almost spectroscopically silent.

The efficiency of acetonitrile as electron donor solvent [29], is manifested through its donor number of 14.1. This plays an important role in the solvation of ionic solutes, has been related to the donor and acceptor electron capacity [28]. Acetonitrile with a lower donor number than ethanol, acetone or water, is

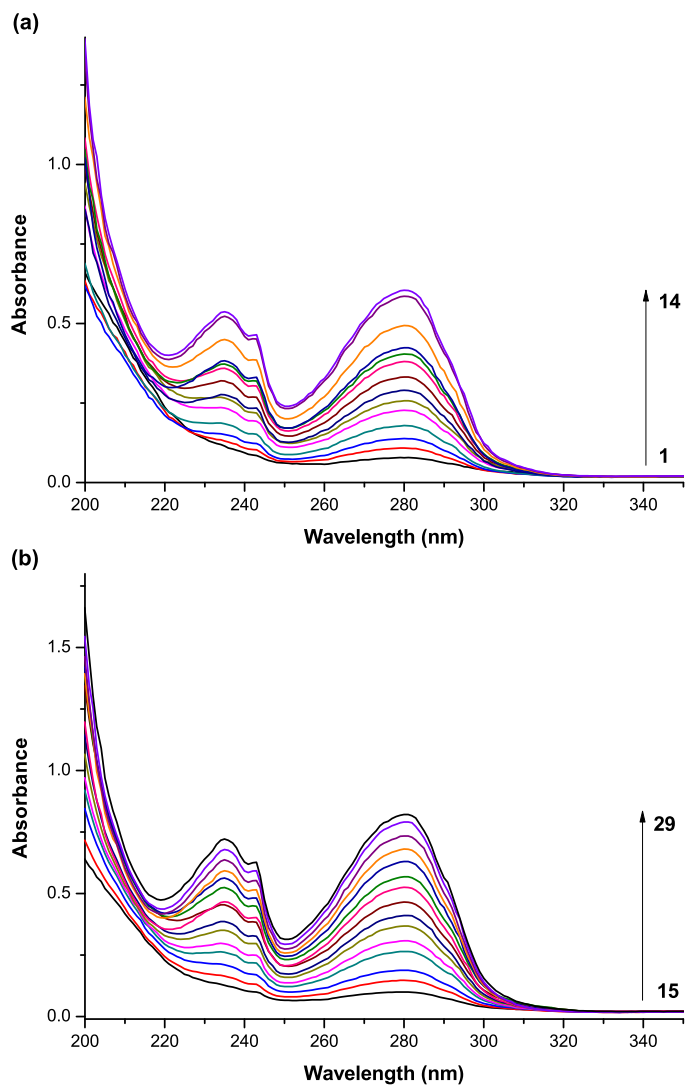


Fig. 1. (a) Absorption spectra of Ca(II)–2,2'-Bipyridyl system in acetonitrile for spectra 1 to 14, $[Ca^{2+}] = 16.6 \mu M$ and 2,2'-Bipyridyl concentration (μM): (1) 2.51; (2) 5.02; (3) 7.52; (4) 10; (5) 12.5; (6) 15; (7) 17.6; (8) 20.1; (9) 22.6; (10) 25.1; (11) 27.6; (12) 30.1; (13) 37.6; (14) 40.1; (b) for spectra 15 to 29, $[Ca^{2+}] = 23.72 \mu M$ and 2,2'-Bipyridyl concentration (μM): (15) 3.58; (16) 7.17; (17) 10.75; (18) 14.34; (19) 17.92; (20) 21.50; (21) 25.09; (22) 28.67; (23) 32.26; (24) 35.84; (25) 39.42; (26) 43.01; (27) 46.52; (28) 50.18; (29) 53.76.

capable of generating into the metal a weaker solvation sphere. Allowing a better association between the ligand and the metal [37]. This capacity is taken into account as an important factor in the difference between the equilibrium constants obtained in previous studies (Table 1). On the other hand, among the factors presented by the metal complexes with 2,2'-bipyridyl and 1,10-phenanthroline, they have very interesting photochemical properties which make them potentially suitable for applications in solar energy conversion [38]. Due to its synthesis and the chelating properties of these ligands, they have been widely used in the syntheses of complexes with metal ions. These ligands have redox stability and ease of functionalization [39]. On the other hand, Ca^{2+} is classified as a hard Lewis acid [15,40], considering this, if both species, metal, and ligand,

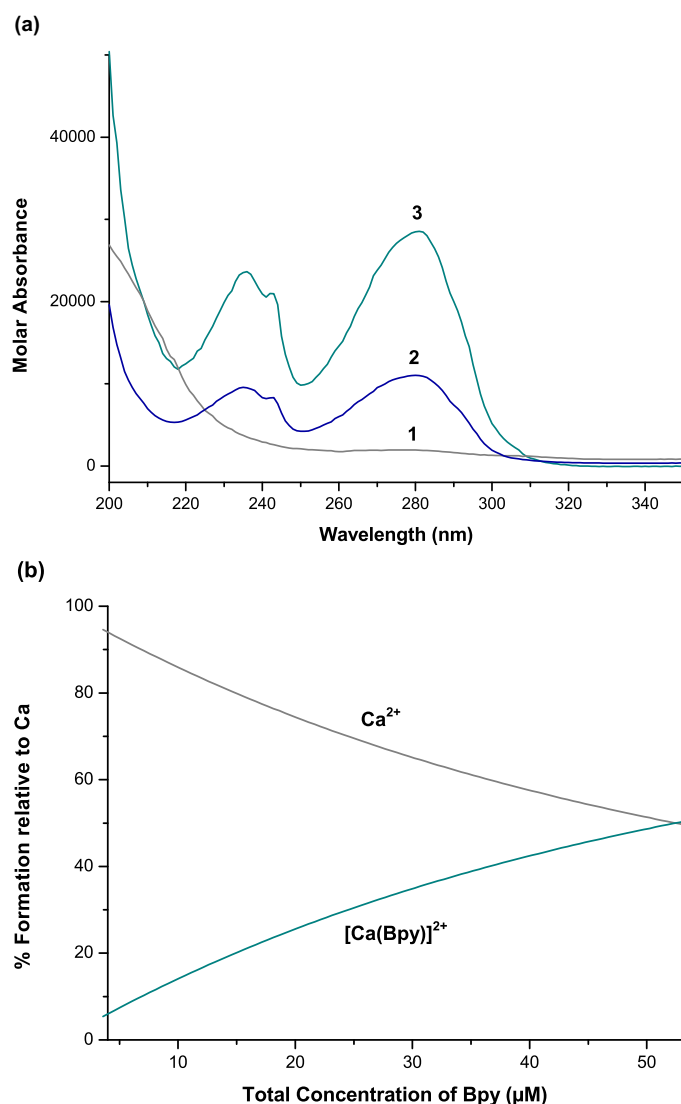


Fig. 2. (a) Electronic spectra of the Ca(II)–2,2'-Bipyridyl complex in acetonitrile: (1) Ca^{2+} ; (2) Bpy; (3) $[Ca(Bpy)_2]^{2+}$. (b) Formation curves of the Ca(II)–2,2'-Bipyridyl complex in acetonitrile. $[Ca^{2+}] = 23.72 \mu M$ and 2, 2'-Bipyridyl from range 3.58 to 53.76 μM .

have an acid and base hard character, respectively, the interaction will be greater [40]. Nevertheless, 1,10-phenanthroline and 2,2'-bipyridyl are considered as soft Lewis bases [40], which may promote that the calcium complexes could be unstable in solvents with high donor number.

In this work the complexes with calcium(II), 1,10-phenanthroline and 2,2'-bipyridyl, show an effect of charge transfer from ligand to metal, this can usually be present in complexes with metal ions with low oxidation states and π -donor ligands as 2,2'-bipyridyl and 1,10-phenanthroline [40–42]. On the other hand, considering the size of ionic calcium and the aromatic behavior of 1,10-phenanthroline could generate a higher inductive effect than the 2,2'-bipyridyl, which behave as a soft base [42]. In order to evaluate this theory, it is necessary to obtain a crystal structure of these complexes, characterize by X-ray diffraction and analyze its structure and bond lengths.

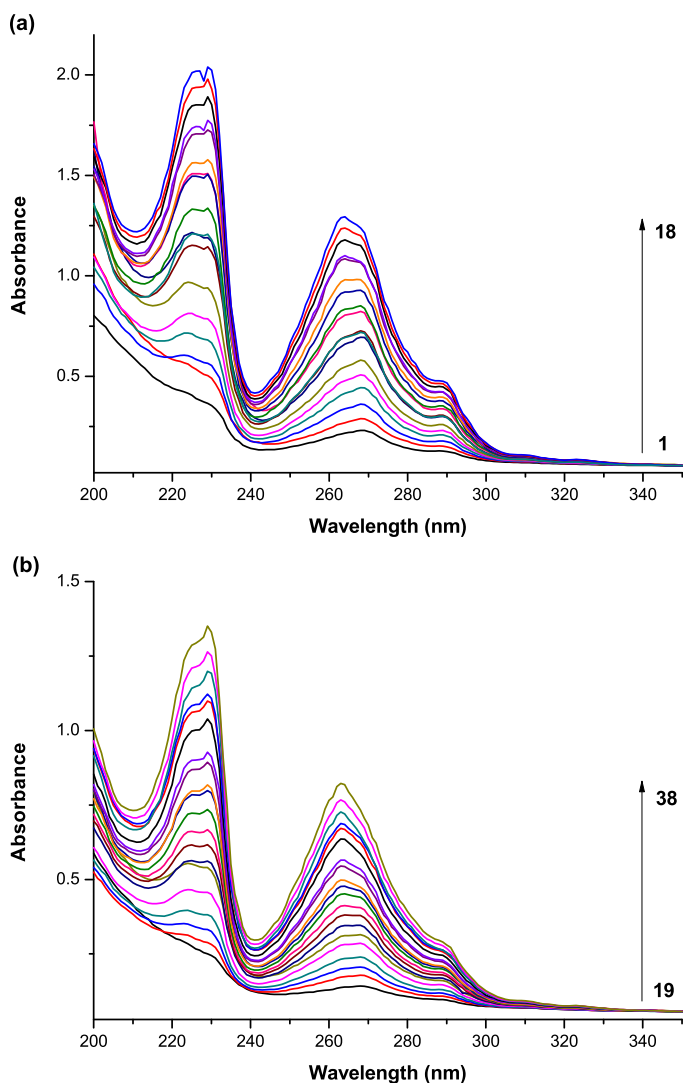


Fig. 3. (a) Absorption spectra of Ca(II)–1,10-Phenanthroline system in acetonitrile for spectra 1 to 18, $[Ca^{2+}] = 23.72 \mu M$ and 1,10-Phenanthroline concentration (μM): (1) 2.8; (2) 5.6; (3) 8.40; (4) 11.20; (5) 14.0; (6) 16.80; (7) 19.60; (8) 22.40; (9) 25.20; (10) 30.80; (11) 33.60; (12) 36.40; (13) 39.20; (14) 44.80; (15) 47.60; (16) 50.40; (17) 53.20; (18) 56.0. (b) for spectra 19 to 38 $[Ca^{2+}] = 10.17 \mu M$ and 1,10-Phenanthroline concentration (μM): (19) 1.2; (20) 2.4; (21) 3.6; (22) 4.8; (23) 6.0; (24) 7.2; (25) 8.4; (26) 9.6; (27) 10; (28) 12.0; (29) 13.2; (30) 14.4; (31) 15.6; (32) 16.8; (33) 18.0; (34) 19.20; (35) 20.4; (36) 21.6; (37) 22.8; (38) 24.0.

3.2. Distribution curves of the calcium(II)–2,2′-bipyridyl and calcium(II)–1,10-phenanthroline systems

The distribution curve of the Calcium–2,2′-bipyridyl system, is shown in Fig. 2(b). For a solution with an equimolar concentration of calcium and 2, 2′-bipyridyl, generates about 30% of $[Ca(Bpy)]^{2+}$ and 70% of ionic calcium. On the other hand, a concentration of 1 mol of ionic calcium and 2 mol of 2,2′-bipyridyl, yields about 50% of the *mono*-complex and reduces the abundance of free calcium to 50%.

The distribution curve for the Calcium(II)–1,10-phenanthroline system is shown in Fig. 4(b). For a solution of an equimolar concentration of Calcium(II) and 1,10-phenanthroline generates a 90% of $[Ca(Phen)]^{2+}$, 10% of a

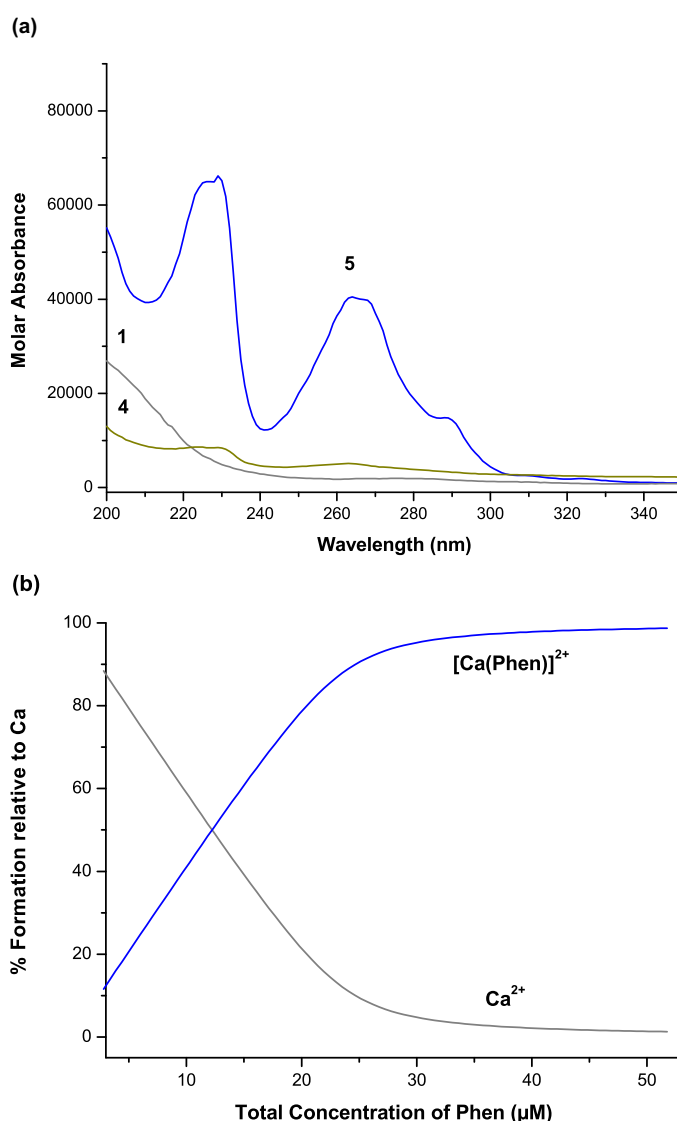


Fig. 4. (a) Electronic spectra of Ca(II)–1,10-Phenanthroline complex in acetonitrile (1) Ca^{2+} ; (4) Phen; (5) $[Ca(Phen)]^{2+}$. (b) Formation curves of Ca(II)–1,10-Phenanthroline complex in acetonitrile. $[Ca^{2+}] = 23.72 \mu M$ and 1,10-Phenanthroline from range 2.80 to 24.0 μM .

mixture of ionic calcium and 1,10-phenanthroline. On the other hand, a combination containing a 1 mol concentration of ionic calcium and 2 mol of 1,10-phenanthroline the $[Ca(Phen)]^{2+}$ increases its abundance to 98% and decreases the mixture of ionic calcium and 1,10-phenanthroline to a 2%. When the π -donor capacity of the 1,10-phenanthroline and 2,2′-bipyridyl is compared, it can be shown that a high π donor capacity promotes an increase in the affinity for ionic calcium, which is consistent with the formation constant for both calcium complexes (Table 2).

4. Conclusions

The purpose of this work was to obtain the formation constants of the calcium complex with 1,10-phenanthroline and 2,2′-bipyridyl, which leads to calculate their electronic spectrum, to compare between them. Further studies should

Table 2

Summary of experimental parameters for the two systems: Ca(II)-2,2'-bipyridyl and Ca(II)-1,10-phenanthroline in acetonitrile.

Solution composition	[T _L] range from 2.51 to 40.10 and 3.58 to 53.76 μM L ⁻¹ [T _M] constant at 16.6 and 23.72 μM L ⁻¹		
Ionic strength, electrolyte			Not used
pH range			Not used
Experimental method	Spectrophotometric		
Temperature	298 K		
Total number of data points	Ca complexation: 29 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
[Ca(Bpy)] ²⁺	Ca ²⁺ + Bpy ⇌ [Ca(Bpy)] ²⁺	Log β ₁₁₀ = 4.391 ± 0.02	0.007
Solution composition	[T _L] range from 1.20 to 24.0 and 2.80 to 56.0 μmol L ⁻¹ [T _M] constant at 10.17 and 23.72 μmol L ⁻¹		
Ionic strength, electrolyte			Not used
pH range			Not used
Experimental method	Spectrophotometric		
Temperature	298 K		
Total number of data points	Ca complexation: 38 solution spectra		
Method of calculation	HypSpec		
Species	Equilibrium	Log β	σ
[Ca(Phen)] ²⁺	Ca ²⁺ + Phen ⇌ [Ca(Phen)] ²⁺	Log β ₁₁₀ = 5.942 ± 0.04	0.057

estimate the potential of the calcium complexes as photocatalysts. Also, additional studies complementing experimental information presented in this work should be done. Some of these studies are the luminescent spectra of the calcium complexes. This study might help to truly establish an electronic structure of these complexes. Also some complementary studies such as cyclic voltamperometry and crystallographic studies can be aids to correlate geometry, redox potential and its possible photocatalytic activity.

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