Available online at www.sciencedirect.com

ScienceDirect

Green Energy & Environment 2 (2017) 51–57

www.keaipublishing.com/gee

Research paper

Spectrophotometric determination of the formation constants of Calcium(II) complexes with 1,2-ethylenediamine, 1,3-propanediamine and 1,4-butanediamine in acetonitrile

Jacqueline González González [a], Mónica Nájera-Lara [b], Varinia López-Ramírez [c], Juan Antonio Ramírez-Vázquez [d], José J.N. Segoviano-Garfias [d,*]

[a] *Programa de Maestría en Biociencias, División de Ciencias de la Vida (DICIVA), Universidad de Guanajuato, Campus Irapuato-Salamanca, Ex Hacienda El Copal, Carretera Irapuato-Silao Km. 9, Irapuato, Gto., 36500, Mexico*

[b] *Colegio del Nivel Medio Superior de Salamanca (ENMS), Prolongación Tampico No. 904, Salamanca, Gto., 36730, Mexico*

[c] *Departamento de Ingeniería Bioquímica, Instituto Tecnológico Superior de Irapuato (ITESI), Carretera Irapuato-Silao Km. 12.5, Irapuato, Gto., 36821, Mexico*

[d] *Departamento de Ciencias Ambientales, División de Ciencias de la Vida (DICIVA), Universidad de Guanajuato, Campus Irapuato-Salamanca, Ex Hacienda El Copal, Carretera Irapuato-Silao Km. 9, Irapuato, Gto., 36500, Mexico*

Received 7 July 2016; revised 7 January 2017; accepted 9 January 2017
Available online 18 January 2017

Abstract

In this work, with the purpose to explore the coordination chemistry of calcium complexes which could work as a partial model of manganese–calcium cluster, a spectrophotometric study to evaluate the stability of the complexes: Calcium(II)-1,2-ethylendiamine, Calcium(II)-1,3-propanediamine and Calcium(II)-1,4-butanediamine in acetonitrile, were carried on. By processing the spectrophotometric data with the HypSpec program allows the determination of the formation constants. The logarithmic values of the formation constants obtained for Calcium(II)-1,2-ethylendiamine, Calcium(II)-1,3-propanediamine and Calcium(II)-1,4-butanediamine were $\log \beta_{110} = 4.69$, $\log \beta_{110} = 5.25$ and $\log \beta_{110} = 4.072$, respectively.

Keywords: Calcium(II) complexes; Solution equilibria; Artificial photosynthesis; Absorbance molar; Speciation

1. Introduction

In order to promote a sustainable development for civilization, several research groups have focused on the development of alternative and renewable energy sources [1]. A promising alternative, is the use of solar radiation reaching the surface of the earth [2], for its storage two major approaches should be considered: direct conversion of solar energy to electricity or the use of solar energy to generate fuels such as molecular hydrogen from water [3]. In nature, the most efficient method to harvest solar energy, is the photosynthesis [4]. In this process, water oxidation occurs in the Oxygen-Evolving Complex (OEC), which is metallic cluster consisting in a Calcium atom oxo-bridged to four Manganese atoms (Mn_4Ca) and bonded to several amino acids [5]. In order to design a sustainable energy system with analogies to the natural photosynthesis, a biomimetic approach has been considered since nineteenth century [6], this theorized technology tries to imitate the photosystem II (PSII), wherein the main analogies in photosynthesis reactions, can be used in a conceptually simple system and accomplish similar results to natural photosynthesis [7].

---

* Corresponding author.
E-mail addresses: segovi@ugto.mx, jose.segoviano@gmail.com (J.J.N. Segoviano-Garfias).

http://dx.doi.org/10.1016/j.gee.2017.01.002

Replication of the OEC is extremely difficult, the scientific community have searched a metal complex, that could combine a chemical stability with an adequate catalytic activity [8]. There have been notable developments related to the water splitting reaction catalyzed by complexes with ruthenium-, iridium-, manganese-, cobalt- and iron [9]. In particular, The complex: *tris*-(2,2′-bipyridyl)ruthenium(II) or $[Ru(Bpy)_3]^{2+}$ has been extensively studied, as active compound in photoelectrochemical cells of Grätzel [10] and as catalyst in water oxidation [11]. On the other hand, ruthenium may present several disadvantages as its high cost [9,12,13] and its low water oxidation activity compared to the presented by the OEC [14].

The presence of Calcium in the Oxygen-evolving complex is of main importance, this fact was demonstrated by several treatments to remove calcium from PSII, inhibiting the oxygen evolution and later reactivated by the addition of Ca^{2+} [15]. Although many other metal ions (Na^+, K^+, Cd^{2+}) might compete for the calcium binding sites in PSII, none of them is capable to reactivate the activity of oxygen evolution [16]. On the other hand, the biological role of Calcium is widely spread. Calcium ions are related to thermal stability in proteins [17], which is present in a wide variety of different activities, such as: muscle contraction, glycolysis, gluconeogenesis, cell division [18], promotes the activation of several proteins such as calmodulin or troponin C [17], which is contained in the core of bones and teeth as octacalcium phosphate. Finally, calcium is incorporated in enzymatic cofactors of the proteases trypsin and thermolysin. Also in enzymes that degrade nucleic acids (nucleases) and lipids (lipases) [19]. Besides the calcium presence in the OEC, as far as we know, the calcium complexes have not been considered for its use in artificial photosystems. Nevertheless, some studies involving calcium oxides have been tested as catalysts for water oxidation showing a limited activity [20,21]. Other study also indicates that ionic calcium could promote a strong interaction to water molecules and change its geometry [22]. In order to explore the coordination chemistry of calcium complexes and evaluate its electronic properties, in this work, we report the formation constants of the complexes generated of Calcium(II) with 1,2-ethylenediamine, 1,3-propanediamine and 1,4-butanediamine in acetonitrile solution, their speciation and the calculated individual electronic spectrum of each species. This is the second part of a previous study, in which the formation constants of calcium and 2,2′-bipyridyl and 1,10-phenanthroline were reported [23]. It is widely accepted that the electronic spectrum of a compound can be usually associated to their electronic structure. Because of this, the purpose of the present work is to explore the electronic spectrum of the calcium complexes obtained.

2. Experimental

In the determination of the formation constants, acetonitrile HPLC grade, was used as solvent (Tecsiquim, Mexico), Calcium nitrate tetrahydrate, $Ca(NO_3)_2 \cdot 4H_2O$, 1,2-ethylenediamine, 1,3-propanediamine and 1,4-butanediamine (Sigma-Aldrich), were of analytical grade and used without further purification. All spectral measurements were made in a Shimadzu Spectrometer UV-1800, at 295 K (RT) using a quartz cell of 1 cm of path length and 3 mL of volume. For all the experiments, the observed spectral region was from 220 to 300 nm. For the determination of formation constants, the spectrophotometric data were fitted with the HypSpec software [24], using the same methodology as reported in previous studies [25]. The distribution diagrams of species were calculated using the software Hyperquad Simulation and Speciation (HySS) [26].

2.1. Calcium(II)-1,2-ethylenediamine equilibrium studies

Experiments were performed using two different stock solutions of 1,2-ethylenediamine (3.590 and 10.770 mM). The $Ca(NO_3)_2 \cdot 4H_2O$ was used to prepare the ionic Calcium stock solutions (2.370 and 7.110 mM). In each experiment, the final concentration of Calcium was set constant at 0.240 and 0.710 mM, in where the 1,2-ethylenediamine concentrations were varied from 0.036 to 0.570 mM and 0.120–0.860 mM, respectively. A total of 14 spectra were used in the refinement in the HypSpec software, using the methodology mentioned above.

2.2. Calcium(II)-1,3-propanediamine equilibrium studies

Experiments were performed using two different stock solutions of 1,3-propanediamine (3.830 and 7.660 mM). The $Ca(NO_3)_2 \cdot 4H_2O$ was used to prepare Calcium stock solutions (2.370 and 4.740 mM). In each experiment, the final concentration of Calcium was set constant at 0.237 and 0.475 mM, the 1,3-propanediamine concentrations were varied from 0.038 to 0.345 mM and 0.153–0.537 mM, respectively. A total of 14 spectra were used for the refinement in the HypSpec software, also using the methodology mentioned above.

2.3. Calcium(II)-1,4-butanediamine equilibrium studies

Experiments were performed using two different stock solutions of 1,4-butanediamine (6.370 and 12.750 mM). $Ca(NO_3)_2 \cdot 4H_2O$ was used to prepare Calcium stock solutions (4.740 and 9.490 mM). In both experiments, the final Calcium concentration was set constant at 0.475 and 0.949 mM and the 1,4-butanediamine concentrations were varied from 0.064 to 0.638 mM and from 0.128 to 1.275 mM, respectively. A total of 12 spectra were used for the refinement in the HypSpec software.

3. Results and discussion

The calcium complexes reported here, are highly insoluble in several solvents, such as water, methanol and ethanol, also the ionic strength was avoided because of increasing the precipitation of the complexes. In order to increase the solubility