Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 143 (2015) 187–191

Contents lists available at ScienceDirect

Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy

journal homepage: www.elsevier.com/locate/saa

Spectrophotometric quantification of the thermodynamic constants of the complexes formed by dopamine and Cu(II) in aqueous media

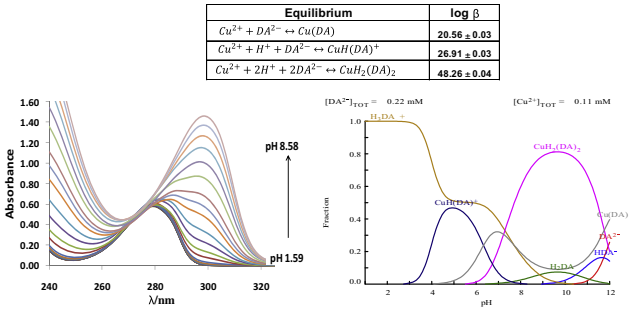
B. Verastegui-Omaña [a], M. Palomar-Pardavé [b], A. Rojas-Hernández [a], S. Corona Avendaño [b], M. Romero-Romo [b], M.T. Ramírez-Silva [a,*]

[a] Universidad Autónoma Metropolitana-Iztapalapa, Departamento de Química, Área de Química Analítica, San Rafael Atlixco 186, Col. Vicentina, Del. Iztapalapa, C.P. 09340 México DF, Mexico
[b] Universidad Autónoma Metropolitana-Azcapotzalco, Área Ingeniería de Materiales, Departamento de Materiales, Av. San Pablo 180, Col. Reynosa-Tamaulipas, C.P. 02200 México DF, Mexico

HIGHLIGHTS

- The thermodynamic constants of the complex Cu(II)–dopamine in aqueous solution were evaluated.
- Experimental spectrophotometric data and the software SQUAD were used.
- It was found that there exist Cu(II):DA complexes with 1:1 and 1:2 stoichiometries.
- Their predominance depends on both the solution pH and the [Cu(II)]/[DA] ratio.
- $Cu(OH)_{2(s)}$ solubility increases drastically when these complexes are formed.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 23 May 2014
Received in revised form 9 December 2014
Accepted 27 January 2015
Available online 17 February 2015

Keywords:
Dopamine
Copper(II)
Spectrophotometry
SQUAD
Complexation constants

ABSTRACT

The thermodynamic constants of the complex Cu(II)–dopamine in aqueous solution were evaluated from spectrophotometric data using the software SQUAD. It was found that there exist Cu(II):DA complexes with 1:1 and 1:2 stoichiometries and that their predominance depends on both the solution pH and the [Cu(II)]/[DA] ratio. Moreover, it is shown that the solubility of $Cu(OH)_{2(s)}$ increases drastically when these complexes are thermodynamically stable.

Introduction

Metal ions such as Cu(II), Zn(II) and Ni(II) [1] are required for normal metabolism of humans. In particular, copper is an essential trace element for all [2], since it plays a key role as an integral component of many enzymes [3,4], in which the ceruloplasmin is responsible for the transport of 95% copper in blood [5,6]. Furthermore, it has been reported that Cu(II), and some other metal ions, are responsible for the storage and transport of one of the major neurotransmitters in mammalians, dopamine (DA), through the cell membrane [7–9]. DA is the main catecholamine in the central

* Corresponding author.
E-mail address: mtrs218@xanum.uam.mx (M.T. Ramírez-Silva).

http://dx.doi.org/10.1016/j.saa.2015.01.067
1386-1425/

nervous system, so much so that abnormal DA concentrations have been associated with neurological diseases such as Parkinson's (low DA in certain brain areas) or schizophrenia (DA too causes hallucinations and paranoid thoughts) [10]. It is clear that the interaction of DA with Cu(II) ions is a key aspect for the full understanding of these processes. Due to this, there have been some studies on the subject [7–9,11–13]. Most of these studies have been performed to estimate the stability constants of such complexes using L-dopa, the metabolic precursor of DA, in different media such as mixtures of alcohol/water and organic solvents such as DMF DMSO [7], methanol/water and ethylene glycol/water using experimental techniques, such as potentiometric titration, UV–VIS spectrometry and electron spin resonance [8,9]. Also, the experimental data have been processed by computer programs as Psequad, Superquad [11] and Miniquad [12] for calculating the thermodynamic constants of this sort of complex formation. Given the importance of calculating the constants of the complex formed by DA and Cu(II) in aqueous media, and that so far the information from the estimation of these constants are not reported, in this paper this interaction was studied through UV–VIS spectrophotometry using the SQUAD program [14].

Experimental

Reactants

All DA (Merck 98.5%) and $CuCl_2{\cdot}2H_2O$ (J.T. Baker 99%) solutions were prepared using analytical grade reagents, just as the NaOH (Merck 99%) and $HClO_4$ (J.T. Baker 72%), using deionized water free from organic matter from a US Filter PURE LAB PLUS. Prior to any experiments, each fresh solution was bubbled with nitrogen and precluded from light incidence, to carry out quality spectro-electrochemical studies. Following the point-by-point analysis method described elsewhere, see Sánchez et al. [15] both: dilution and DA oxidation complications were avoided. All the solutions were made with $HClO_4$ 0.1 M and the pH was adjusted with NaOH 2 M (keeping a constant 0.1 M ionic strength). A thermostated 10 mL reaction cell was used in order to maintain a constant temperature (25 ± 0.5) °C aided by a Cole-Palmer bath and a magnetic stirrer.

Equipment

A UV–VIS spectrophotometer (Perkin Elmer Lambda 20) was used. The pH of the dissolutions was measured by means of a pH-meter Mettler Toledo MP230, with a Mettler Toledo InLab 413 SG combined electrode (pH interval 0–14).

Results and discussion

As the DA is a bidentate ligand then the Cu(II) could form a complex either through the catechol or the amine group. Thus, the aim of this research is to demonstrate the formation of these complexes. Hence, it is appropriate to state the working conditions, then to present the results obtained concerning the spectrophotometry study followed by an electrochemical one of the Cu(II) with DA mixes.

Working conditions

Fig. 1a shows the absorbance behavior of the DA solution for a 2.14×10^{-4} M DA sample at pH 1.35. An absorption maximum became evident at 277 nm. It should be noted that there were no signals apparent at wavelengths greater than 300 nm.

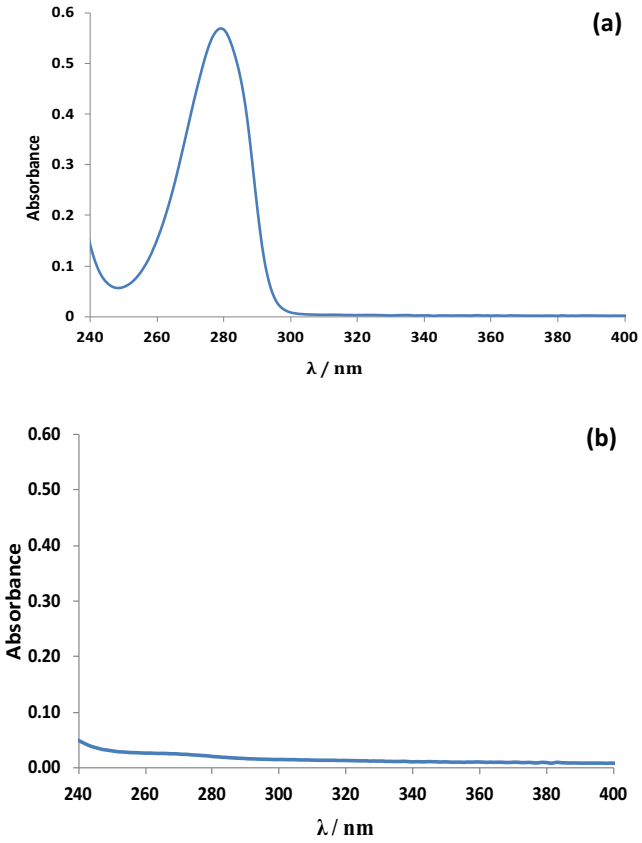


Fig. 1. Absorption spectrum at pH 1.35 in $HClO_4$ 0.1 M of (a) DA 2.14×10^{-4} M, and (b) Cu(II) 2.11×10^{-4} M.

Next, the spectrophotometry study was carried out with a 2.11×10^{-4} M Cu(II) solution at pH 1.35, see Fig. 1b. No absorbance peaks from the Cu(II) were displayed: therefore, there should not be expected any interference for the DA.

Once the Cu(II) and the DA working conditions were established, then the spectrophotometric and the electrochemical study were carried out for mixtures of DA and Cu(II) in order to evaluate if a chemical interaction between this molecules is occurring.

Spectrophotometric study

Fig. 2a shows a family of absorption spectra recorded in the system DA 2.14×10^{-4} M, pH 4.18 for different [Cu(II)] values. It is possible to note that the respective spectra were not similar in all cases to those recorded in the absence of Cu(II), see Fig. 1a. The same experiment was carried out for pH < 4.18 and the same similar results were obtained. However, at pH 6.53 (Fig. 2b) the corresponding spectra displayed notable changes, as a shoulder appeared at approximately 308 nm that increased with increasing metal–ligand molar ratio, and a shift in wavelength of the absorption maximum (bathochromic and hyperchromic effects), which strongly suggest a Cu(II)–DA interaction. Therefore, a molar ratios' study was carried out [16,17] of the system Cu(II)–DA, in order to propose the possible stoichiometric relation of the complex formed.

Fig. 3 depicts the variation of the absorbance recorded at 308 nm, see Fig. 2b, as a function of the [Cu(II)]/[DA] molar-ratio. At least two slope changes can be observed that lead into the preliminary conclusion that there exist Cu(II):DA complexes with 1:1 and 1:2 stoichiometries.