Contents lists available at SciVerse ScienceDirect

Electrochimica Acta

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

Electrochemical metallation with Ni(II) and Al(III) of 5,10,15,20-tetrakis(p-hydroxyphenyl)porphyrin: Effect of ultrasound

Elsa N. Aguilera^{a,*}, Leonor M. Blanco Jerez^b, Jorge L. Alonso^b

^a Corporación Mexicana de Investigación en Materiales, S.A. de C.V., Ciencia y Tecnología No. 790, Fracc. Saltillo 400, C.P. 25290, Saltillo, Coah., Mexico ^b Laboratorio de Electroquímica, Facultad de Ciencias Químicas, Universidad Autónoma de Nuevo León, Guerrero y Progreso S/N, Col. Treviño, C.P. 64570 Monterrey, N.L., Mexico

ARTICLE INFO

Article history: Received 2 February 2013 Accepted 5 March 2013 Available online 13 March 2013

Keywords: 5,10,15,20-Tetrakis(phydroxyphenyl)porphyrin Nickel porphyrins Aluminum porphyrins Electrosynthesis Ultrasound

JILIASOUIIU

1. Introduction

Research on porphyrin and metalloporphyrin has evolved from the first synthesis by Fisher in 1920 to their use as selective catalysts in molecular electronic devices, photodynamic therapy agents and others applications in material chemistry [1,2]. Since then, the porphyrins and their complex salts have been obtained by the interaction of free base porphyrins and a metal salt in suitable reaction conditions.

Template synthesis and direct synthesis are the methods currently used to prepare metalloporphyrins [3]. In direct synthesis, which is the most widely used method, free base porphyrins react with metallic salt ions under drastic reaction conditions [4].

Electrolysis is commonly used to synthesize coordination compounds. Advantages of electrolysis include higher yields and higher purity of the resulting compounds than those obtained by classic methods. Also, electrosynthesis is carried out under milder conditions and with lower reaction times than those of classic methods [3].

The porphyrin ring system can be reduced or oxidized during the electrolysis process. Electrochemical studies by cyclic voltammetry (CV) show that porphyrins can be reduced or oxidized in two one-electron-transfer steps to form π anionic or cationic radicals

ABSTRACT

The electrochemical synthesis of Ni(II) and Al(III) metalloporphyrins by reaction of the dianion radical of the 5,10,15,20-tetrakis(p-hydroxyphenyl)porphyrin (TpOHPP) with Ni(II) and Al(III) ions is reported. The electrosynthesis conditions were established by cyclic voltammetry of TpOHPP. The electrosynthesis process was carried out in an undivided cell at the potential corresponding to the formation of the porphyrin dianion radical. A sacrificial anode of Ni or Al was used to electrogenerate the ions. The experiments were carried out in aprotic solvents. The effect of the application of 20 kHz ultrasound on the electrochemical process was evaluated. The electrosynthesis products were characterized by spectroscopy and electrochemical techniques. The results indicate the formation of metalloporphyrins in the different solvents in silent conditions and with ultrasound. The application of 20 kHz ultrasound and protic solvents enhance the reaction yields without affecting the structure of the obtained products.

© 2013 Elsevier Ltd. All rights reserved.

[5–8]. Therefore, the application of an electric field will produce a π anionic radical, which reacts with the positive metallic ions to form the metalloporphyrin. The solvent plays a very important role in metalloporphyrin

synthesis. Kadish et al. reported that the reaction of cobalt acetate with meso-tetrakis(pentafluorophenyl)porphyrin (TF_5PP) H_2 leads to the formation of different metalloporphyrin products for different solvents [7]. The spectroscopic, electrochemical and redox properties of metalloporphyrins are also affected by the solvent. Kadish et al. found that nickel metalloporphyrins can be oxidized or reduced on three one-electron-transfer steps depending on the solvent [8].

Another important aspect to consider is the metal ion used for porphyrin metallization. The compatibility of the porphyrin ring dimensions with the metal cation ionic radius is crucial for metalloporphyrin formation. Stable complexes are formed only when both sizes are similar [9].

In recent years, ultrasound irradiation has been used in some chemical reactions to improve yields, selectivity and reaction rate without using harsh conditions [10]. These advantages attributed to the special sonochemical effect, which is primarily resulted from "hot spots" formed during acoustic cavitations (i.e., the formation, growth, and implosive collapse of bubbles in liquids). In particular, the behavior of localized intensity of temperature and pressure in the reaction determines their function feature [11]. The imploding of bubbles creates locally high pressure up to 1000 bar and temperature up to 5000 K. These extraordinary conditions permit access to a range of chemical reaction space normally nor accessible,





^{*} Corresponding author. Tel.: +52 844 411 32 00x1349.

E-mail addresses: eaguilera.gonzalez@gmail.com, elsa.aguilera@comimsa.com (E.N. Aguilera).

^{0013-4686/\$ -} see front matter © 2013 Elsevier Ltd. All rights reserved. http://dx.doi.org/10.1016/j.electacta.2013.03.028



Fig. 1. Cyclic voltammograms of TpOHPP and TPP in TBAP/DMF at 0.5 V/s at a glassy carbon disk electrode (E vs. Fc/Fc⁺); the arrow indicates the sweep direction.

which allows for the synthesis of a wide variety of unusual materials [12,13].

This paper reports the results of electrochemical metallization of 5,10,15,20-tetrakis(p-hydroxyphenyl)porphyrin with Ni(II) and Al(III) in different solvents. We also report the effect of ultrasound on the metalloporphyrin electrosynthesis process.

2. Experimental

2.1. Electrochemical study

An electrochemical study was carried out to determine the formation potential of the porphyrin dianion radical. Linear and voltammetric techniques were applied in a conventional threeelectrode cell using an Epsilon potentiostat/galvanostat (BAS). Porphyrin voltammograms were obtained using a glassy carbon disk as the working electrode, a platinum disk as the auxiliary electrode (both from BAS) and a silver wire as the pseudo-reference electrode. MeOH and AN were used as solvents. The glassy carbon disk was polished before each experiment with alumina/methanol paste. Different sweep rates were applied to 10 mL of 2 mM TpOHPP with 0.1 M TBAP (Sigma–Aldrich) as the supporting electrolyte. All the potential values are reported with reference to the Fc/Fc⁺ system.

2.2. Metalloporphyrins electrosynthesis

The metalloporphyrins electrosynthesis was carried out at controlled potential. An undivided electrochemical cell containing 75 mL of a 0.1 mM porphyrin solution with 0.1 M TBAP as the supporting electrolyte was used. The working electrode was a glassy carbon cylinder (BAS) with a large surface area. A nickel and aluminum sheets of $2 \times 3 \text{ cm}^2$ were used as the sacrificial anodes and a silver wire was used as the reference electrode. To evaluate the solvent effect, the electrosynthesis was carried out in DMF and MeOH at room temperature for nickel metalloporphyrins and AN and MeOH at room temperature for aluminum metalloporphyrins. For ultrasound-assisted electrosynthesis, a 1/8-in. probe (or horn) was introduced in the reaction mixture, and a Fisher Scientific Sonifier (500 Model) was used to generate a 20 kHz ultrasound signal. The solvent was removed in a rotative evaporator and the products, obtained by precipitation with water, were washed with $\mbox{CH}_2\mbox{Cl}_2$ and vacuum dried.

2.3. Characterization

Metalloporphyrins were analyzed using various techniques. The atomic absorption technique was carried out in a GBC spectrometer (932AA model). The samples were previously dissolved in concentrated HNO₃ to destroy the organic material. The UV-Vis spectra of the starting material and the electrosynthesis products were obtained in a Varian UV spectrophotometer (Cary 100 CONC model). The samples (0.01 mg/mL) were analyzed in the 200–800 nm spectral region. FTIR analysis was carried out in a Bruker IR spectrophotometer (Tensor 27 model) using a KBr tablet. Finally, the ¹H NMR and ¹³C NMR studies were carried out in a Varian spectrometer (Mercury 200 model) and a 400 MHz Bruker spectrometer (Avance DPX model), respectively.

3. Results and discussion

3.1. Porphyrin electrochemical study

Fig. 1 depicts the electrochemical behavior of TpOHPP and 5,10,15,20-tetraphenylporphyrin (TPP) in TBAP/DMF at 0.5 V/s.

TpOHPP shows three reduction processes. The first two processes, labeled (A) and (B) in the figure, occur at $Epc_1 = -75 \text{ mV}$ and $Epc_2 = -222 \text{ mV}$; a less defined third process (labeled (C)) occurs at $Epc_3 = -703 \text{ mV}$ TpOHPP also shows three oxidation processes, labeled (a)–(c).

As reported in the literature [5–8], porphyrins experience two reductions and two oxidations by transfer of two electrons. Therefore, the processes shown for TpOHPP are likely associated with the porphyrin ring oxidation and reduction. However, the chem-

Table 1

Potential for the formation of $(TpOHPP)^{2-}$ (Epc) and applied potential (Eapp) for metalloporphyrin electrosynthesis (E vs. Fc/Fc⁺).

Solvent	Epc (mV)	Eapp (mV)
DMF	-222	-235
MeOH	-73	-93
AN	-585	-600

ical structure of TpOHPP has OH groups that can also oxidize or reduce. To identify and differentiate the reduction and oxidation processes of the porphyrin ring and the OH groups, we performed the cyclic voltammetry of TPP, which is similar to TpOHPP, but lacks OH groups. The conditions for this cyclic voltammetry were the same as that TpOHPP.

TPP shows two reduction and two oxidation processes. The reduction processes, labeled (A') and (B'), occur at $\text{Epc}_1 = -20 \text{ mV}$ and $\text{Epc}_2 = -219 \text{ mV}$; the oxidation processes ((a') and (b')) take place at $\text{Epa}_1 = 1636 \text{ mV}$ and $\text{Epa}_2 = 1914 \text{ mV}$. These processes should be the porphyrin ring redox processes, because TPP does not contain other constituents that can be reduced or oxidized. Therefore, the processes observed in TpOHPP (A and B) correspond to the porphyrin ring reduction, and are associated with the formation of a dianion radical, according to the following equations:

 $P(PhOH)_4 + e^- \rightarrow P^-(PhOH)_4 \quad Epc_1 = -75 \text{ mV}$ (1)

$$P^{-}(PhOH)_4 + e^- \rightarrow P^{2-}(PhOH)_4 \quad Epc_2 = -222 \text{ mV}$$
 (2)

TpOHPP also showed an oxidation process at Epa = 2.336 V that is not present in TPP (c). This process can be associated with phenolic TpOHPP groups.

For negative potential sweeps, the reduction of each hydroxyl likely leads to the formation of a phenoxide ion by losing a proton as shown in Eq. (3).

$$PhOH \rightarrow PhO^{-} + H^{+}$$



Fig. 2. UV-vis spectra in DMF of electrosynthesis products obtained in silent conditions and with ultrasound application.

For positive potential sweeps, the phenoxide ions may oxidize to form quinones, as shown in Eq. (4).

$$PhO^{-} \rightarrow PhO + e^{-} Epa = 2336 \,\mathrm{mV}$$
 (4)



(3)

Fig. 3. IR spectra of the Ni electrosynthesis products in DMF and MeOH in silent conditions and with ultrasound, and of the commercial Ni-TpOHPP.



Fig. 4. ¹H NMR spectrum (400 MHz) in DMSO-d₆ of the Ni electrosynthesis products obtained in silent conditions: (a) in DMF and (b) in MeOH.

These results indicated that dianion radical $(TpOHPP)^{2-}$ can be electrogenerated in situ at potential values slightly more negative than the second peak potential and its reaction with the electrogenerated Ni(II) and Al(III) ions allows obtaining the corresponding metalloporphyrins.

Table 1 shows the potential for the formation of $(TpOHPP)^{2-}$ (Epc) and applied potential (Eapp) for metalloporphyrin electrosynthesis using different solvents. The formation of $(TpOHPP)^{2-}$ using MeOH as a solvent takes place at a less negative potential than the potential for which this radical is formed when using DMF. In contrast, formation of $(TpOHPP)^{2-}$ in the presence of AN occurs at a more negative potential than in the presence of DMF. These results indicated that using different solvents can affect the rate and efficiency of the electrochemical metallation process with TpOHPP. In this case, the formation of $(TpOHPP)^{2-}$ is more favorable in MeOH.

As reported in the literature [14–16], factors affecting stability of the ionic forms of the macrocyclic compounds (both cationic



Fig. 5. UV-vis spectrum of the Al electrosynthesis product synthesized in AN.



Fig. 6. ¹H NMR spectrum (400 MHz) in acetone- d_6 of the Al electrosynthesis product synthesized in AN with ultrasound application.

and anionic) yielded by proton transfer are: electronic factors (or polarization), structural (or steric) and solvation factors. These factors are particularly significant for weak acids and bases with rigid reaction centers, as porphyrins. The contributions of these factors on the overall stabilization of the ionic species depend on the group to which belong the porphyrin macrocycle and the solvent.

Porphyrins are usually subdivided into classical (with moderate distortion of the planarity of the macrocycle and well-known properties), and non-classical (with non-traditional structures and properties) [14]. The lightly non- planarity of *meso*tetraphenylporphyrins makes the NH centers are more accessible to an attack of a base or a deprotonation. Donor solvents, with electron properties pronounced, like DMSO and DMF which have high donor number (DN 29.8 and 26.6), increase the acidic properties of classical porphyrins [14], and make deprotonation of the NH acids thermodynamically more favorable than donor solvents with poor properties as AN or MeOH (DN 14.1 and 19). However, MeOH is a protic solvent with high acceptor number (AN 41.5) and tends to form hydrogen bonds with lonely electron pairs of highly electronegative elements (such as O or N). The methanol protons are bonded with the —OH groups of phenols substituents of TpOHPP, which may share electron pairs more easily than the N of the porphyrin macrocycle (sterically more hindered). The formation of these hydrogen bonds provides delocalization of electron density excess of ring substituents increasing the acidity of the NH proton. This fact makes more easy the porphyrin deprotonation. It has also been reported in the literature that the effect of solvation, stabilizes the ionic species of porphyrins (either anionic or cationic) [15]. Hence, the formation of radicals mono and dicationic of TpOHPP is more favorable in MeOH and require less negative potential values.

3.2. Metalloporphyrin electrosynthesis

3.2.1. Nickel metalloporphyrins

Fig. 2 depicts the UV-vis spectra of electrosynthesis products with Ni (II) using DMF in silent conditions and with ultrasound



Fig. 7. IR spectrum of the Al electrosynthesis product.

Table 2

Efficiency of electrochemical metallation process of TpOHPP with Ni(II) and Al(III).

Ni(II) metallation		Al(III) metallation	
Condition	Electrolytical efficiency (%)	Condition	Electrolytical efficiency (%)
DMF	82	AN	66
DMF-US	99	AN-US	82
MeOH	92	MeOH	74
MeOH-US	95	MeOH-US	80

application. The absorption pattern for products using MeOH as solvent is the same. The electrosynthesis products have two absorption bands (beta and alpha bands). This result indicates a symmetrical change of porphyrin macrocycle $(D_{4h}-D_{2h})$ because of the metal insertion in the porphyrin cavity.

IR spectra of the products obtained in DMF and MeOH in silent conditions and with ultrasound application, and the commercial Ni-TpOHPP are showed in Fig. 3. The electrosynthesis products show the same absorption pattern than commercial Ni-TpOHPP (stretching vibrations of the O–H group of phenolic groups at 3425 cm^{-1} , folding and torsion vibrations of C–N bonds at 1170 and 1001 cm⁻¹).

Fig. 4 shows the ¹H NMR spectra of products obtained using DMF and MeOH as solvent in silent conditions .The peak at δ = 12.47 ppm corresponding to the internal protons of the porphyrin macrocycle N—H bond is absent. This confirms that Ni insertion in the porphyrin core shifts the pyrrolic protons, and the same product is obtained. All these results suggest the formation of the same metalloporphyrin using different solvents, with and without ultrasound application.

Spectrometric analysis revealed a nickel content of about 8% in the products. This result suggests a possible metal:ligand ratio of 1:1.

3.2.2. Aluminum metalloporphyrin

The UV–vis spectra of the electrosynthesis products obtained in AN and MeOH show a Soret band and four Q bands similar to those of a free-base porphyrin spectrum. Fig. 5 shows one of these spectra. However, in the ¹H NMR spectra (see Fig. 6) the N–H bond peak of the pyrrolic groups is absent, indicating the possible coordination of aluminum ions in the porphyrin core.

The IR spectra of the products obtained in AN and MeOH (see Fig. 7) show the stretching vibrations of O–H groups. This fact suggests that the aluminum atom is not bound by oxygen in the product obtained. Also, the decrease in the C–N bond signal intensity suggests insertion of aluminum in the porphyrin cavity.

Product spectrometric analysis showed aluminum content of 3%, which corresponds to a possible metal/ligand ratio of 1:1 for an aluminum complex with one ClO_4^- ion as a counterion.

The characterization results show the obtention of Ni(II) and Al(III) metalloporphyrins in protic and aprotic solvents. Apparently, the porphyrin ring dimensions (3.7 Å) are compatible with the ionic radius of Ni and Al (0.78 and 0.50 Å), hence stable complexes are formed.

Table 2 shows the efficiency values of the electrochemical metallation process of TpOHPP with Ni(II) and Al(III) under silent conditions and with ultrasound application. The efficiency values were calculated as q_i/Q ratio-net charge used for the porphyrin

4. Conclusions

The electrochemical reduction of TpOHPP to the dianion radical and its further chemical reaction with the Ni(II) and Al(III) ions lead to metalloporphyrins in protic and aprotic solvents with efficiencies higher than 60%. Application of 20 kHz ultrasound enhances the electrochemical metallation process efficiency without affecting the product chemical structure. The solvent used in metalloporphyrin electrosynthesis affects the process efficiency. Protic solvents enhance the reaction yields.

Acknowledgement

The authors gratefully acknowledge funding provided by CONA-CyT project No. 83253.

References

- K.S. Suslick, N.A. Rakow, M.E. Kosal, J.-H. Chou, The materials chemistry of porphyrins and metalloporphyrins, Journal of Porphyrins and Phthalocyanines 4 (2000) 407.
- [2] A. Kumar, S. Maji, P. Dubey, G.J. Abhilash, S. Pandey, S. Sakar, One-pot general synthesis of metalloporphyrins, Tetrahedron Letters 48 (2007) 7287.
- [3] A.D. Garnovskii, I.S. Vasilchenko, D.A. Garnovskii, Synthetic coordination and organometallic chemistry, Ch.3, Marcel Dekker, NY, USA, 2003, p. 151.
- [4] R. Singh, Geetanjali, Novel synthetic metodology for metalloporphyrins in ionic liquid, Journal of the Brazilian Chemical Society 16 (2005) 666.
- [5] K.M. Kadish, D. Sazou, Y.M. Liu, A. Saoiabi, M. Ferhat, R. Guilard, Electrochemical and spectroelectrochemical studies of nickel (II) porphyrins in dimethylformamide, Inorganic Chemistry 27 (1988) 1198.
- [6] G. Wilkinson, Comprehensive Coordination Chemistry, first ed., Pergamon Press, Oxford, 1987, p. 864.
- [7] K.M. Kadish, C. Araullo-McAdams, B.C. Han, M.M. Franzen, Synthesis and spectroscopic characterization of (T(p-Me₂N)F₄PP)H₂ and (T(p-Me₂N)F₄PP)M where T(p-Me₂N)F₄PP is the dianion of meso-*Tetrakis*(o,o,m,m-tetrafluoro-p-(dimethylamino)phenyl)-porphyrin and M=Co(II), Cu(II), or Ni(II). Structures of (T(p-Me₂N)F₄PP)Co and (meso-*Tetrakis*(pentafluorophenyl)porphinato)cobalt(II), (TF₅PP)Co, Journal of the American Chemical Society 112 (1990) 8364.
- [8] K.M. Kadish, E.V. Caemelbecke, P. Boulas, F. D'Souza, E. Vogel, M. Kisters, C.J. Medforth, K.M. Smith, First reversible electrogeneration of triply oxidized nickel porphyrins and porphycenes. Formation of nickel (III) π dications, Inorganic Chemistry 32 (1993) 4177.
- [9] J.W. Buchler, in: K.M. Smith (Ed.), Porphyrins and Metalloporphyrins, Elsevier, Amsterdam, 1975, p. 157.
- [10] T.J. Mason, J.P. Lorimer, Applied Sonochemistry: The uses of the Power Ultrasound in Chemistry and Processing, Wiley-VCH Verlag, Weinhein, 2002, p. 115.
- [11] Ch, Sun, B. Hu, W. Zhou, S. Xu, Z. Liu, Investigations on the demetalation of metalloporphyrins under ultrasound irradiation, Ultrasonics Sonochemistry 18 (2011) 501.
- [12] G. Chael, C. Goux-Henry, N. Kardos, J. Suptil, B. Andrioletti, Ultrasound and ionic liquid: an efficient combination to tune the mechanism of alkenes epoxidation, Ultrasonics Sonochemistry 19 (2012) 390.
- [13] J.H. Ang, K.S. Suslick, Applications of ultrasound to the synthesis of nanostructured materials, Advanced Materials 22 (2010) 1039.
- [14] D.B. Bezerin, N.I. Islamova, O.V. Malkova, V.G. Andrianov, NH-acid properties of porphyrins in acetonitrile, Russian Journal of General Chemistry 76 (2006) 997.
- [15] D.B. Bezerin, A.S. Semeikin, M.B. Berezin, The influence of the macroring structure on solvation of nonplanar porphyrins in organic solvents, Russian Journal of Physical Chemistry A 83 (2009) 1315.
- [16] K.M. Kadish, E.V. Caemelbecke, Electrochemistry of porphyrins and related macrocycles, Journal of Solid State Electrochemistry 7 (2003) 254.