



Electrolysis of V(IV) and free *meso*-tetraphenyl porphyrin in two immiscible liquids

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Abstract

The electrochemical decomposition of free and vanadyl tetraphenyl porphyrin in xylene solutions, and in the presence of water, using K₂SO₄ as electrolyte, was studied. Electrolysis of the two-phase system was carried out at constant current density and potential. It was observed that the electrochemical decomposition of the porphyrins, using a two-phase liquid system, is possible. An inexpensive organic solvent (xylene instead of THF, acetonitrile, methylene chloride etc.) can be very effectively used in such a system. The decomposition occurs through an oxidation process, with the subsequent formation of cationic and dicationic radicals, and a final breakdown of the macrocycle.

1. Introduction

Around 70% of Venezuelan crude oil reserves are of the heavy and extra heavy type, and these represent about 21% of world reserves. These types of crude oil are characterized by high contents of heteroatoms, that is, sulphur, nitrogen and metals. Metals, mainly Ni and V, are associated to organic molecules (usually porphyrins) which are located in the asphaltenic fractions. In order to obtain useful products from this crude oil, it is of great importance to find new processes that can lead to economic treatment of such feedstocks. Electrochemical upgrading of heavy oil may be a feasible alternative. In fact, several reports deal with the upgrading (demetallization, desulphurisation, and aromatic hydrogenation) of fuel oil, shale oil and porphyrinic petroleum extracts using electrochemical methods [1–7]. Thus, Bell et al. [1] reported the electrochemical desulfurization of fuel oil using water emulsions and a surfactant (calcium hydroxide or sodium hydroxide). Yen and Wen [2,3] used an electrochemical system to upgrade an oil shale in the presence of ethylenediamine as solvent and lithium chloride as electrolyte. Sugihara et al. [4] also studied the treatment of crude oil in the presence of ethylenediamine as solvent and lithium chloride as electrolyte. On the other hand, Dongmei et al. [5,6] reported the hydrogenation of naphthalene in ethanol/water mixtures and lithium chloride or tetra butyl ammonium bromide. Finally, Ovalles and coworkers [7] studied the electrochemical decomposition of petroporphyrin extracts, crude oil and its fractions and of synthetic vanadyl

porphyrin, in THF, lithium perchlorate and methanol mixtures. In all this work the potential of the electrochemical process for the upgrading of crude oil and related feeds was demonstrated. However, the use of expensive solvents or electrolytes renders any industrial application of the process impractical. Also, little is known about the mechanism for the electrochemical upgrading of such feeds. In the present paper the decomposition of free and vanadyl tetraphenyl porphyrin in xylene solutions, and in the presence of water, have been studied.

2. Experimental details

Electrolysis was carried out at controlled potential and constant current density, using an EG&G PAR potentiostat (model 362). UV–visible spectra were recorded in a Shimadzu 1601PC photometer. Cell potential was measured with a Gold Star DM-6335 digital voltmeter. In a typical experiment, 5 cm³ of aqueous K₂SO₄ saturated solution were added to a one-compartment 25 cm³ cell containing 5 cm³ of porphyrin or metallo porphyrin solution (5 × 10⁻⁴ M in xylene). The mixture was vigorously stirred with a magnetic stirrer until a microheterogeneous suspension was formed. In fact, if a microheterogeneous suspension is not obtained the reaction does not take place. The electrolysis was carried out at 298 K. A Pt sheet of 2 cm² surface area was used as working electrode, and a Pb sheet (2 cm²) was used as counter electrode. The cell was fitted with

Table 1. Time required for 98% conversion, or higher, for H₂TPP and VOTPP

		<i>t</i> (H ₂ TPP)/s	<i>t</i> (VOTPP)/s
Potential vs NHE /V	4.0	1	50
	3.5	8	70
	3.0	8	240
	2.5	8	360
	1.5	∞	∞
Current density /mA cm ⁻²	200	16	30
	150	20	90
	100	30	120
	50	105	240
	12.5	180	720
	5.0	∞	∞

three or two electrodes for constant potential and constant current density experiments, respectively. Potential was measured against the hydrogen normal electrode (NHE). The values for the potential and current densities are presented in Table 1.

UV–visible spectra were recorded at different time intervals in order to follow the decomposition reaction. Porphyrin conversions were measured by decrease in the absorbance of the bands at 549 nm and 515 nm, for metal and free porphyrin, respectively.

Four repeated experiments at 100 mA cm⁻² were carried out in which the aqueous phase was separated and analysed for vanadium by u.v.–vis. spectroscopy [8].

3. Results and discussion

3.1. Free tetraphenyl porphyrin (H₂TPP)

Figure 1 shows the u.v.–vis. spectra for H₂TPP solutions treated at 4 V vs NHE, at different times. For the initial sample a characteristic four-band spectrum (in the region 450–800 nm) is observed. The bands are located at 515, 549, 591 and 648 nm. Also a shoulder at 479 nm and the very intense Soret band can be observed. As electrolysis time is increased (from 16 to 180 s) a decrease in the four free porphyrin bands is observed, which

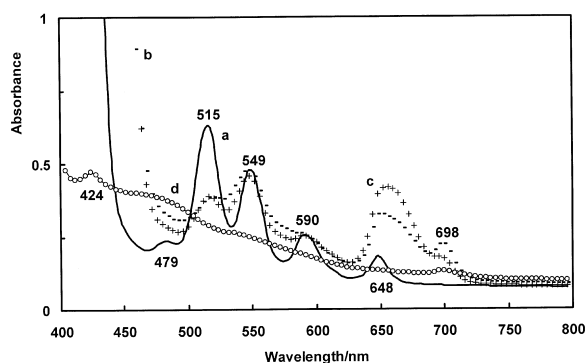


Fig. 1. Evolution of u.v.–vis. spectrum as a function of time of electrolysis for the H₂TPP. (a) Initial; (b) 16 s; (c) 30 s; (d) 180 s.

completely disappear at the longest time. Also, the band at 648 nm shifts to 659 nm. The intensity of this band increases and goes to a maximum for 16 s of reaction, and for longer times it decreases and also completely disappears. At the same time, a shift in the Soret band (not shown) towards longer wavelengths is observed. This band is also totally lost at the end of the reaction. A similar behaviour is observed for the other voltages, only the time needed for complete decomposition of the porphyrin macrocycle is different.

The modification observed in the u.v.–vis. spectra is indicative of the transformation of the porphyrinic system with loss of aromaticity and formation of one (or may be two) reaction intermediates. A similar effect has been reported for the oxidation of Zn and Mg porphyrins in one-phase systems [9,10]. The changes have been attributed to the formation of radical mono- and dications. So, in our case, the same kind of reaction pathway is taking place; that is, first a radical monocation is formed, which in turn, is converted into a radical dication. This process produces a destabilization of the macrocycle and its final breakdown. In order to see whether the process was an oxidation, an experiment was carried out in a cell with two compartment separated by a glass frit. The reaction was found to occur only in the anodic compartment. In addition, the aqueous phase pH was found to change from neutral to about 11 at the end of the electrolysis. All these experimental facts clearly indicate that the process is an oxidation.

UV–vis. spectra for experiments carried out at constant current density show a behaviour similar to that found at constant voltage, indicating porphyrin decomposition by a similar mechanism.

3.2. Vanadyl tetraphenyl porphyrin (VOTPP)

In Figure 2 the u.v.–vis. spectra for electrolysis of VOTPP at constant voltage (2.5 V vs NHE) are shown. For the initial solution a three band spectrum is observed; an intense band at 548 nm and two smaller bands at 584 and 512 nm. Also a very intense band,

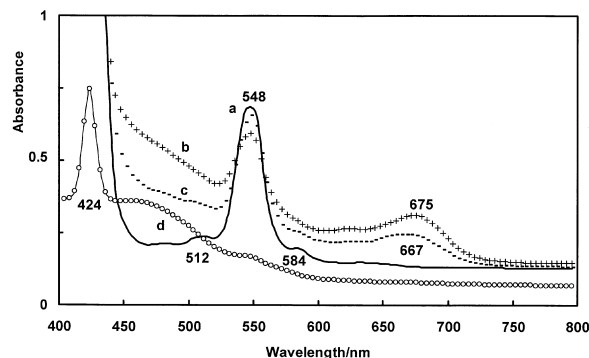


Fig. 2. Evolution of u.v.–vis. spectra as a function of time of electrolysis for the VOTPP. (a) Initial; (b) 1800 s; (c) 3000 s; (d) 16200 s.

which corresponds to the Soret band, is obtained. This spectrum is characteristic of the VOTPP. As electrolysis time increases the bands at 584, 512 and 548 nm completely disappear and the Soret band shifts to higher wavelengths. A new broadband at around 670 nm is developed. This band decreases in intensity as electrolysis proceeds and finally disappears at 16200 s. Even though there are significant differences in u.v.-vis. spectra for the free porphyrin and the vanadyl porphyrin, the changes are due to the same phenomenon (i.e., formation of the cation and dication radicals which finally destabilizes the porphyrin macrocycle) leading to a break down of the molecule. In fact, similar spectra have been reported for this type of radical in the oxidation of other metal tetraphenyl porphyrins [11,12]. As for the free H₂TPP, the u.v.-vis. spectra are similar for all potentials studied, the only change being the time needed for complete porphyrin decomposition. Another important observation is that bands that can be assigned to the free porphyrin are not observed in the experiments with the vanadyl porphyrin, which suggests that a mechanism of a direct metal extraction of the macrocycle is unlikely.

In Table 1, the times required for 98% conversion of the porphyrins (free and metal) at different potential and intensities are also shown. The time for 98% is a function of the potential and current density, but, in general, shorter times are needed at constant potential rather than at constant current densities.

On the other hand, it was also found that a high potential is required for demetallization/deporphyrinization to take place. High potential is required because the system forms a microheterogeneous suspension, which increases the resistance to current flow. Also, the second oxidation potential for the oxidation of the H₂TPP has been reported to be around 1.2 V vs NHE [9], in CHCl₃ solution. This potential will be even higher for the breaking of the macrocycle. Moreover, when the process is carried out in a two-phase system, where the current does not pass directly through the organic solvent, which contains the porphyrin, the process can be expected to be even more difficult.

It is also observed, that the times needed for the macrocycle decomposition are shorter for the free porphyrin than for the vanadyl porphyrins, which is consistent with the fact that introduction of a metal to the porphyrin ring increases the stability of the macrocycle. The values for anode potentials (V vs NHE), at constant current density, are presented in Table 2. At constant potentials, cell current varied between 220 and 20 mA cm⁻², for potentials of 4 and 2.5 V vs NHE, respectively.

To check that the disappearance of the bands due to the metal porphyrin is proportional to the demetallization, four repeated experiments at 100 mA cm⁻², until total porphyrin decomposition was obtained, were carried out, and the reaction was followed by u.v.-vis. chemical analysis for vanadium in the aqueous solutions. The aqueous solution was found to contain

Table 2. Anode potential at different cell current densities, for the electrolysis of the VOTPP

Current density /mA cm ⁻²	Anode potential vs NHE /V
25	2.65
50	2.99
100	3.32
200	4.15

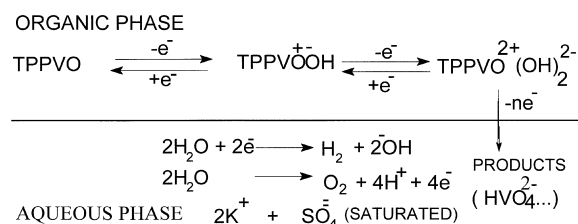


Fig. 3. Scheme for decomposition of the VOTPP in a two immiscible liquid system.

31.5 ppm of vanadium, which is equivalent to 92% of the vanadium originally present as VO-porphyrin (initially 34.2 ppm). This amount is slightly lower than that expected from total porphyrin decomposition, however, ICP analysis of the organic phase showed that some vanadium remains dissolved (around 3 ppm). These results indicate that the metal released during the electrochemical process is solubilized in the aqueous phase. In fact, due to the pH of the solution (~11) vanadium should remain dissolved as HVO₄²⁻ [13].

Finally, the results obtained for two immiscible liquids may be explained by the mechanism presented in Figure 3, which is similar to the those proposed for other metallo-porphyrins oxidation, that is Zn-etio porphyrin and Mg-octaethyl porphyrin [11,12] in one-liquid-phase systems (THF, CH₂Cl₂). According to this scheme, the porphyrin molecule (H₂TPP or VOTPP) loses one electron to form the radical cation, and undergoes a second electron extraction to produce the dicationic radical. This process leads macrocycle destabilization and to a complete breakdown of the porphyrinic ring, with the metal passing to the aqueous solution.

In the present study current efficiency has not been measured; however, oxidation of the porphyrin macrocycle is produced during the process together with H₂O electrolysis. H₂O electrolysis produces hydrogen at the cathode, which could eventually be recovered, thus increasing current efficiency.

4. Conclusions

It has been shown that the electrochemical decomposition of free H₂TPP and VOTPP, using a two-phase

liquid system, is possible. A demetallization near to 100% is obtained. In fact an inexpensive organic solvent and electrolyte (i.e., K_2SO_4 instead of $LiClO_4$ and xylene instead of THF, acetonitrile, methylene chloride, etc.) can be used very effectively in such a system. It has also been demonstrated that, under the conditions used in the present work, free and vanadyl tetra phenyl porphyrins decompose through an oxidation process. This, in its initial steps, leads to the formation of a radical cation followed by the formation of the radical dication, and finally to macrocycle break up.

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