Article

Electrochemical Nitration of Naphthalene in Micellar Systems

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Foi estudada a nitração do Naftaleno (NapH) em um eletrodo de Pt em soluções aquosas de NaNO2, na ausência e na presença de Brij 35, um surfactante não-iônico. O comportamento eletroquímico dos reagentes NapH e NaNO2 e de suas misturas foi investigado por voltametria cíclica para determinar as condições de eletrólise. A corrente de pico do NapH decresce monotonamente com a concentração de NaNO2, indicando que o produto da oxidação do íon NO2⁻ interage com o NapH•+. Foram realizadas eletrólises a potencial controlado e os produtos foram analisados por HPCL.

Na solução micelar foram obtidos 1-nitronaftaleno, 2-nitronaftaleno, 1,2-naftoquinona, 1,4-naftoquinona e 1,1'-Binaftilo (BinapH) enquanto que, na falta de Brij 35, somente foram detectados naftoquinonas e BinapH. A maior seletividade para 2-nitronaftaleno em comparação com meios homogêneos não-aquosos pode ter sido induzida pelo microambiente nas micelas.

The nitration of naphthalene (NapH) at a Pt electrode in $NaNO_2$ aqueous solutions in the absence and presence of a non-ionic surfactant, Brij 35, was studied. The electrochemical behavior of the reactants NapH and $NaNO_2$ and their mixture was investigated by cyclic voltammetry to determine their electrolysis conditions. The peak current of NapH decreases monotonically with the $NaNO_2$ concentration, indicating that the oxidation product of NO_2^- ion interacts with NapH•+. Controlled potential electrolysis were carried out and the products were analyzed by HPLC. 1-nitronaphthalene, 2-nitronaphthalene, 1,2-naphthoquinone, 1,4-naphthoquinone and 1,1'-Binaphthyl (BinapH) were obtained in the micellar solution while in the absence of Brij 35 only naphthoquinones and BinapH were detected. The higher selectivity for 2-NO_2NapH in comparison to non-aqueous homogeneous media may be induced by the micelles microenvironment.

Keywords: *electro oxidation, micelles, nitration, naphthalene*

Introduction

Electrochemistry on micelles has mostly developed in the last twenty years[1]. Monomeric molecules of amphiphilic compounds (tensoactives) possess regions of hydrophilic and hydrophobic character. In aqueous solutions, aggregates of these monomeric molecules (organized structures or micelles) can be reached when the monomeric concentration exceeds a critical value or critical micelle concentration (cmc)[2].

An important feature of these so-called microheterogeneous systems is that by careful election of the amphiphilic molecule and making use of the mode of distribution and location of solutes in the aggregates, it is possible to organize reactants at a microscopic (molecular) level[3]. Probably, the most important property of micellar solutions is their capacity to solubilize water-insoluble compounds, a process described by the dynamic equilibrium monomer-micelle in the action mass model[4]. The solubilization phenomenon is very important in chemistry, industry and biology[5].

The nature of the micelle-substrate interaction determines the substrate electrochemical behavior[6]. Moreover, micellar effects have been studied from various perspectives, such as cmc and diffusion coefficients determinations[5,7],

electrode kinetic and thermodynamic parameters[8], solubilization[9], catalysis[1,10], electrosynthesis[11], and electrode adsorption[12].

In a previous article we reported a mechanistic study of the nitration of naphthalene (NapH) by its electrochemical oxidation in the presence of nitrite ion in acetonitrile solution[13]. In the present communication, similar experiments are reported in aqueous solution where the non-ionic surfactant, Brij 35, was used to solubilize naphthalene in water. The electrosynthesis of nitro derivatives was performed by controlled potential electrolysis (CPE) on Pt electrodes. The product distribution was analyzed by high performance liquid chromatography (HPLC).

Experimental

Naphthalene (NapH) from Fluka AG was purified by sublimation prior to use. 1-Nitronaphthalene (1-NO$_2$NapH) was synthesized from NapH with 53% HNO$_3$ in acetic anhydride[14], and recrystallized from ethanol- water mixtures (mp. 61 ± 0.2 °C). 2-Nitronaphthalene (2-NO$_2$NapH) from Aldrich was recrystallized five times from ethanol + water mixtures, and then sublimated (mp. 78.5 ± 0.2 °C). 1,2-Naphthoquinone (1,2-NaphQ), Aldrich was used as received. 1,4-Naphthoquinone (1,4-NaphQ), Fluka was recrystallized from ethanol (mp. 128.2 ± 0.2 °C). 1,4-Dinitrobenzene (Fluka) was recrystallized three times from acetone (mp 173 ± 0.2 °C) and used as the internal standard in HPLC. The other reagents, NaNO$_2$ (Merck p.a. min. 99%), NaClO$_4$ (Merck p.a. min. 99%), and Brij35 (poly(oxyethylen)$_{23}$ lauryl ether, Merck) were analytical grade and used as received. Brij 35 is a non-ionic surfactant whose cmc is 0.65 μM and aggregation number is 40, at 25 °C. HPLC analyses were performed in a Varian 5000 chromatograph with a MicroPak MCH-10 column and an isocratic 30:70 mixture of triply distilled water and methanol (Sintorgan, HPLC, water content 0.05%) as the mobile phase at a flow rate of 0.5 mL/min. A Varian 2550 detector was used. The retention times in minutes were 8.79 for 1,2-NaphQ, 11.53 for 1,4-NaphQ, 21.51 for 1-NO$_2$NapH, 23.65 for 2-NO$_2$NapH, and 25.89 for NapH.

The standard solutions of NapH, nitro derivatives and other products were prepared by weighing. The exact concentration of NapH was determined by UV spectroscopy ($\lambda_{max} = 276$ nm, log ε = 3.75) in a Hewlett-Packard HP 8452 spectrophotometer.

For cyclic voltammetry (CV) and CPE measurements, a potentiostat-galvanostat EG&G PAR model 273 was employed. The current and potentials were registered either on an X-Y EG&G PAR model RE 0150, x-t REC 61 Servograph Radiometer recorder or with a Keithley 194A high speed voltmeter connected to a PC computer. Conventional three-compartment Pyrex cells were used for CV and CPE experiments. The cell for CPE was efficiently agitated by

vertical hydrodynamic movements of the electrode support. The working electrodes were Pt disks of variable areas for CV, and Pt electrodes of larger areas, *ca.* 4 cm^2, for CPE experiments. The counter electrode was a stainless steel foil with a large area. All the potentials were referred to a saturated calomel electrode (SCE) and were corrected for iR drop by positive feedback techniques. The experiments were performed at 20 °C.

Results and Discussion

Control experiments in the absence of Brij 35

The solubility of NapH in aqueous solutions is low (*i.e.*, 1.58×10^{-4} M at 20 °C), as determined by UV spectroscopy. In the presence of NO$_2^-$ ion, no changes in the aqueous solubility were detected. Cyclic voltammograms showed only the oxidation peak of nitrite, but the NapH oxidation occurred at 1.4 V because a saturated solution of NapH without nitrite decreased the UV 276 nm band after EPC. When a saturated solution of NapH + 1×10^{-2} M NaNO$_2$ was electrolyzed at 1.4 V, no nitration products were detected. At this potential value, NO$_2^-$ ion oxidation is very important, but the reaction between NapH$^{\bullet+}$ and NO$_2$ is very slow. The faster reaction occurs between NapH$^{\bullet+}$ and H$_2$O, to give only quinonic products (1,2-NaphQ, 1,4-NaphQ), as were detected by HPLC.

Solubility of Naphthalene in micellar solutions

In order to obtain evidence of NapH distribution between water and Brij 35 micelles, the partition parameter (K$_p$) was evaluated from the solubility measurements, following a previously described procedure[15,16].

K$_p$ is defined as:

$$K_p = \frac{[NapH]_{WS}}{[NapH]_M} = \frac{[NapH]_{WS}}{[NapH]_{MS} + [NapH]_{WS}} \qquad (1)$$

where [NapH]$_{WS}$ and [NapH]$_{MS}$ represent the solubilities of NapH in water /0.4 M NaClO$_4$ and in the micellar solution, water /0.4 M NaClO$_4$ /Brij 35 (2.5×10^{-2} M), respectively. [NapH]$_M$ represents the NapH bound to the micelle. This method gives the value of K$_p$ at NapH saturation concentration and does not permit studies at different NapH concentrations below this solubility value. The NapH water solubility is [NapH]$_{WS} = 1.58 \times 10^{-4}$ M and in the micellar medium [NapH]$_{MS} = 6.17 \times 10^{-3}$ M giving a K$_p = 0.026$. This means that NapH is almost completely solubilized in the micelle subphase at saturation. Thus, it is expected that under the electrolysis conditions, the NapH solubilization is even more favorable because the total substrate concentration is 2×10^{-3} M.

Cyclic Voltammetry

NaNO$_2$

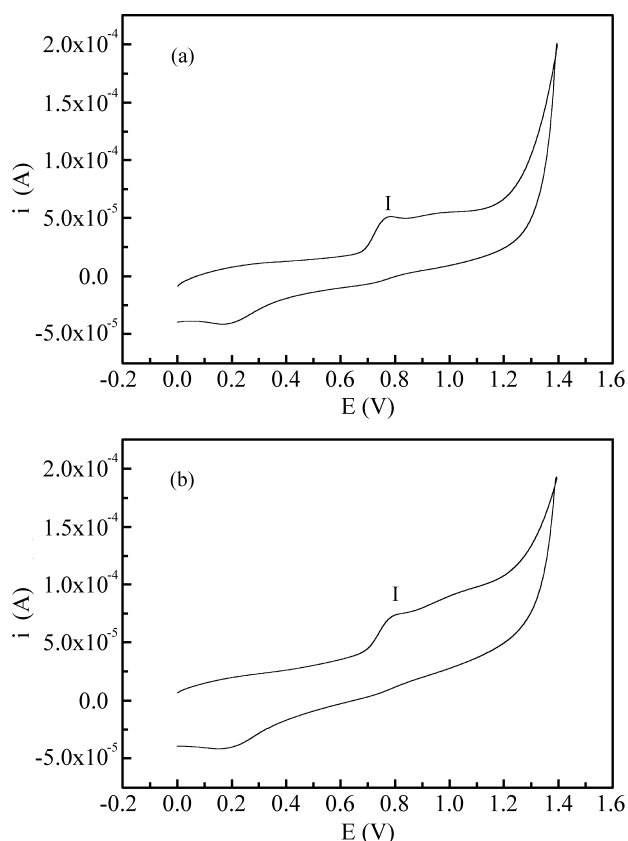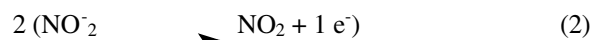**Figure 1.** Cyclic voltammogram of the $NaNO_2$ oxidation a) in aqueous solution; b) in micellar solution, [Brij 35] = 0.025 M, [$NaNO_2$] =

The electrochemical oxidation of the nitrite ion in aqueous solution[17] is well established. Figure 1 shows the cyclic voltammograms obtained in aqueous solution (a) and with Brij 35 (b); in both cases only one peak at $E_{p,a}$ = 0.800 V is detected in the anodic scan. No cathodic current is observed when the scan is reversed. This fact indicates a chemical complication coupled to a first charge transfer. In aqueous and micellar media the CV patterns are similar, indicating no interaction of NO_2^- ion with Brij 35 micelles, as expected for an ionic substrate. This implies that NO_2^- ion is not partitioned into the micelles. In both cases, the peak current varies linearly on $v^{1/2}$ and on the NO_2^- concentration, but in the micellar medium the current is only about 80% of the value in the aqueous system. This fact can be explained by an increase of the viscosity of the micellar system[18].

The electrochemical reaction in aqueous solution has been interpreted in terms of a complex mechanism[17] (Eqs. 2-4):

$$2\ (NO_2^- \longrightarrow NO_2 + 1\ e^-) \tag{2}$$

$$2\ NO_2 + H_2O \longrightarrow NO_3^- + NO_2^- + 2\ H^+ \tag{3}$$

$$NO_2^- + H_2O \longrightarrow NO_3^- + 2\ H^+ + 2\ e^- \tag{4}$$

The principal product formed in the first charge transfer reaction is NO_2. Subsequently, NO_2 suffers disproportionation to give NO_3^- and NO_2^- ions (Eq. 3), in an irreversible way. The rate constant value obtained by electrochemical measurement[17] is k = 4 x 10^6 l mol^{-1} s^{-1}. Hence, the NO_2 concentration is only appreciable in a reaction layer near the electrode surface. This layer can be estimated to be less than the thickness of the diffusion layer of NO_2^- ion[19]. However, the NO_2 concentration profile is enough to react with the NapH radical cation, NapH$^{•+}$ (see below). Therefore, under voltammetric conditions the overall electrode process is given by Eq. 4. In CPE experiments in a unbuffered medium the reaction of the NO_2^- ion with H_3O^+ gives:

$$NO_2^- + H_3O^+ \rightleftharpoons HNO_2 + H_2O \tag{5}$$

The pK_a value[20] of this reaction is 3.25, but this fact is not important for CPE conditions since the proton transfer kinetic in water is fast. In order to confirm this hypothesis, the CPE of NO_2^- solution with Brij 35 was performed at 1.45 V. The current decayed exponentially with time at a value near the blank current, and the pH of the solution decreased from 6.31 to around 1.1. The apparent electron number n_{app})1.8 Faraday per mole of NO_2^- ion is in agreement with Eq. 4. These facts show that the HNO_2 concentration is negligible at the end of the electrolysis, supporting our hypothesis.

Naphthalene

A typical cyclic voltammogram of NapH in Brij 35 solution is illustrated in Fig. 2. An oxidation wave (E = 1.40 V) due to the NapH oxidation to give NapH$^{•+}$ is observed on the first sweep. This wave is not defined as a peak probably due to the O_2 evolution. It is highly irreversible and no complementary cathodic peak is observed even at 50 V s^{-1}. This is an indication of a very short life time for NapH$^{•+}$ and/or a fast follow-up reaction coupled to the
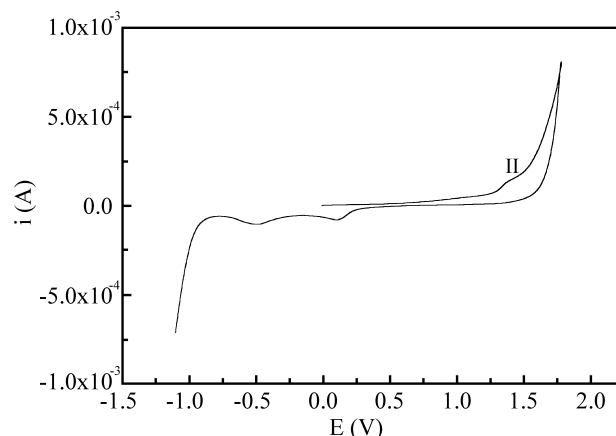

Figure 2. Cyclic voltammogram for NapH oxidation in micellar solution. [NapH] = 5.5 x 10^{-3} M, [Brij 35] = 0.025 M. The other conditions

charge transfer, as observed for the NapH[•+] stability in another organic medium[13]. Assuming that NapH is only in the micellar subphase, its microenvironment would be more like an organic solvent and a similar behavior could be expected.

The current limit i_{LI} shows a linear dependence on $v^{1/2}$ in the sweep rates range from 0.01 to 0.3 V s^{-1}. This observation reinforces the idea of a fast reaction coupled to the charge transfer. Typical reactions of the aromatic radical cations are the dimerization and even further polimerization reactions[21]. The more probable dimerization product of this radical cation is 1,1'-Binaphthyl (BinapH)[13]. Another possibility is that NapH[•+] reacts with a nucleophile, water for example, to give oxygenate substitution products such as quinones[22].

In the negative sweep, two peaks are observed. The peak at 0.15 V is assigned to the PtO reduction in this medium, as confirmed by blank experiments (without NapH). The other peak at -0.40 V is assigned to the solvated protons released by the dimerization reaction of NapH[•+], as confirmed by the addition of perchloric acid to the solution. No new peak was detected by cycling between -1.10 and 1.75 V. Therefore, the electrooxidation of NapH in micellar medium can be interpreted by the following global process:

$$M(NapH) \longrightarrow M(NapH^{•+}) + e^- \quad (6)$$

$$2\,M(NapH^{•+}) \longrightarrow M(BinapH) + 2\,H^+ \quad (7)$$

$$M(NapH^{•+}) \xrightarrow{\ H_2O\ } M(Q) + 6\,H^+ + 5e^- \quad (8)$$

Where M(NapH), M(NapH[•+]), M(BinapH) , M(Q) stand for NapH, NapH[•+], BinapH, and Quinone in the micelle subphase, respectively.

NaNO₂ + NapH solution

A typical cyclic voltammogram obtained when both substrates are in solution is illustrated in Fig. 3. Two well-defined peaks are observed which correspond to the NO$_2^-$ ion oxidation (peak I) and NapH oxidation (peak II). The peak potentials are the same as those of the separate substrates (Fig. 1b and Fig. 2). The peak current i_{pI} does not change with respect to its value in Figure 1b, however, the peak current for the NapH electrooxidation (peak II) changes when NO$_2^-$ ion is present. Thus, to determine this dependence, systematic studies were carried out keeping NapH constant and changing the NO$_2^-$ ion concentration. In all cases, i_{pI} changes linearly with the concentration, but i_{pII} decreases when NO$_2^-$ increases (Fig. 4). This suggests that either the NO$_2^-$ ion or its oxidation product interacts with NapH[•+], changing its route of degradation, in agreement with similar results obtained in a non-aqueous system[13].

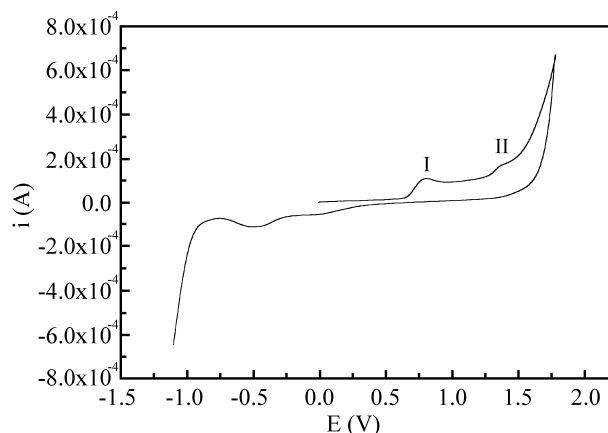**Figure 3.** Cyclic voltammogram for NapH and NaNO₂ oxidation in micellar solution. [Brij 35] = 0.025 M, [NapH] = 5 x 10^{-3} M [NaNO₂] = 5 x 10^{-3} M. The other conditions are the same as in Fig. 1
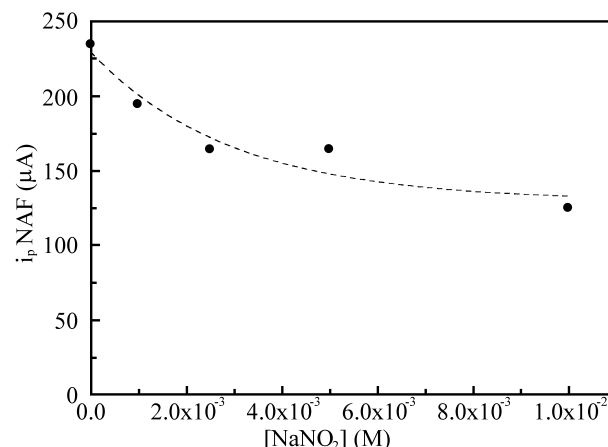

Figure 4. Dependence of i_{pII} as a function of the NO$_2^-$ ion concentration. [NapH] = 5.5 x 10^{-3} M, [Brij 35] = 0.025 M. The other conditions are the same as in Fig. 1

Controlled-Potential Electrolysis (CPE)

In view of the CV results reported above, CPE was performed for two different micellar solutions: (a) only NapH present, and (b) both substrates NapH + NaNO₂.

a) CPE of NapH

Following the conditions in Fig. 2, CPE of a 2 x 10^{-3} M NapH solution with 2.5 x 10^{-2} M Brij 35 and 0.4 M NaClO₄ as the supporting electrolyte was performed at 1.45 V. The initial colorless solution turned to pale yellow at the end of the electrolysis. The experiment was concluded when NapH was no longer detected by the HPLC technique. Under these conditions, the detected products are only 1,2- and 1,4-NaphQ. However, the mass balance with respect to NapH suggests another product, probably the dimer BinapH or an insoluble oligomer. In addition, the pH of the solution decreased to pH ﹥2, as expected when H$^+$ is released in chemical reactions (Eqs. 7 and 8). The electrolysis

Table 1. Yield of products for CPE of NapH in different conditions.

Product	Brij 35 + NapH/%	Brij 35 + NapH + NaNO$_2$/%
1,2-NaphQ	3.3	4.2
1,4-NaphQ	10.7	14.3
1-NO$_2$NapH	—-	32.4
2-NO$_2$NapH	—-	2.0
BinapH	43	23.6

current decayed exponentially with time, and the $n_{app} \cong 4.6$ per molecule of NapH was calculated at the end of the electrolysis. The n_{app} value observed is consistent with the electrooxidation of NapH under these conditions to give quinones and binaphthyl or an oligomeric product.

Typical result fors this CPE are shown in Table 1.

b) CPE of NapH + NaNO$_2$

The possibility of the NapH nitration by the electro oxidation product of the NO$^-_2$ ion was explored by CPE performed at 1.2 V. At this potential, only the NO$^-_2$ ion is electrolyzed. Under these conditions, no nitration nor quinonic products are detected by HPLC. This provides the evidence that NapH is not attacked by the intermediate product of the NO$^-_2$ ion electro oxidation. The absence of the quinonic and nitrated products would indicate that NapH$^{\bullet+}$ mediates in their formation. Thus, CPE was performed at 1.45 V, and the products detected by HPLC were 1-NO$_2$NapH, 2-NO$_2$NapH, 1,2-NaphQ, and 1,4-NaphQ. Also, the formation of BinapH was assumed, and its yield was calculated from the mass balance. Typical results are shown in Table 1. It should be noted that the ratio 1-NO$_2$Naph/2-NO$_2$NapH is lower than that observed in previous studies in acetonitrile medium[13], indicating a micellar effect that may be due to preferred orientations of the substrate in the organized media.

Conclusions

In aqueous systems in the presence of the NO$^-_2$ ion , no nitration is observed. NapH$^{\bullet+}$ reacts fast with water to form quinones. On the other hand, the electrogenerated NO$_2$ (Eq. 2) decomposes, as shown in Eq. 3. Both reactions are faster than those of nitration.

In micellar systems, nitrated products are obtained. Probably, the micellar microstructure increases the NO$_2$ solubilization in a micelle subphase, favoring its encounter with NapH$^{\bullet+}$. The ratio of 1- NO$_2$Naph/2-NO$_2$NapH is lower than in non-aqueous media, where the ratio is always greater than 50[13]. The higher yield of 2-NO$_2$NapH may be explained by intramolecular selectivity induced by the micelles microenvironment.

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