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ULTRASOUND-ASSISTED CATHODIC REDUCTION OF 4,4' - DINITRODIBENZYLE

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RESUMÉ. Reduction cathodique du 4,4'-dinitrodibenzyle assistee par ultrasons. Le travail présente la voltammétrie du 4,4'-dinitrodibenzyle en millieu alcoholique acide sur électrode-disque Pt/Hg, en absence et en présence des ultrasons produits d'une sonde ultrasonique (20 kHz) localisée à une courte distance de celle-ci, et directionés sur la surface d'électrode. On a étudié les effets de la distance entre l'extrémité de la sonde et la surface de l'électrode et de la vitesse de balayage sur le courant limite, et on les a comparé avec les mesures effectuées sur une électrode disque-tournante. Les conditions hydrodinamiques sont exprimées en termes de la vitesse de rotation necessaire dans la voltammétrie sur disque tournant pour obtenir des vitesses de transport de masse similaires.

1. Introduction

Mass transport is a very important aspect of electrochemical processes as well as of heterogeneous processes in general. Many heterogeneous reactions proceed under mass transport control and variation of the flux of material transported to and from the interface has been reported to cause in same cases a "switching" to a different reaction pathway [1]. In the literature there is widespread agreement on the dominant effect of ultrasound in electrochemistry being a strongly enhanced mass transport [2-24].

A macroscopic beam of liquid generated by ultrasonic horn ("acoustic streaming") [16, 25], a strong turbulent flow and microjets of liquid formed by transient cavitation [26, 27] close to the electrode surface may all contribute to this effect, and their relative contributions may be solvent and reactor geometry dependent. Furthermore, the intense soundfield causes changes at the electrode surface which have been described as cleaning [28, 29] or activation [30, 31].

The aim of this paper is to present experiments related to the ultrasound-assisted electroreduction of 4,4'-dinitrodibenzyle (DNDB) in ethanolic 2.5N H_2SO_4 solution. The role played by acoustic streaming and turbulence on one side, and microjetting on the other, in mass transfer enhancement will be shown.The effect of distance from sonicator tip to the electrode surface as well as the horn tip to the cell floor distance on limiting currents are considered and compared to measurements made at a rotating disk electrode. Hydrodynamic conditions are described in terms of the effective rotation rate which would be needed in rotating disk voltammetry to achieve similar transport rates.

2. Experimental

An ultrasonic cell disrupter (Sonics & Materials, CT) with an ultrasonic horn (titanium alloy, surface area 1cm^2) working at 20kHz frequency was used as the source of ultrasound. The output setting ca. 4 W, which correspond to an intensity of 4 W/cm^2 at the horn tip was found to be well adapted for sonication.

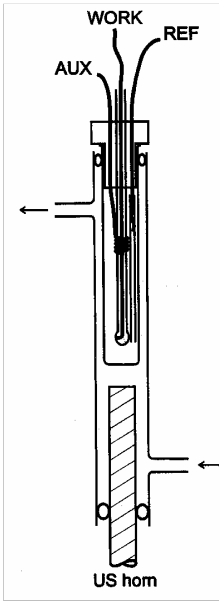

Figure 1. The sonoelectrochemical cell
working electrode: Pt/Hg
auxiliary electrode: Pt wire
refererence electrode: Ag wire

The electrochemical experiments were carried out with the help of the arrangement represented in Fig.1. An electrochemical cell of cylindrical shape (external diameter 16 mm) with a flat bottom was immersed in a larger glass tube (internal diameter 22 mm). The ultrasonic horn was situated at the bottom of this tube. Water flowing through this tube serves as a both a cooling agent and a coupling medium for transfer of ultrasound from the horn to the cell. An overpressure of 3 to 4 atm. was maintained inside the cooling water. In the absence of overpressure, an intense cavitation, *i.e.* formation of microbubbles, was observed near the horn tip inside the cooling water. It indicates that a large amount of ultrasonic energy was absorbed, and consequently only a low ultrasonic intensity was transferred to the vicinity of the electrode. With overpressure, the cavitation in the vicinity of the horn tip was much weaker, *i.e.* the transferred ultrasonic intensity was higher, and so formation of cavitating bubbles was observed in the vicinity of the electrode. Table 1 gives the values of the limiting reduction currents i_l of 4,4'-dinitrodibenzyle (DNDB) recorded at the stationary disc electrode under the following conditions of sonications: horn without and with overpressure. It indicates that the mass transfer coefficient $m = i_l / nFA$ [substrate] is ca **2.2 times higher** with overpressure than without. Table 1 also gives the rotation speeds, which would be obtained at a rotating electrode (Levich equation).

Table 1.

Voltammetric data associated to the cathodic reduction of 4,4'-dinitrodibenzyle (2mM) in ethanolic 2.5 N H_2SO_4 solution under sonication on a stationary electrode, and under silent conditions at a rotating electrode; electrode / horn tip separation distance 5 mm and horn tip / cell floor separation distance 12 mm (scan rate 5 mVs^{-1}).

	Stationary electrode		**Rotating electrode**
	US horn with overpressure	**US horn**	**No sonication**
Limiting current [mA]	0.523	0.240	0.144
Rotation rate [rps]	659*	139*	50

* Equivalent rotation rate from the Levich equation (ν = 56.07 cm^2/s; D = $5 \cdot 10^{-6}$ cm^2/s; n = 12)

The main advantages result from this arrangement: (i) the horn is electrically isolated from the electrolyte and (ii) due to the cylindrical shape of the whole assembly all the acoustic energy is passing through a constant area of cca. 4 cm^2 and is not decreasing with the increasing distance from the horn.

The cell was equipped with three electrodes. A vertical position of the working electrode was used since it allows a free vertical movement of bubbles formed in the solution. A cylindrical Pt-net was used as an auxiliary electrode. An Ag wire quasi-reference electrode was placed near the surface of the solution where the intensity of ultrasound is low. A Pt/Hg-disc (ϕ = 1.5 mm) [32] was used as a working electrode. Voltammetric experiments were carried out using a PGSTAT 20, ECO CHEMIE potentiostat and for rde experiments a BAS-100 B/W electrochemical system was employed.

The cell without electrodes was filled with 10 ml ethyl alcoholic 2.5 N H_2SO_4 solution of DNDB and an aluminium kitchen foil was immersed. According to Pugin [33] the observation of the destruction of the foil by sonicaton allows the space in the cell with the most intense transient cavitation to be found, and the location of areas with and without transient cavitation to be discriminated. The foil was rapidly destroyed in the area at ca. 5 mm from the bottom of the cell, which proves an intense transient cavitation. Another area was observed where the destruction of the foil occurred (ca. 35 mm from the bottom of the cell). However, the destruction was much slower owing to weaker transient cavitation. Sporadic holes were sometime found on other parts of the foil but concentrated surface damage was located in only these two areas. These results show that the intensity of ultrasound varies with the distance from the horn being greatest near the bottom of the cell, and then decreases under the transient cavitations threshold and increases again above it after ca. 3.5 cm.

The cell was then washed, equipped with the three electrodes, the working electrode being positioned at 5 -12 mm from the bottom of the cell. It was filled with the electrolyte up to exactly the same level as previously in order to maintain the same distribution of ultrasonic energy, that is the volume of solution was ca. 8 ml.

Ethyl alcohol (Aldrich), sulfuric acid (Aldrich) and 4,4'-dinitrodibenzyle (Aldrich), recrystalised from toluene were used. The temperature was 20°C

without sonication, under sonication the temperature increased from 20^{o}C up to ca.22^{o}C.

3. Results and discussion

Voltammetric studies of 2 mM 4,4'-dinitrodibenzyle in ethyl alcoholic 2.5N H_2SO_4 solution on Pt/Hg electrode allow well-defined voltammograms to be recorded, both under silent conditions and under sonication, over a wide potential range. In Fig. 2 cyclic voltammogram (a) and sonovoltammogram (b) are shown.

Figure 2a illustrates that an irreversible $8e^-$ reduction (process 1) at $\varepsilon_{1/2}$ = - 0,55 V/Ag is followed by an irreversible $4e^-$ reduction (process 2) with a peak potential ε_{cp} = - 0,69 V/Ag.

$$O_2N–\phi–(CH_2)_2–\phi–NO_2 + 8e^- + 8H^+ \rightarrow HOHN–\phi–(CH_2)_2–\phi–NHOH \quad (1)$$

$$HOHN–\phi–(CH_2)_2–\phi–NHOH + 4e^- + 4H^+ \rightarrow H_2N–\phi–(CH_2)_2–\phi–NH_2 \quad (2)$$

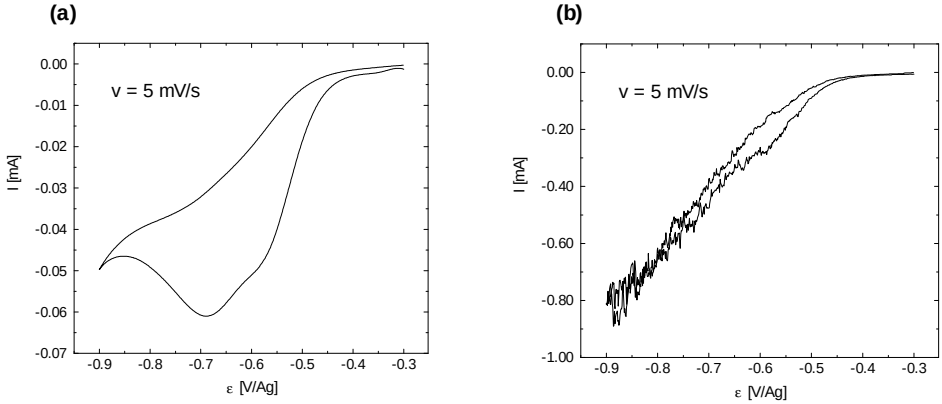

Figure 2. Cyclic voltammograms of 2 mM DNDB in the absence (a) and in the presence (b) of ultrasound

Figure 2b shows an analogous measurement except that 20 kHz ultrasound of intensity 2,8 W/cm^2 has been directed at the electrode surface, using the experimental arrangement described in figure 1 with a horn tip-electrode separation d = 5 mm. The average transport limited current is significantly enhanced as compared to the silent case, and the form of the voltammogram is qualitatively changed from that of a familiar cyclic voltammogram to a sigmoidal shape, indicative of a constant rate of transport of the electroactive species to the electrode surface so as to sustain an, in average, steady current. The magnitude of the current is considerably greater than that of the peak current seen under silent conditions.

In figure 3 two successive potential scans are shown. The limiting current decreases during the second potential scan, since it is as low as ca. 5-15 %

of its initial value. The same current is obtained after five successive scans as for the second scan.

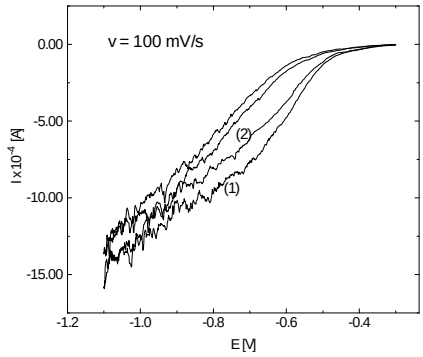

Figure 3. Succesive sonovoltammograms of 2 mM DNDB.

An important variable in sonoelectrochemical experiments is the distance between the electrode surface and the tip of the amplifying horn. Figure 4 confirms the expected current increase as the electrode is positioned closer to the region of highest cavitational intensity, near the tip of the amplifying horn. These experiments were performed maintaining a constant distance between the horn tip and the floor of the sonoelectrochemical cell.

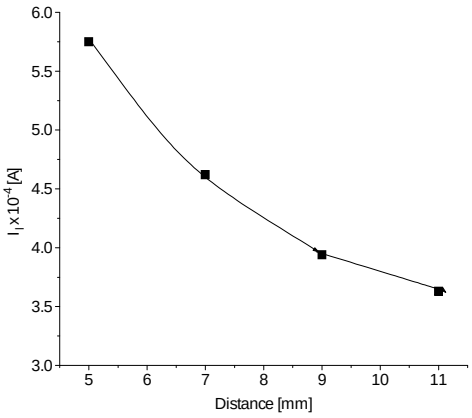

Figure 4. Limiting current *vs* separation distance between horn tip and electrode surface; horn tip/cell floor distance 12 mm, 2 mM DNDB in ethanolic 2.5 N H_2SO_4 solution.

Results presented in the table 2 indicate that scatter resulting from fluid profile changes at various horn tip/cell floor separation distances. It is minimized when small horn tip/electrode separation distances are employed. As is shown, if a distance of 5 mm is maintained between horn tip and electrode, a relative deviation of only 2 - 4% is found for limiting currents measured with horn tip/cell floor separation distances ranging from 1.5 to 12 mm.

Table 2.

Effect of distance from sonicator tip to cell floor on limiting current;
2 mM DNDB in ethanolic 2.5 N H_2SO_4 solution

Height above cell floor [mm]	$I_{II} \cdot 10^{-4}$ [A]	**Electrode / horn tip separation distance** [mm]
1.5	5.57	5
3	5.79	5
6	5.54	5
9	5.66	5
12	5.75	5

The mass transport limited current, I_{lim}, observed in sonovoltammetry may be described by the equation (3) [34,35]:

$$I_{lim} = n \cdot F \cdot A \cdot [substrate] \cdot m \qquad (3)$$

where [substrate] is the bulk concentration, $m = D/\delta$ is the average mass transport coefficient and the other symbols have their usual meanings.

Table 3 presents the limiting currents obtained from cyclic voltammetry, the equivalent rotation rates and the average mass transfer coefficients for the electroreduction of 2 mM DNDB in the presence of ultrasound.

Table 3

Limiting currents, equivalent rotation rate and average mass transfer coefficients for electroreduction of 2 mM DNDB in the presence of ultrasound; two successive potential scans.

v [V/s]	$\mathbf{I_{lim} \cdot 10^{-4}}$ [A]		**rotation rate*** [rps]		$\mathbf{m \cdot 10^{-2}}$ [cm/s]	
	1st cycle	2nd cycle	1st cycle	2nd cycle	1st cycle	2nd cycle
0.005	1.36	1.26	45	38	1.18	0.92

* Equivalent rotating rate - determinate from the equation:

$$I_l = 0{,}62 \cdot n \cdot F \cdot [substrate] \cdot A \cdot D^{2/3} \cdot \nu^{-1/6} \cdot \omega^{1/2}$$

By comparison, to duplicate the mass transport coefficient of 0.0273 cm/s calculated for the sonovoltammogram obtained at a scan rate of 0.010 V/s, a rotation rate of 75780 rpm would theoretically be necessary, an experimental improbability, as the onset of turbulence occurs rotation rates of > 10.000 rpm.

The significance of **m** obtained from sonovoltammetry is somewhat different from that for a rde. In the case of the rde, fluid velocity normal to the electrode surface remains constant from the bulk up to the outer edge of the hydrodynamic layer and is independent of the radial (r) and angular (φ) coordinates [34].

The mass transport coefficient then represents the volume flow per time per unit area ($cm^3/s \cdot cm^2$ = cm/s) [9]. In the cavitational environment of sono-voltammetry however, fluid velocity is expected to be highest at the sonicator tip,

to decrease normal to the tip, and then to increase again close to the electrode surface (due to the presence of fluid macrojets formed during interfacial bubble collapse), before finally dropping to zero at the solid/liquid interface. Furthermore, due to the turbulence nature of the flow patterns, the component of the fluid velocity normal to the electrode surface is not expected to be constant with respect to the radial or angular coordinates at a given distance from the electrode surface. For this reason, a mass transport coefficient measured in such an experiment represents a spatially average value over the electrode surface and is a time-varying quantity consisting of a steady-state component (m_{dc}) and a transient portion (m_{ac}) which sum to give the instantaneous value of the coefficient [34].

Characterization of the high rates of mass transport observed during sonovoltammetry, in terms of **m**, is useful due to the potential importance of these results in the areas of both sonochemistry[36] and industrial electrochemistry [37].

In table 4. are presented the mass transport coefficients determinated using a rotating-disk.

Table 4

Limiting currents and mass transport coefficients for electroreduction of 2 mM DNDB on Pt/Hg rotating disk electrode, in ethanolic 2,5 N H_2SO_4 solution; v = 0.005 V/s

ω [rps]	$\mathbf{I_{lim} \cdot 10^{-4}}$ [A]	$\mathbf{m \cdot 10^{-2}}$ [cm/s]
16.67	0.95	0.69
33.33	1.24	0.90
50	1.44	1.05
83.33	1.78	1.30

Using a comparison with a “classical” hydrodynamic technique, a rotating disk-electrode with a rotation speed of approximately 50 rps (3000 rpm) would be necessary to achieve an equivalent steady-state current as for cyclic voltammetry (at scan rate of 0,005 V/s) assisted by sonication (20 kHz, 4W/cm^2) (see also fig. 5).

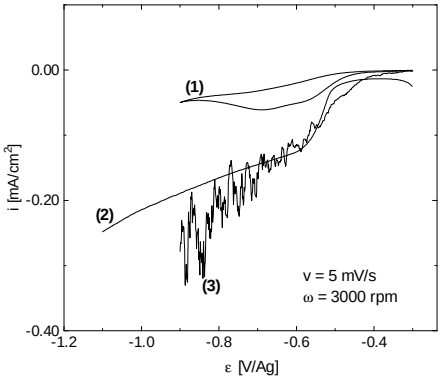

Figure 5. Voltammograms of 2 mM DNDB on stationary electrode, in absence (1), in presence (3) of ultrasound and on rotating disc electrode (2).

4. Conclusions

Examination of limiting currents obtained under a variety of sonochemical conditions yields information concerning the identity of the factors, which influence

the mass transport coefficient. Comparison of sonoelectrochemical experiments with rde measurements illustrates how acoustic cavitation and turbulence can influence steady-state currents. Minimisation of electrode-sonicator tip separation distance yields current values that are cell geometry independent.

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