

Application of an electrochemical pulsed flow reactor to electroorganic synthesis: Part I: Reduction of acetophenone

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Received 2 January 1996; revised 9 September 1996

The aim of this work is to investigate the use of a new type of reactor for electroorganic synthesis. The concept of the reactor is based on the principle of the porous percolated pulsed electrode (E3P) which was primarily developed at commercial scale for metal recovery in waste waters. The reactor is fitted with a three-dimensional electrode, of axial configuration, consisting of ordered stacks of discs of expanded metal. It can be supplied either by a homogeneous electrolyte or by an emulsion generated by an external ultrasonic system. The pulsation of the electrolyte represents a very effective means of improving mass transfer rates at the electrode. Under two phase conditions, the role of the pulsation is also to ensure the hydraulic transport of the emulsion and to increase the three phase contacts between the aqueous phase, the organic phase and the electrode. The efficiency of the reactor was tested using both homogeneous and two phase liquid–liquid electrolytes in the direct reduction process of an aromatic ketone. This study reports the effects of the pulsation on the mass transfer rate of acetophenone at the electrode. A comparative study of the behaviour of the E3P reactor towards different media is accomplished. Particular attention is paid to the chemical and faradaic yields, as well as to the selectivity of the reaction.

Keywords: *acetophenone, electrochemical reactor, electroorganic synthesis*

1. Introduction

Electroorganic synthesis has found a rather limited number of applications on an industrial scale. These include electrohydrodimerization of acrylonitrile, the Nalco process for tetraalkyllead and sebacic acid for the manufacture of polyamide resins [1, 2]. However, electroorganic processes that have been investigated on a pilot plant or semicommercial scale cover a wide range of reaction types [1]. The weakness in the industrial development of such processes can be partially attributed to the lack of suitable reactors. Although many kinds of electrolyzers have been developed on a laboratory scale, filter-press reactors are still predominant. Adaptable reactors are not easy to find on the market and the development of reactors suited to electroorganic synthesis proves to be a real need.

The aim of this paper is to show the potentialities in electroorganic synthesis of a new kind of reactor. This reactor is based on the principle of the E3P reactor (E3P: porous percolated pulsed electrode) which is at present commercialized for the recovery of metals and for effluent treatment [3]. The most important advantages of this reactor come from the possibility to use a three-dimensional electrode and from the pulsation of the liquid phase. The use of a three-dimensional electrode allows for a high exchange surface area and increases the electrode surface/reaction volume ratio which is important in the design of electrolyzers [4]. The pulsation enhances mass transfer at the electrode [5, 6]. Pulsation induces stirring of the electrolyte which is easily controlled by means of two parameters: the amplitude, a , and the frequency, f . In electroorganic synthesis, stirring is sometimes a key parameter, strongly influencing the selectivity of the reaction. The reactor was first

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adapted to electrolysis in two phase liquid–liquid media with an emulsion prepared by ultrasonication [5]. The efficiency of this reactor has been demonstrated using well-known oxidation–extraction reactions such as the oxidation of iodide to iodine and the oxidation of ferrocene to ferricinium. Furthermore, an example of the application of the E3P reactor to electroorganic synthesis was given by Cognet [7] concerning the electrooxidation of benzyl alcohol on nickel foam electrodes. In an axial configuration, the use of porous electrodes is necessary for the working of this electrolyser. The open structure of expanded metal electrodes is also suited to this reactor.

The interest of using expanded metal electrodes in electroorganic synthesis has been demonstrated for a variety of electrolysers and, in particular, for processes involving two phase electrolytes [8–11]. Generally, two-phase electrolytes are used when solubility problems are encountered and the need to reach an emulsion state in order to enhance mass transfer and chemical rates [12]. In this way, the open structure of expanded metal protects the emulsion from coalescence when passing through the electrode bed. Ultrasonication yields microemulsions which limit the use of surfactants or phase transfer agents that make the recovery of products more difficult and can react or adsorb at the electrode. Under these conditions, the electron transfer reaction is carried out in the conductive phase and the product is extracted by the nonconductive phase. In electroorganic synthesis, these processes are interesting because they may protect the products from further oxidation or reduction.

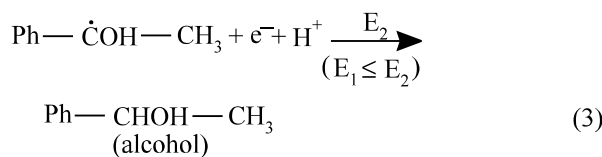
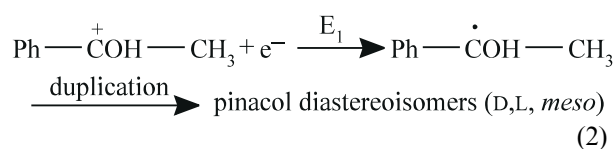
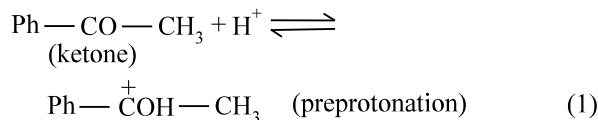
We report below results for the direct reduction of an aromatic ketone (acetophenone) to alcohol and pinacol. These reactions have been studied in homogeneous and in two phase liquid–liquid media and we have paid particular attention to the influence of the medium and the pulsation on the electrolysis efficiency.

2. Direct reduction of aromatic ketones

Direct reduction of acetophenone in aqueous media has initially been chosen as a model reaction. Its mechanism is well known. Although much work has been done on this subject [13–20], the reaction was only investigated in homogeneous or pseudo homogeneous media (aqueous micellar media [16]). To our knowledge, no work has been devoted to the reduction of acetophenone circulating as an emulsion through the pores of a three-dimensional electrode.

The reaction was studied in an aqueous homogeneous medium and in an emulsion at neutral pH on a cadmium cathode. Cadmium electrodes were chosen for their high hydrogen overvoltage and their hardness when manufactured as expanded cadmium grids. One product is the 2,3 diphenyl-2,3-butanediol under two diastereoisomers *D,L* and *meso*. It is obtained by one-electron reduction followed by radical duplication. The other product is the 1-phenylethanol and is obtained by a 2 electron reduction which

consists of an electrochemical dihydrogenation. After a preliminary analytical study of the reaction and taking into account the reaction mechanism mentioned in the literature concerning aromatic ketones in a protic medium [19, 20], the electroreduction is represented by the following reaction scheme:



In alkaline aqueous media, the formation of alcohol is favoured while the reductive coupling to pinacol is favoured in acidic media. In neutral or slightly acidic aqueous medium, the two mono-electronic stages are not clearly distinguished. The voltamperometric curves exhibit one single wave and the whole shape of the curves indicates a slow or irreversible system.

The result of the electrolysis depends strongly on the ketone concentration because the dimerization reaction (reaction order 2) is in competition with the alcohol production reaction (reaction order 1). In macroelectrolysis, pinacol is generally the major product [21] and the *D,L/meso* ratio remains in the range 0.7–0.95 in spite of changes in the electrolysis conditions. Similarly, stirring plays an important part in the chemoselectivity of the reaction. Under conventional stirring, enhancement of the stirring velocity favours the transfer of the electrogenerated radicals towards the bulk solution. This leads to a greater amount of pinacol in the medium [20]. In this context, the study of the influence of pulsation a and f , the stirring parameters of the E3P reactor, is of great interest.

3. Experimental details

3.1. Apparatus

The reactor and the equipment have been described previously [6]. Electrolyses were carried out in an undivided E3P reactor whose internal volume was 10^{-3} m^3 [6] (Fig. 1). A peristaltic pump (6) was used to control the permanent superficial velocity U_0 in the range $0\text{--}0.1 \text{ cm s}^{-1}$; the overflow was returned to the storage tank (7) which was used for sampling. The pulsation was achieved by a Teflon piston (1), with an amplitude of $0 < a < 0.012 \text{ m}$ and a frequency of $0 < f < 1.33 \text{ Hz}$). The instantaneous velocity of the liquid is given by $U = U_0 + a\omega \sin \omega t$ and the hydrodynamic

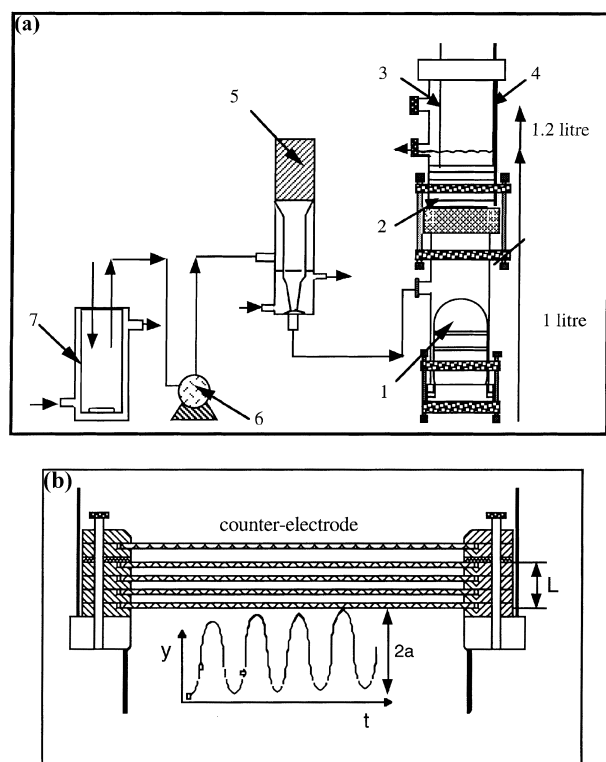


Fig. 1. (a) Schematic view of experimental apparatus: (1) Teflon piston, (2) electrodes, (3) Luggin capillary (SCE reference electrode), (4) current feeder, (5) sonication cell, (6) peristaltic pump and (7) storage tank. (b) Electrodes stand; L is the electrode stack height.

conditions are characterized by the Strouhal number $Sr = a\omega/U_0$. The maximum velocity that could be obtained with the pulsation was around 10 cm s^{-1} . In the present study, as $Sr \gg 1$, the electrochemical cell can be considered as a perfectly stirred tank. Under two phase conditions, high velocities were necessary to ensure the stability of the emulsion and to prevent the coalescence of droplets within the electrode.

The reactor was fed either with a homogeneous electrolyte or by an emulsion generated by a continuous ultrasonic cell consisting of a piezoelectric transducer. In both cases, the feeding solution is brought from the mixing tank (a storage tank) to the reactor by means of a peristaltic pump. The solution was totally recycled (closed circuit). The electrolyte volume was about 1.2 dm^3 . For a homogeneous electrolyte or for an emulsion composed of a dispersed organic phase with a density inferior to that of the aqueous continuous phase, feeding took place at the bottom of the reactor and it was recycled at the top. In the special case of an emulsion consisting of a dispersed organic phase having a density greater than the aqueous continuous phase (water/acetophenone emulsion), feeding took place at the top of the reactor and it was recycled at the bottom by use of a second pump.

3.2. Electrolysis cell

The reactor was equipped with an undivided cell in an axial configuration with a diameter of 8 cm. The electrical configuration was monopolar and each

electrode was fitted with its own current feeder. The working electrode consisted of a stack of circular expanded cadmium grids especially supplied for this work by the company Le Métal Déployé [22]. The space between two electrodes was 4 mm. The counter electrode was placed 1 cm over the working electrode (Fig. 1). A stack of three grids (overall geometrical surface area of $2.6 \times 10^{-2} \text{ m}^2$) was used. The counter electrode consisted of a spiral made of platinum (surface area of $0.12 \times 10^{-2} \text{ m}^2$) for preparative electrolyses or an expanded Ti/Pt (surface area of $0.67 \times 10^{-2} \text{ m}^2$) grid for recording the I/E curves.

3.3. Electrolysis

All experiments were run at room temperature (around 20°C). The storage tank was fitted with a cooling jacket to ensure control of the temperature by circulating water. Solutions were degassed in an ultrasonicated tank for 30 min before the experiment. The organic phase was degassed separately before being weighed and mixed with the aqueous phase. Permanent degassing of the electrolytic solution during experiments was achieved by nitrogen bubbling.

I/E curves were recorded using a three electrode configuration by means of a potentiostat (Tacussel PJT 35 V-2 A). The potential scanning rate was 0.025 V s^{-1} . Preparative electrolyses in the E3P reactor were conducted galvanostatically (three-electrode configuration or two-electrode configuration with a Heinzinger 32 V-6 A current supplier). To measure or to set the potential to the three dimensional working electrode, a double junction reference saturated calomel electrode (SCE) was used. It was immersed in the solution through a Luggin capillary. This could be shifted inside a groove along the stack of electrodes in order to measure the potential at any height of the three-dimensional electrode.

3.4. Electrolyte composition

Three electrolytic systems were used:

- aqueous solution saturated with acetophenone (homogeneous medium)
Supporting electrolyte : Na_2SO_4 0.1 M, pH 6;
 $[\text{PhCOCH}_3]_{\text{sat}} = 4 \times 10^{-2} \text{ M}$
- water/acetophenone emulsion (binary system)
Organic phase (10 vol %): acetophenone (124 g)
Aqueous phase (90 vol %): Na_2SO_4 0.1 M, pH 6
- water/toluene/acetophenone emulsion (ternary system)
Organic phase (5 vol %): acetophenone (5 g) + toluene
Aqueous phase (95 vol %): Na_2SO_4 0.1 M, pH 6

In the case of the binary system, the acetophenone concentration in the aqueous phase was continuously equal to the saturation concentration ($4 \times 10^{-2} \text{ M}$). In the case of the ternary system, acetophenone was dissolved in an electrochemically inert solvent and

was present in both phases of the emulsion. The initial ketone concentration in the aqueous phase at the equilibrium is 4.2×10^{-3} M and the mass related distribution coefficient ($m_{\text{tol.}}/m_{\text{aq.}}$) was 7.3.

3.5. Products analysis

Unreacted materials and products were first extracted with diethyl ether. Their concentrations were then determined by HPLC on a grafted C18 $5 \mu\text{m}$ column with the following conditions:

eluent: acetonitrile (60%), water (40%)
 detector: u.v. with wavelength 220 nm
 flow rate: 0.8 ml min^{-1}

The HPLC determinations give the alcohol/pinacol ratio and the acetophenone conversion:

Conversion

$$= \frac{\text{Acetophenone}_{\text{initial}} - \text{Acetophenone}_{\text{measured}}}{\text{Acetophenone}_{\text{initial}}} \times 100$$

The percentage current efficiency CE was then calculated from the theoretical charge Q_{th} needed for the acetophenone reduction to alcohol (two electrons) and pinacol (one electron) against the measured electric charge Q_{cons} :

$$\text{CE} = \frac{Q_{\text{th}}}{Q_{\text{cons}}} \times 100$$

4. Results and discussion

4.1. Homogeneous medium

Figure 2 shows the positive effect of pulsation on the diffusion current of acetophenone reduction. It represents the ratio of the diffusion current under pul-

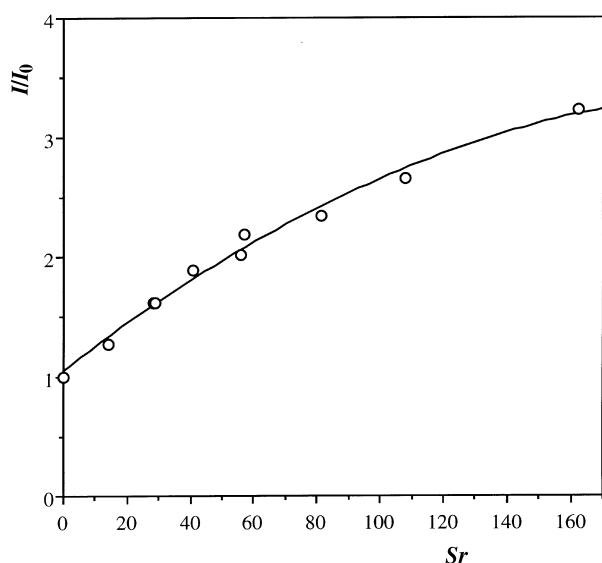


Fig. 2. Ratio III_0 as a function of Sr number ($U_0 = 1 \text{ cm min}^{-1}$) for the reduction of acetophenone (8.5×10^{-3} M) in an aqueous solution (pH 6, $[\text{LiCl}]$: 0.1 M) at one expanded cadmium electrode. I_0 diffusion current without pulsation; I diffusion current under pulsation.

sation, I , in comparison to that without pulsation, I_0 , as a function of the Strouhal number Sr . Under the pulsation regime, the currents were smoothed because they followed the sine function of the pulsation. The currents were measured on the I/E curves recorded at one cadmium grid and for a solution of 8.5×10^{-3} M acetophenone while the other grids were disconnected and used as turbulence promoters. In the explored range ($0 \leq Sr \leq 165$), the ratio III_0 increases with Sr number and shows an asymptotic behaviour for high Sr . The currents are related to the mass transfer rate and pulsation enhances mass transfer [6]. At $Sr = 160$, the currents were tripled and the mass transfer coefficient was around 10^{-5} m s^{-1} . Comparisons of the mass transfer performance of the E3P reactor with filter-press reactors were undertaken for nickel foam electrodes [6]. The mass transfer coefficient could reach $2 \times 10^{-5} \text{ m s}^{-1}$ and correlations indicated that mass transfer was higher for the E3P reactor than for a filter press reactor [6]. As the mass transfer rates are higher under pulsation, electrolysis can be carried out with current densities higher than in plug flow conditions (without pulsation). This may lead to higher performance.

To determine the contribution of each pulsation parameter to the mass transfer performance, a correlation, $III_0 = K a^x \omega^y$, was investigated. The following correlation was found for $0 \leq Sr \leq 165$ and $U_0 = 1 \text{ cm min}^{-1}$.

$$I/I_0 = 2.22a^{0.38} \omega^{0.37} \quad (1)$$

where a is in cm and $\omega = 2 \pi f$ is in rad s^{-1} .

This correlation accounts for the positive influence of the pulsation on mass transfer rates. The amplitude and frequency show the same effect, which is in agreement with the relation between mass transfer and instantaneous velocity depending on $a\omega$ at high Sr values. These results are in good agreement with the study of mass transfer at nickel foam electrodes in an E3P reactor under pulsation [6].

Taking into account the electroactivity of acetophenone at the electrode (curve (c) in Fig. 3), electrolyses of saturated acetophenone solutions were carried out under the same galvanostatic conditions for different values of the pulsating parameters. The applied current corresponded to I_0 , the diffusion current in plug flow conditions (without pulsation) at the 3 Cd grids. The results are reported in Table 1. The conversions are of the same order of magnitude, ranging from 65 to 75%. The conversion and the current efficiency CE follow the same variations with Sr number. An optimum Sr number is around 100 in order to obtain the highest conversion. It is observed that the alcohol/pinacol ratio depends on Sr but no simple relation was found. For a small amplitude (0.37 cm), an increase in frequency from 0.52 to 1.18 Hz modifies the pinacol selectivity from 32 to 60% (runs 2 and 4). Pinacol formation is enhanced under pulsation at high frequency and low amplitude. Radical coupling to pinacol is favoured in strongly turbulent zones (high frequency) while direct reduc-

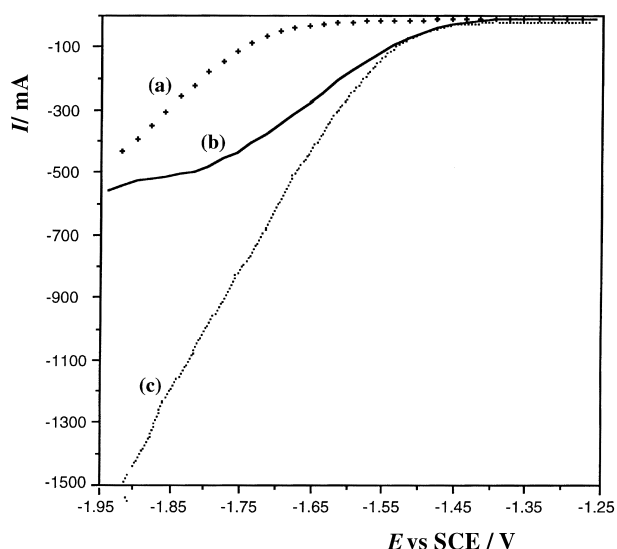


Fig. 3. I/E curves in pulsed flow conditions ($U_0 = 1 \text{ cm min}^{-1}$; $a = 0.6 \text{ cm}$; $f = 1 \text{ Hz}$): (a) Na_2SO_4 0.1 M (residual current); (b) aqueous acetophenone saturated solution + Na_2SO_4 0.1 M (homogeneous medium); (c) emulsion: water + Na_2SO_4 0.1 M / acetophenone 10 vol% (binary system).

tion to alcohol is favoured when pulsation is low. As the mass transfer increases under pulsation, the enhancement of the pinacol formation under pulsation indicates that duplication occurs in solution. To increase pinacol formation, we studied the electrochemical reduction of acetophenone in two phase media.

4.2. Two phase media

The influence of the composition of the two-phase mixed electrolyte and pulsation on the interfacial transfer conditions was investigated. The current distribution between the reduction of acetophenone and the side reaction of hydrogen evolution was also studied. This distribution can be represented by the ratio $(|i_{\text{total}}| - |i_{\text{hydrogen}}|)/|i_{\text{total}}|$. This ratio has been calculated for a potential in the range $[-1.85 \text{ V to } -1.40 \text{ V}]$. Figure 4(a) (without pulsation) and 4(b) (with pulsation) show the potential domain which corresponds to the best current distribution and therefore to the optimum electrolysis conditions. Acetophenone electroreduction was then conducted

in an E3P reactor for each two phase system to compare the runs with results obtained in a homogeneous medium (Table 1).

4.2.1. Ternary system. In pulsed flow conditions, the reduction of acetophenone, which is present in each phase of an emulsion water/toluene, is performed under diffusional control. The diffusion plateau is not well defined (Fig. 3). The transfer rate is three times lower than in aqueous saturated solution. When acetophenone is replaced by benzophenone, which is insoluble in water, no reduction current is detected. This demonstrates that the reaction occurs only at the aqueous phase/electrode interface. Although the ketone concentration in the aqueous phase at equilibrium ($4.2 \times 10^{-3} \text{ M}$) is nine times lower than the concentration in saturation conditions, the detected intensity is only three times lower than in a homogeneous medium. Thus, the presence of the dispersed phase (toluene phase) takes part in increasing the mass transfer rates at the electrode. Furiet *et al.* [21], who studied a similar system (iodine/iodide in water/toluene medium) in a stirred tank, found that in the diffusional regime, intensity values were enhanced by a factor between three and four in the presence of a dispersed phase. They reported that this mass transfer enhancement could be attributed to a resaturation of the diffusional zones by the reactant present in the dispersed phase. The same assumption can be made concerning the system water/toluene/acetophenone. Indeed, the organic 'storage phase' (toluene/acetophenone) can compensate the loss of electroreducible species in the aqueous phase near the electrode by liquid/liquid transfer and then improve the liquid/electrode mass transfer.

Concerning hydrogen evolution, it is interesting to note in Fig. 4(a) and (b) that the efficient distribution zone is larger under pulsed flow conditions. This allows for a higher potential drop in the electrode during electrolysis under pulsation. In other respects, the optimum value of the current distribution curve is 10 to 15% lower than in a homogeneous medium. Runs 4 and 5 (Table 1), performed under the same electrolysis conditions, show that conversion and faradaic yield obtained in homogeneous medium are respectively 27 and 11% higher than for the ternary

Table 1. Influence of pulsating parameters on the current efficiency and the selectivity: operating conditions and results

Run	Medium	a /cm	f /Hz	Sr^{\ddagger}	i /A m ⁻²	Electrolysis time /h	Conversion /%	Current efficiency /%	Alcohol/pinacol molar ratio [§]
1*	homogeneous (1)	0	0	0	12	6.08	69	66	58/42
2*	homogeneous (1)	0.37	0.52	86	12	6.08	75	77	68/32
3*	homogeneous (1)	1.06	1.03	486	12	6.08	65	58	50/50
4*	homogeneous (1)	0.37	1.18	194	12	6.08	70	60	40/60
5 [†]	two phase (ternary) (3)	0.37	1.18	194	12	6.08	43	49	95/5
6 [‡]	two phase (binary) (2)	0.37	1.18	194	6	7.00	20	60	30/70

* Potential of cathode is higher than or equal to -1.65 V/SCE and the order of magnitude of the potential drop in the stack is 10 mV; pH variation between the beginning and the end of the electrolysis is negligible.

[†] Potential of the cathode is higher than -1.80 V/SCE (ΔE was not measured); pH 5 (final).

[‡] $U_0 = 1 \text{ cm min}^{-1}$ for all runs.

[§] D,L and meso diastereoisomers are formed in equal proportion.

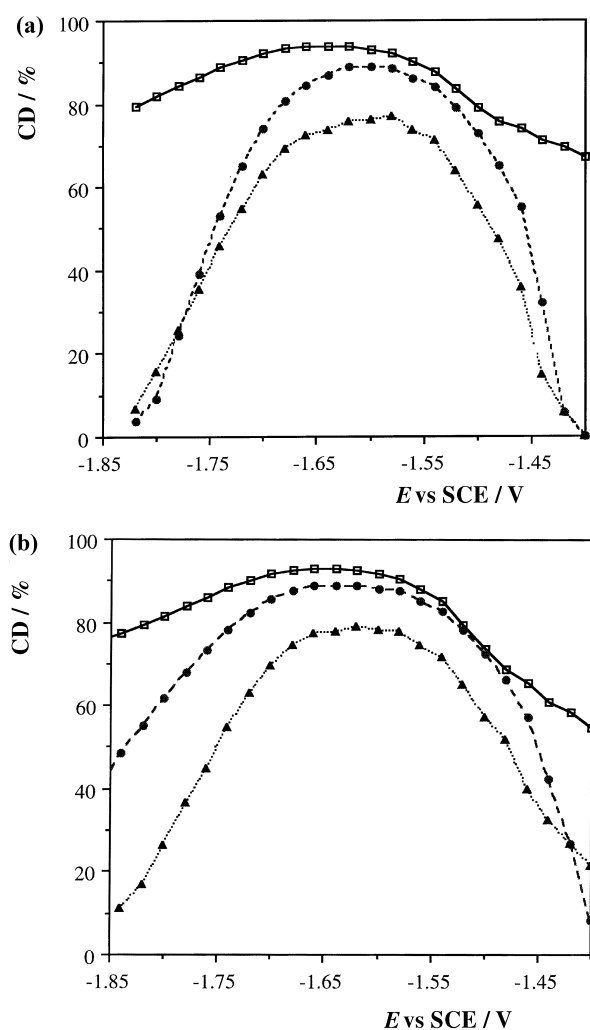


Fig. 4. current distribution, CD, between the hydrogen evolution I_{H_2} and the acetophenone reduction: (a) without pulsation, (b) under pulsation ($a = 0.6$ cm, $f = 1$ Hz). $CD = 100 \times (I_{total} - I_{H_2}) / I_{total}$. Legend: (\square) water/acetophenone emulsion; (\blacktriangle) water/toluene/acetophenone emulsion; (\bullet) homogeneous medium.

two phase system. The low faradaic yield is consistent with analysis of the current distribution curves. Despite the low yields obtained in the ternary two phase system, electrolysis leads selectively to alcohol (molar yield of 95%). Under the same conditions, the homogeneous medium leads to pinacol (molar yield of 60%). This significant difference of selectivity can be attributed to a concentration effect. For the ternary system, the dimerization reaction is not favoured because of the very small ketone concentration in the aqueous phase.

The presence of a nonpolar solvent like toluene does not lead to satisfactory yields because of the low ketone concentration in the aqueous phase. Nevertheless, it could be interesting when applied to moderately soluble ketone reduction in the presence of a non electroactive olefin. In an acidic medium, ketones are more easily reducible than olefins. Mixed dimers can be obtained by coreduction. They are formed by an attack on the olefin by the cetyl radical. In this way, cyclization products can also be obtained [17]. In this case, the organic phase plays the part of the

reactant and the extractant and takes part in the enhancement of the transfer rates.

4.2.2. Binary system. In the case of a water/acetophenone emulsion, the aqueous phase is constantly saturated with acetophenone and the reacting organic phase (acetophenone) enables the *in situ* extraction of pinacol that is insoluble in water. *I/E* curves of Fig. 3 show that, the electrode works under kinetic control. This result is interesting since at a given potential corresponding to the plateau domain in homogeneous medium, the intensity is multiplied by a factor of three under a pulsed flow regime. This phenomenon had been observed by Quéméré [5] who studied the behaviour of a water/nitrobenzene emulsion (binary system) at an expanded copper electrode. The appearance of a kinetic current can be explained by the total resaturation of the aqueous phase in reducible substrate, leading to the suppression of the diffusion limitation in the proximity of the electrode.

Concerning the hydrogen evolution, it is shown, on Fig. 4(a) and (b), that the distribution curve profile is flat and that the binary system corresponds to the most favourable profile. Electrolysis of a water/acetophenone emulsion (run 6, Table 1) gives far better results than electrolysis of a saturated aqueous solution or a ternary electrolyte. After seven hours of electrolysis at a 60 A m^{-2} current density, 20 g of pinacol were obtained with a corresponding 60% current efficiency and a 70% selectivity. Taking into account these results, the pinacol production in an E3P reactor and with a binary two phase electrolyte previously dispersed by ultrasonication is of great interest.

5. Conclusion

We have tested the efficiency of the E3P reactor for the electroreduction of acetophenone. The advantage of liquid pulsation on electrolysis performance has been demonstrated. Analysis of pulsation parameters has raised the following interesting points:

- (i) pulsation has an impact on mass transfer but also on the chemoselectivity of the reactions,
- (ii) each pulsating parameter plays a similar role in mass transfer but not in selectivity.

The same conclusions apply to benzyl alcohol oxidation in an E3P reactor [19].

From the studies conducted in two phase liquid-liquid media, it can be concluded that electrolysis of an emulsion generated by an external ultrasonic cell, without surfactant, gives good results in the case of a binary water/organic reactant electrolyte where the reactant is sparingly or moderately soluble in water and is in direct contact with the aqueous phase. In the case of a water/acetophenone binary system, it was observed that the electrode worked in the regime of kinetic control and that electrolysis could be conducted with currents higher than limiting currents obtained for an aqueous saturated solution.

When applied to an electrochemical process involving the conversion of an organic substance which is sparingly or moderately soluble in water, electrolysis in a pulsed flow reactor offers interesting prospects. Another advantage of the pulsation is that performing the electrolysis in an E3P reactor does not require devices to generate high emulsion circulation velocities, as is necessary for filter press type reactors.

Experiments in the presence of a nonpolar solvent (ternary electrolyte water/toluene/acetophenone) did not lead to satisfactory results. Ultrasound permits considerable enhancement of the exchange surface but can not replace a phase transfer agent. It would be interesting to operate with a small quantity of phase transfer agent or to perform electrolyses activated by ultrasound [12].

Acknowledgements

The financial support of this work by E.D.F. is gratefully acknowledged. Métal Déployé S.A. is also acknowledged for supplying the non commercialized expanded cadmium grids.

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