ELECTROCHEMICAL REDUCTION OF TETRACHLOROMETHANE. ELECTROLYTIC CONVERSION TO CHLOROFORM

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The feasibility of electrolytic removal of tetrachloromethane from industrial effluents has been investigated. A new method based on the electrochemical reductive dechlorination of CCl_4 yielding chloroform is described. The main goal was not only to remove CCl_4 but also to utilize the process for obtaining chloroform, which can be industrially reused. GC-MS analysis of the electrolysed samples showed that chloroform is the only product. Voltammetric experiments were made in order to select experimental conditions of the electrolysis. Using energetic and economic criteria, ethanol–water (1 : 4) and LiCl were found to be the optimum solvent and supporting electrolyte tested. No great differences were found while working at different pH values. Chronoamperometric and voltammetric experiments with convolution analysis showed low k_f^0 and α values for the reaction. A new differential pulse voltammetric peak deconvolution method was developed for an easier and faster analysis of the electrolysis products. Electrolysis experiments were carried out using both a bulk reactor and a through-flow cell. Thus, three different kinds of galvanostatic electrolyses were carried out. Under all conditions, CCl_4 conversions ranging from 60 to 75% and good current efficiencies were obtained.

Keywords: Carbon tetrachloride; Chlorinated compounds; Reductions; Electroreductions; Electrochemistry; Voltammetry.

Because of the increasing care of environment over the last twenty years, environmental policies in the developed countries have focused on new strategies for waste management. They are based on the promotion of the best available techniques (BAT) as well as recycling, as a way to minimise or avoid the occurrence of pollutants in chemical processes/industries.

Electrochemical technologies could play an important role as environmental tools/clean techniques due to their environmental friendliness, the relative simplicity of the equipment and the easy control of the process[1,2]. Chlorinated organic pollutants are especially sensitive to electrochemical transformation: they can undergo dechlorination in a relatively simple pro-

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cess of electrolysis[3]. By controlling the electrochemical and medium parameters, it is possible to achieve partial or total dechlorination making products less toxic and more amenable to reusing or recycling.

Tetrachloromethane has been one of the most restricted pollutants in the last decade owing both to its toxicity and its role as a precursor of CFCs (chlorofluorocarbons)[4]. The Montreal Protocol suppressed the production of CCl_4 and other CFCs in most of the developed countries and, because of their toxicity, the EPA (Environmental Protection Agency) has classified them as a possible human carcinogen[5]. Despite these restrictions, CCl_4 is still indirectly produced mainly in two ways: in the industrial synthesis of chloromethanes and in the disinfection of drinking water with chlorine[6,7].

Many studies for elimination of CCl_4 have been proposed including a wide range of techniques such as chemical reduction[8–10], hydrolysis[11] hydrogenation/hydrogenolysis[12], pyrolysis[13], incineration[14], and chemical reaction[15]. Electrochemical reduction of chlorinated aliphatic compounds but only for mechanistic reasons[16–18] but so far, there has been no attempt to develop an electrolytic process that could be used as an effective way of removing CCl_4 at industrial scale.

Our goal is to evaluate the suitability of the reductive electrolysis of CCl_4 to obtain chloroform, a less toxic and profitable product that could be industrially used. This objective is a first step in the design of a subsequent industrial application. This process would be of environmental and economic interest for industry because the chloroform obtained from CCl_4 wastes could be commercialised.

First, we have studied the voltammetric behaviour of CCl_4 under many different conditions to determine the influence of the solvent, supporting electrolyte and pH on its reduction. Using these experiments, it will be possible to obtain a useful energetic and economic criterion for selection of the solvent composition to be used in electrolysis. Further, a deconvolution methodology based on differential pulse voltammetry has been developed for the quantification of the CCl_4 and chloroform in solution. Gas chromatography-mass spectrometry has been used for the identification of electrolysis products.

EXPERIMENTAL

Reagents

Chloromethanes and HPLC grade solvents were obtained from Merck. Tetraalkylammonium salts (tetrabutylammonium chloride, TBACl; tetraethylammonium chloride, TEACl; tetrabutylammonium iodide, TBAI) and lithium chloride, used as supporting electrolytes, were obtained from Sigma. Sodium sulfate, H_3PO_4, LiOH and Li_2CO_3 were obtained from Merck, and LiH_2PO_4 from Carlo Erba. Millipore treated water was used in each of the aqueous solutions prepared.

Instrumentation

Linear-sweep cyclic voltammetric and differential pulse voltammetric measurements were performed with a single-shot triangular wave generator coupled to a microprocessor-based data acquisition and control system equipped with a fast 12-bit A/D converter. Chronoamperometric measurements were carried out with a microprocessor-based system, which can generate appropriate pulses and timing sequences from a 12-bit D/A converter and suitable software. The generator, potentiostat, and acquisition systems were all home-made.

Electrolyses were carried out with a Thandar precision DC power supply, model TS3023S.

Gas chromatographic-mass spectrometric analyses were performed with a Fisons 8000 gas chromatograph coupled to a Fisons mass spectrometer detector model TRIO 1000. Both GC and MS were computer-controlled by the Lab-Base software from Fisons Instruments.

Voltammetric and Chronoamperometric Experiments

Linear-sweep cyclic voltammetric and chronoamperometric measurements were carried out with an aqueous sodium-saturated calomel electrode (SSCE) and a platinum wire as reference and auxiliary electrodes, respectively. As working electrode, a Metrohm EA 290 hanging mercury electrode of the area 1.39 ± 0.03 mm^2 was used. Due to the great volatility of CCl_4, the solution containing only the supporting electrolyte was first added to the cell and de-aerated for 15 min with N_2. After de-aeration, the N_2 flow was stopped and CCl_4 was added to the cell to achieve a final concentration of 1 mmol l^{-1} in voltammetry and 0.63 mmol l^{-1} in chronoamperometry. A scan rate of 100 mV s^{-1} was used in voltammetry.

For the differential pulse voltammetric measurements, a glassy carbon electrode was used as working electrode. The electrode was polished with a Buehler Metadi diamond paste of the size 1 and 0.25 mμ. Prior to the measurements, electrochemical cleaning was performed on the working electrode immersed in a supporting electrolyte solution by applying a potential of 4 V for 2 min. Then, an electrolytic sample was added to the cell, which was previously de-aerated. 0.1 M tetrabutylammonium chloride was used as supporting electrolyte and ethanol–water (4 : 1) as solvent.

Bulk Electrolysis

These experiments were performed using a mercury pool cathode with a surface of 1.3 cm^2 in a static cell. As anode, Pt (2 cm^2) or dimension-stable anode (DSA, 3.5 cm^2) were used. A conventional thermostated 50-ml cell (Metrohm) was used in all the experiments. A constant current density of 15 mA cm^{-2} was used for the galvanostatic electrolysis; 1 M LiCl in ethanol–water (4 : 1) and 0.2 M CCl_4 was the composition of the working solution. Samples were taken throughout the electrolysis and analysed by differential pulse voltammetry. An electrolytic sample of 100 μl was withdrawn from the cell and introduced in to a flask containing 10 ml of 0.1 M TBACl in ethanol–water (4 : 1). The flask was then immediately hermetically sealed.

Single Flow Electrolysis

A solution containing 0.2 M CCl_4, 1 M LiCl and ethanol–water (4 : 1) was pumped from a flask to the cell at 0.12 ml min^{-1}, and the output from the cathode was directed to waste. Samples for analysis were withdrawn from the output following the same procedure as above.

Analysis of Halomethanes Using GC-MS

Chlorinated halomethanes in headspace were identified by GC-MS using a system consisting of a Fisons 8000 gas chromatograph directly coupled to a Fisons Trio 1000 mass spectrometer. A J&W DB-64 column (30 m × 0.32 mm, 1.8 μm film thickness) was used. The head pressure was 70 kPa and He was used as carrier gas with a flow rate of 1 ml min^{-1} and a split of 1 : 7. The oven temperature program was as follows: 30 °C for 5 min, 30–140 °C at 5 °C min^{-1}, 140 °C for 10 min. The ion source was run in the EI mode at 200 °C, at 70 eV ionization energy. Detection was set at a single-ion-register (SIR) mode focusing on *m/z* 35, 37, 79, and 81 corresponding to the most common isotopes of chloride and bromide ions.

The sample was prepared in a 20-ml flask containing 4.2 g Na_2SO_4, 10 ml water, and 150 μl of 1 000 mg l^{-1} bromochloromethane, which was used as an internal standard. A sample of 5 μl from the electrolysis solution was added. Then, the flask was hermetically sealed and heated in an oven at 80 °C for 30 min just before injection. A headspace sample of 1 ml was then injected with the injector in split mode.

RESULTS AND DISCUSSION

General Behaviour

A study of the voltammetric reduction of CCl_4 under different experimental conditions was carried out to find optimum media in which the electrolysis could be performed with the lowest energetic consumption. As a criterion for energy consumption we have taken the peak potential of CCl_4 reduction, which is directly related to the overpotential of the process. Solvent, supporting electrolyte and pH were the experimental variables studied and the cyclic staircase voltammetry was employed as electrochemical technique.

Due to the low solubility of CCl_4 in pure water, DMF–water and ethanol–water mixtures, DMF, DMSO, ethanol, and aqueous solutions were used to study the influence of the solvent.

Figure 1 shows some characteristic voltammograms. As can be seen, the shape and the intensity of the peak are strongly influenced by the nature of the solvent employed; in general, the peak currents are higher for aprotic solvents. The peak potential is also influenced by the medium. Ethanol–water (1 : 4) has shown the lowest overpotential in the CCl_4 electroreduction. The addition of water to ethanol or DMF has a double opposite effect: it reduces

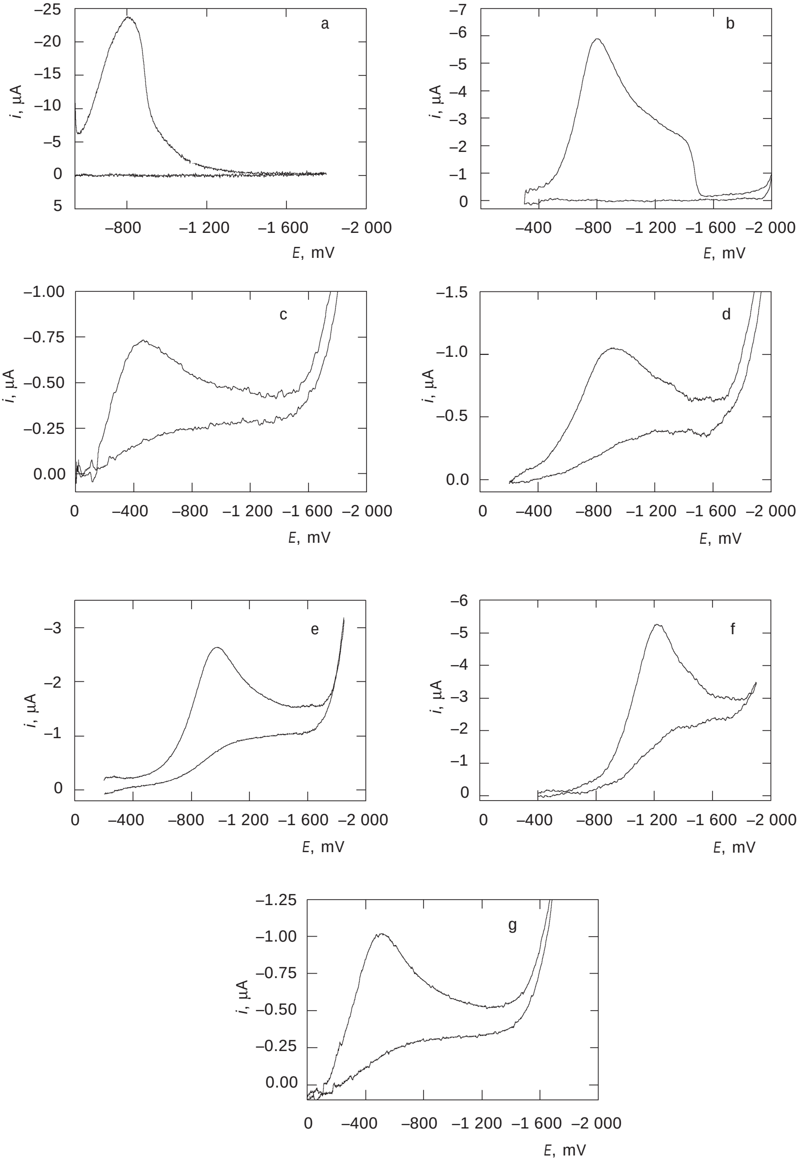

FIG. 1

Staircase voltammograms using various solvents: a DMSO, b DMF, c ethanol–water (1 : 4), d ethanol–water (1 : 1), e ethanol–water (4 : 1), f ethanol, g DMF–water (1 : 1). $1 \cdot 10^{-3}$ M CCl_4, 0.1 M LiCl, *E vs* SSCE, 25 °C; scan rate 100 mV s^{-1}

the overpotential and the peak intensity. Ethanol–water (1 : 4) could be the best of the solvents tested for the electrolysis process. Nevertheless, this solvent and also mixtures of DMF–water (1 : 1) show low solubility of CCl_4, making them unusable for large-scale electrolysis. In order to avoid this problem, we have chosen an organic solvent–water (4 : 1) as a compromise. Although the DMF–water mixtures have somewhat lower overpotential than ethanol–water mixtures, DMF is expensive for practical use. Thus, the ethanol–water (4 : 1) was selected as the working solvent.

Tetraalkylammonium salts and LiCl were used as supporting electrolytes. Some data about the influence of tetraalkylammonium salts on CCl_4 reduction have been previously reported[19] detecting a decrease in the overpotential compared with other inorganic salts. Tetrabutylammonium chloride showed the lowest overpotential (see Table I) and all the tetraalkylammonium salts tested exhibit a lower peak potential than LiCl. This result can be related to a possible change of the electrode surface, due to the adsorption of tetraalkylammonium ions, which could stabilise the reactant or the product of the reaction[19].

Although the energetic criteria are in favour of the use of tetraalkylammonium salts, we have finally chosen LiCl as the supporting electrolyte for the electrolysis of CCl_4 since the improvement due to a decrease in the energy cost does not compensate the cost of tetraalkylammonium salts.

As protons are involved in the reduction of CCl_4 to chloroform, the influence of pH on this reaction has been studied. Ethanol–water (1 : 1) was used as solvent and 0.1 M LiCl as supporting electrolyte. pH of the solution was varied in the range from 1.5 to 9.6; the corresponding peak potentials are given in Table II. At pH < 1.5, it was impossible to record the voltammetric peak of CCl_4 due to the hydrogen evolution. The lowest peak

TABLE I
Peak potentials (*vs* SSCE) from the voltammograms with different 0.1 M supporting electrolytes. Ethanol–water (1 : 1), 25 °C, 1 mM CCl_4

Supporting electrolyte	E_p, mV
LiCl	–914
TEACl	–700
TBAI	–614
TBACl	–486

potential corresponds to pH 2.6 but, nevertheless, there is no great difference between the best and the worst situation. Hence, we do not use a specific pH for the electrolysis experiments.

Chronoamperometric Measurements

In order to obtain kinetic information on the electroreduction of CCl_4, chronoamperometric measurements were carried out in two potential regions: 1) stepwise changes to a very negative value, in the diffusion control

TABLE II
Peak potentials (*vs* SSCE) from the voltammograms of different pH. Ethanol–water (1 : 1), 25 °C, 0.1 M LiCl, 1 mM CCl_4

Buffer	pH	E_p, mV
H_3PO_4/LiH_2PO_4	1.5	–
H_3PO_4/LiH_2PO_4	2.6	–782
H_3PO_4/LiH_2PO_4	5.1	–852
H_3PO_4/LiH_2PO_4	5.5	–918
LiOH	7.1	–906
$Li_2CO_3/LiOH$	9.6	–840

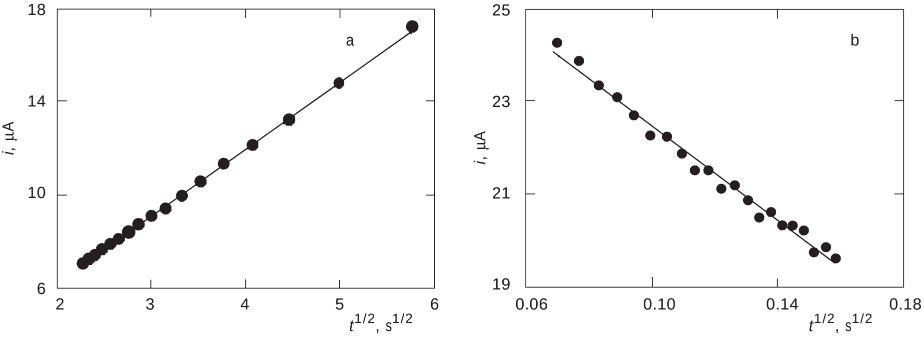

FIG. 2
a Typical i_d–t curve for 0.63 mM CCl_4 in 0.1 M LiCl and ethanol–water (4 : 1). Electrode radius 1.39 mm^2; applied potential –1.5 V (SSCE). b Chronoamperometric analysis at –1.2 V (SSCE), kinetic control

region; 2) stepwise potentials changes in the region where the kinetics of the electron exchange process at the surface exert an influence on the overall process.

Chronoamperometric results obtained under diffusion control have been analysed by using a Cottrel analysis of chronoamperograms, which showed a linear dependence of i on $t^{-1/2}$. Estimates of the diffusion coefficient and the number of exchanged electrons were obtained from ref.[20]:

$$i_\mathrm{d} = \frac{nFAC^0 D^{1/2}}{\pi^{1/2} t^{1/2}} + \frac{nFAC^0 D}{r_0} , \qquad (1)$$

where C^0 is the bulk CCl_4 concentration, D the diffusion coefficient, i_d the diffusion current and r_0 the electrode radius. The Cottrell analysis (Fig. 2a) was consistent with $n = 2 \pm 0.1$ and $D = (9 \pm 0.5) \cdot 10^{-6}$ cm^2 s^{-1}.

The second chronoamperometric experiment series has been carried out at potentials where the process is kinetically controlled. Taking into account the usual boundary condition and solving the diffusion equation for a plane electrode, the i–t equation is obtained[21]:

$$i + nFAk_\mathrm{f} C^0 \left(1 - \frac{2k_\mathrm{f} t^{1/2}}{\pi^{1/2} D^{1/2}} \right) , \qquad (2)$$

where $k_\mathrm{f} = k_\mathrm{f}^0 \exp\left[-\alpha nFE/RT\right]$.

The experiments were performed varying the pulse potential range from –1 160 to –1 250 mV. Assuming $n = 2$, k_f and D can be obtained from the i *vs* $t^{1/2}$ plots. Figure 2b shows a typical chronoamperometric analysis in this potential region. From the E *vs* ln k_f analysis, k_f^0 and αn values were obtained. The analysis gave $\alpha n = 0.36$, independent of the potential, and $k_\mathrm{f}^0 = (1.4 \pm 0.2) \cdot 10^{-6}$ cm s^{-1}. These values imply a slow and irreversible process. The low value of αn is in agreement with a concerted mechanism reported for other aliphatic halides consisting in a first electron transfer associated with the RX bond breaking without formation of the anion radical intermediate[22].

The above results are in agreement with the overall process of CCl_4 reduction.

$$CCl_4 + H^+ + 2\,e \longrightarrow CHCl_3 + Cl^- \qquad (3)$$

Bulk Electrolysis and Identification of Compounds

Once the optimum experimental conditions were selected using the voltammetric studies, electrolytic experiments were carried out. The main goal of these experiments was to study the product or products of the reaction and to improve its efficiency at laboratory scale.

Galvanostatic electrolysis is commonly used in many electrochemical industries, as it provides an easier control and its design is simpler than the potentiostatic one. It can also offer better efficiencies but it is difficult to control the selectivity of the process.

A first study was made using a Hg pool cathode (1.3 cm^2) and a Pt anode (2 cm^2). Hg cathode could have a practical consequence because this is one of the technologies still used in the NaOH-chlorine industrial synthesis. Halomethane production is commonly integrated in a NaOH-chlorine synthesis plant and hence CCl_4 wastes could be treated making use of the same technology. A constant current density of 15 mA cm^{-2} was applied. An initial CCl_4 concentration of 0.2 mol l^{-1} with 1 M LiCl was used in the solvent ethanol–water (4 : 1) as previously optimised. The solution was continuously stirred and cooled to a constant temperature of 5 °C in order to minimise evaporation. The cathode area, concentrations, and current density were chosen in order to prevent hydrogen evolution when the cathode was strongly negatively polarised. Samples from the electrolysis cell were taken at different times and qualitatively analysed by gas chromatography-mass spectroscopy. Figure 3 shows a typical chromatogram obtained

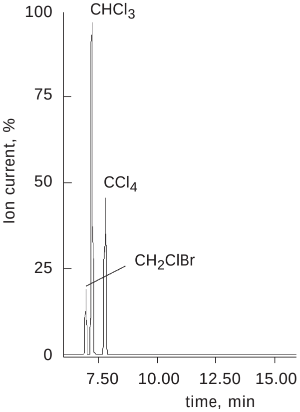

FIG. 3

Typical chromatogram of an electrolysis sample taken after 3 h of galvanostatic electrolysis of CCl_4. For conditions, see the text during the galvanostatic electrolysis of CCl_4: chloroform was the only product observed.

Quantitative analysis of the electrolysis progress was performed by a differential pulse voltammetric method because of its high sensitivity. The main advantage of the voltammetric analysis is its simplicity, compared with the classic GC-MS analysis. The method is based on the linear relationship between the intensity of the voltammetric peaks of CCl_4 and chloroform and their concentration. Previously, two experiments of standard addition of CCl_4 were carried out in order to check the method and to scan the region of a linear relationship between intensity and concentration.

Different solvents and background electrolytes were previously tested in order to achieve an optimum resolution for chloroform and CCl_4 peaks. Finally, ethanol–water (4 : 1) and 0.1 M TBACl were selected. Despite the good resolution of both peaks, the background current due to the glassy carbon used as working electrode influences the voltammograms, in particular the peak corresponding to the electroreduction of chloroform. Thus, a deconvolution algorithm was used in order to avoid this influence and get good and reproducible intensities. Fourteen additions were made.

Both experiments of standard addition showed a good linear range between 10^{-4} and 10^{-3} mol l^{-1} with a regression coefficient of 0.9993 in both cases. Different initial concentrations were used in each experiment and in both cases good predictions of the original concentration were obtained. These experiments were used to analyse CCl_4 and chloroform concentrations using the linear relationship between the concentration and deconvoluted intensity of the voltammetric peaks. Deconvolution technique has also been a useful tool that allowed the evaluation of the influence of the background current on each voltammogram. A typical differential pulse voltammogram with deconvolution analysis can be seen in Fig. 4. The use of glassy carbon as cathode in this method shows that carbon electrodes could be employed in electrolytic experiments for higher extent avoiding the utilisation of mercury.

Samples of 100 μl from the electrolysis cell were taken at different times and analysed by the deconvolution methodology developed.

Due to the direct relationship between deconvoluted intensity and concentration, we were able to estimate CCl_4 and chloroform concentrations throughout the electrolysis. After 4-h electrolysis, only 25% of the initial CCl_4 remained in the electrolysis cell. Figure 5 shows the evolution of the electrolysis process. The calculated current efficiency was nearly 100%. On the course of the electrolysis, differential pulse voltammograms show that the intensities of CCl_4 peaks continuously diminish and the chloroform intensity peak remains approximately constant as can be expected. Thus, the constant intensity of chloroform peaks reflects an increase in its concentration due to the CCl_4 reduction. The intensity of the chloroform peak has two contributions. At the beginning of electrolysis, the intensity comes

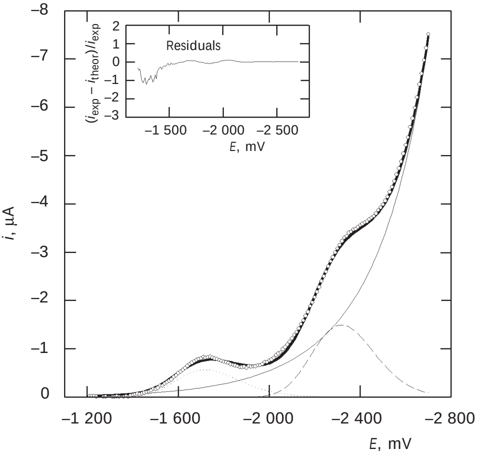

FIG. 4
Typical differential pulse voltammogram with deconvolution analysis: ········ deconvoluted CT, – – – – deconvoluted chloroform, ——— deconvoluted background, ━━━ sum of deconvoluted data, ❍ experimental data

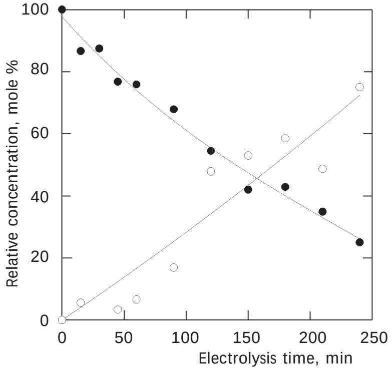

FIG. 5
Evolution of galvanostatic electrolysis of 0.2 M CCl_4 using a Pt anode, current density 15 mA cm^{-2}, Hg pool, 1 M LiCl, ethanol–water (4 : 1) at 5 °C. Concentration is directly related to the deconvoluted intensity (● CCl_4, ❍ $CHCl_3$). Relative concentration of chloroform refers to the generated $CHCl_3$

from the chloroform generated by electroreduction of CCl_4. When the bulk concentration of CCl_4 decreases as a consequence of the electrolysis, this contribution to the peak intensity of chloroform decreases. But, at the same time, the electrolysis process generates chloroform that is prone to be also electroreduced, thus contributing to the peak intensity. The fact that the chloroform intensity peak keeps nearly constant is an evidence that the current efficiency is nearly 100% and also that its evaporation is negligible. The experimental current efficiency measured was 95%.

The applied potentials were in the range from –1.5 to –2 V throughout the electrolysis as shown in the voltammetric experiments (Fig. 4) and overpotential for the hydrogen evolution in this medium was –2 V.

A second galvanostatic electrolysis was performed under the same solution conditions but exchanging the Pt electrode for a dimension-stable anode (3.5 cm^2). This kind of electrodes is currently employed in the chlorine-alkali industry. DSAs are more resistant to corrosion when working with chlorine derivatives. The same current density (15 mA cm^{-2}) as in the previous experiments was used. Similar results were obtained and after 4 h, approximately 60% of CCl_4 in the bulk was converted to chloroform (Fig. 6). Constant intensity of chloroform peak again shows how its concentration increases during electrolysis. No other by-products were observed in the chromatograms.

A single flow experiment with galvanostatic polarisation was carried out in a 20-ml flow-by cell. Larger electrodes were used but current was modified in order to achieve the same current density (15 mA cm^{-2}) as in the previous studies. A DSA was used as anode and a mercury pool as cathode.

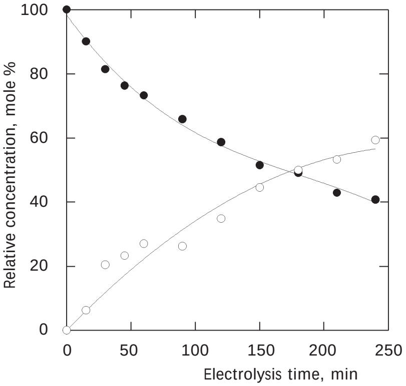

FIG. 6
Evolution of galvanostatic electrolysis using a DSA. Other parameters are the same as in Fig. 5

Samples were taken at the output of the flow cell. The potential throughout the electrolysis was again in the range from –1.5 to –2 V as in the bulk experiments and no hydrogen evolution was detected. Relative concentration of CCl_4 and chloroform are presented in Fig. 7 as a function of electrolysis time. Similar results to those in the bulk electrolysis were obtained. The concentration of chloroform increased throughout the electrolysis, and its intensity remained constant. After 4 h, the solution leaving the cell contained only 27% of the initial CCl_4. Thus, better efficiencies were obtained in the single flow electrolysis since about 73% of the CCl_4 was converted to chloroform while in the bulk electrolysis with the same anode, conversion was only about 60%.

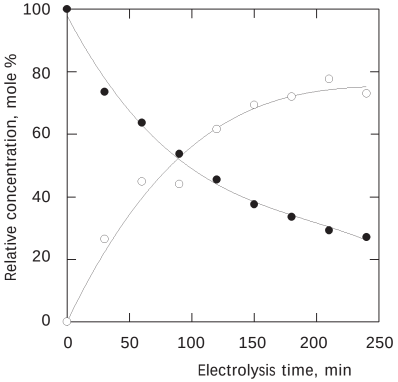

FIG. 7
Single flow galvanostatic electrolysis; flow rate 0.12 ml min^{-1}, DSA. Other parameters are the same as in Fig. 5

CONCLUSION

We have shown that the electrolytic conversion of CCl_4 to chloroform is possible and that chloroform is the only reaction product. A new electrochemical procedure that allows a faster analysis of products from the electrolysis has also been developed. The experimental conditions employed in the electrolysis were very economical and simple; the fact increases the interest in this process from the practical point of view.

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