Use of ion exchange membranes in preparative organic electrochemistry. II. Anodic dimethoxylation of furan

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Anodic dimethoxylation of furan can be performed by electro-oxidation of a solution of furan in methanol in the absence of supporting-electrolyte at a platinum grid lying on a cation exchange membrane. Yields of up to 80% of 2,5-dimethoxy-2,5-dihydrofuran are reached. The process is studied by investigating the influence of different factors (cell voltage, substrate concentration, nature of the membrane) on electrolysis results such as chemical yield, current efficiency and energy consumption.

1. Introduction

In a preliminary note [1], we indicated how some electro-oxidations or reductions of organic compounds can be performed in poorly or non-conducting media.

Recently, we applied this new process to anodic dimethoxylation of some olefins [2]. The results are rather similar to those obtained by classical electrolysis methods (i.e. electro-oxidation of a methanolic solution of an olefin in the presence of a supporting electrolyte, generally sodium methoxide [3]). In particular, with most of the tested olefins, mixtures are formed and such substrates are not suitable for a systematic study.

Nevertheless, furan was found to give only 2,5-dimethoxy-2,5-dihydrofuran:

$$\text{[furan]} + 2CH_3OH - 2e - 2H^+$$

$$\longrightarrow H_3CO \quad O \quad OCH_3$$
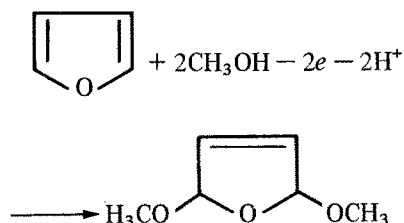
Electrolytic dimethoxylation of furan has been extensively studied after the pioneering work of Clauson-Kaas [4] and was reviewed by Weinberg

and Weinberg [5]. Industrial applications are in progress in Japan [6] and Germany [7] and this well-known electrochemical reaction is often chosen to test new electrolysis cells [8].

So we also selected anodic dimethoxylation of furan, according to Fig. 1, to explore the influence of various parameters on the chemical yield in dimethoxylated compound and on the current efficiency of the process.

2. Experimental details

2.1. *Electrolytic cells*

Electro-oxidation was carried out in a previously described [9] electrochemical batch reactor.

The working compartment equipped with a vertical condenser contained $80\,cm^3$ methanolic solution of furan; the anode was a platinum grid (thread ϕ 0.06 mm; 1024 meshes cm^{-2}) or a disc of woven graphite (Le Carbone–Lorraine, thickness 1 mm). The auxiliary compartment was filled with 0.1 M aqueous sodium sulphate in which a graphite rod was introduced as a counter electrode. The two solutions were separated by a cation exchange membrane in order to remove, towards the aqueous phase, the protons formed by the electrochemical reaction. Four membrane samples were investigated: Selemion AMV, Ionac
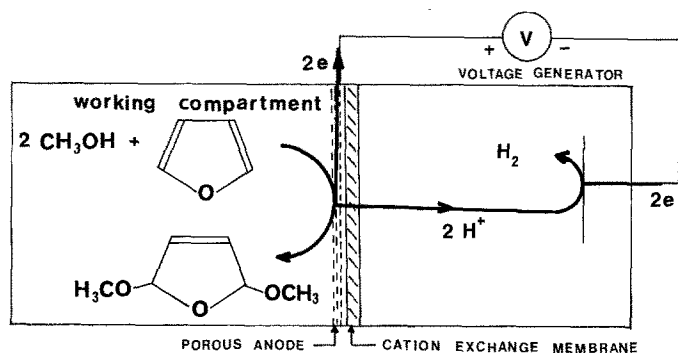
Fig. 1. The electrolysis process.

MC 3470, Nafion 425 and Raipore R-4010. A constant voltage was applied between the two electrodes.

2.2. Procedure

Before assembling the cell, the membrane had been prepared by immersion for a few days in aqueous 0.5 M sulphuric acid at room temperature.

Three steps can be distinguished in the experimental procedure.

First, aqueous sodium sulphate was introduced to the auxiliary compartment while the working one was filled with methanol (without furan).

Secondly, the chosen cell voltage was applied and left overnight, in order to achieve stabilization of the current intensity. Thirdly, after replacement of methanol (to ensure the absence of impurities cf. Section 3.1.) the desired amount of furan was introduced. The amount of electricity passing through the cell was measured and samples of the methanolic solution were progressively analysed by means of GLC (column Carbovax 20 M 10%, 120° C, carrier gas N_2, $P = 1.5$ atm, diethyl oxalate added as an internal standard for quantitative measurements); 2,5-dimethoxy-2,5-dihydrofuran was also characterized at the end of electrolyses by its NMR spectrum according to literature data [10]. No significant quantities of by-products were thereby detected in the working compartment.

Experiments were stopped after consumption of an amount of electricity between two and three faradays per mole of furan. In any case, the quantity of remaining furan in the working compartment was then below 10%.

3. Results and discussion

3.1. General and qualitative aspects of membrane behaviour

Fig. 2 summarizes the species transfer that may occur through the membrane from one compartment to the other.

Transport of sodium ions towards the working compartment during electrolysis is expected not to occur because of the applied electrical field. On the contrary, the membrane being a cation exchange one, charged species transferred through it should be the protons formed by the electrochemical reaction and, to a less extent, sulphate ions because of the imperfect selectivity of the membrane. It has previously been pointed out [2] that the transport number of sulphate ions under the experimental conditions is very small ($t^- < 10^{-2}$). This is confirmed by the fact that the pH of the aqueous phase remains constant during the electrolysis.

As for uncharged species, osmosis may be responsible for the transfer indicated in Fig. 2. Moreover, under electrolysis conditions, methanol and organic solute transport in or through the membrane may be enhanced by electro-osmosis whereas water transfer should decay. These phenomena can actually be observed at the different steps of the experimental procedure. As a rule, at step one, when no voltage is applied to the cell, an increase of the volume of the methanolic phase occurs resulting from major water transfer. This remains true at the second or third steps if the current intensities are rather small. However, at large current intensities, electro-osmosis prevails:
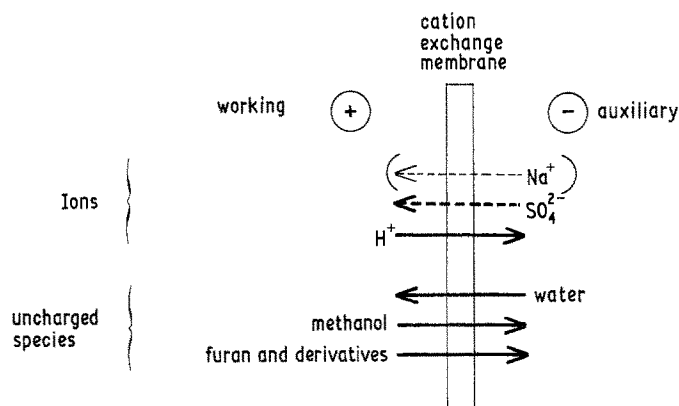
Fig. 2. Transport in the separator.

the volume of the auxiliary solution may then increase. The extent of these phenomena depends dramatically on the investigated membrane: while it is very limited with an Ionac membrane, the volume decrease of the organic solution can reach a quarter of the initial volume with Nafion over the duration (4 h) of an electrolysis performed at a high voltage value.

Since the electric resistance of the separator depends on the solvents with which it is swollen, osmosis and electro-osmosis are the reasons why it is necessary to wait for the stabilization of the current intensity (second step of the procedure).

The transfer of the organic solutes is revealed in two ways:

(a) a yellowish or brown colour sometimes appears in the auxiliary compartment (when a graphite anode is used, or when electrolyses are performed at high furan concentrations and voltages). The presence of a small amount of 2,5-dimethoxy-2,5-dihydrofuran could then be detected in the auxiliary compartment, but most of organic substance is damaged when crossing the membrane.

(b) when auxiliary solution darkening occurs, a decrease is simultaneously observed in the current intensity, probably because of an increase in the membrane electric resistance. This point will be reviewed later, but it is obvious that such transfers have to be minimized.

3.2. *Effects of membrane and cell voltage on preparative electrolyses*

A constant amount of furan (3×10^{-2} mol) was added to methanol and different runs were per-

formed with the four membrane samples at various cell voltages. The current efficiency and chemical yield were determined as the electrolysis progressed. Except in Section 3.2.4. data refer to a platinum anode.

3.2.1. Chemical yields. Results are shown in Fig. 3.

The importance of the membrane is obvious. With Ionac, chemical yields over 80% can be reached (Fig. 3b), whereas with the others, they are limited to 50–60%. The amount of remaining furan being small, no by-products having been detected in the organic solution and precautions having been taken to avoid evaporation from the working compartment, the loss of organic material has to be assigned to transfer through the membrane. From that point of view, the existence of a maximum on Fig. 3c and the fact that the working compartment progressively empties through the membrane are not independent. With the Raipore sample (Fig. 3d), we had, surprisingly, to wait until almost one faraday per mole had passed through the cell before detecting 2,5-dimethoxy-2,5-dihydrofuran in the methanolic solution, whereas a yellowish colour had already appeared in the auxiliary compartment: it appears as though the product was preferentially penetrating the membrane at the beginning of the electrolysis instead of diffusing in methanol. So, this study, even if not exhaustive, clearly shows that permeability to the involved organic substances is an important feature of the membrane, and that good chemical yields can be obtained with materials such as the tested Ionac sample.

The influence of the cell voltage can also be seen in Fig. 3: chemical yields increase when
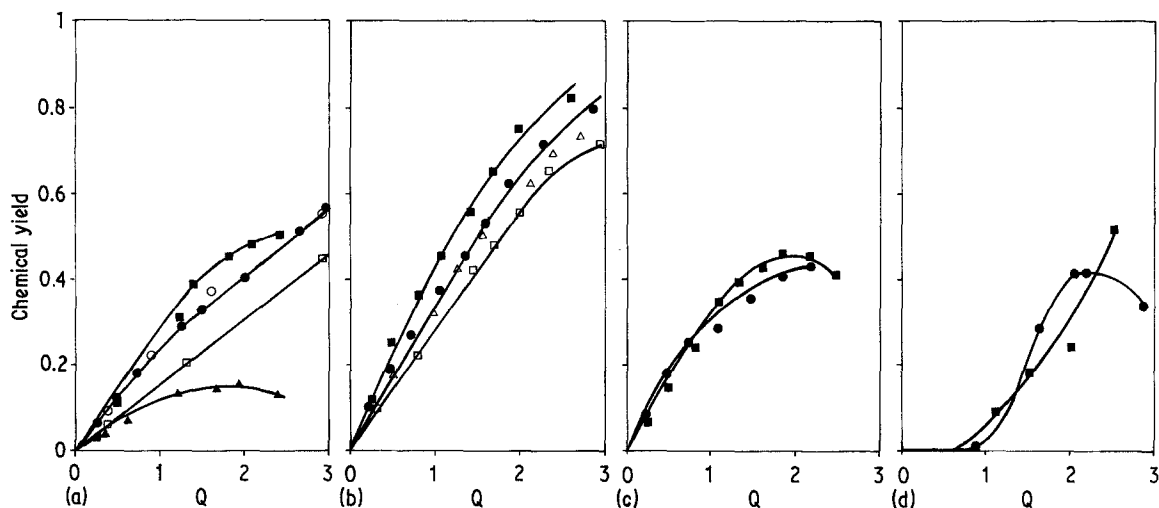
Fig. 3. Variations of chemical yields as functions of the amount of electricity, Q (faradays per mole of furan). 3×10^{-2} mol furan ($c = 0.375 \, \text{mol} \, l^{-1}$), platinum anode.

Graph	Membrane	Cell voltages and current intensities
(a)	Selemion	▲: 5 V, 30 mA; □: 8 V, 80 mA; ○: 10 V, 170 mA; ●: 15 V, 350–400 mA; ■: 20 V, 550–600 mA.
(b)	Ionac	□: 8 V, 85 mA; ●: 15 V, 280 mA; ■: 20 V, 350–400 mA; △: 30 V, 500 mA.
(c)	Nafion	●: 15 V, 280–200 mA; ■: 20 V, 500–400 mA.
(d)	Raipore	●: 15 V, 200–150 mA; ■: 20 V, 450 mA.

increasing the cell voltage and the corresponding current intensity. Nevertheless, Fig. 3a shows that, over a certain value, there is little advantage in applying a higher cell voltage and from the data of Fig. 3b, it is clear that an excessive voltage is harmful. So, we note an optimum range for the cell voltage situated at about 10–15 V. It is however difficult to state whether electrochemical factors (current density, working potential) or other factors such as temperature or material transport in membranes are responsible for this phenomenon.

3.2.2. Current efficiencies. These are indicated in Fig. 4 as functions of the amount of electricity passed through the cell.

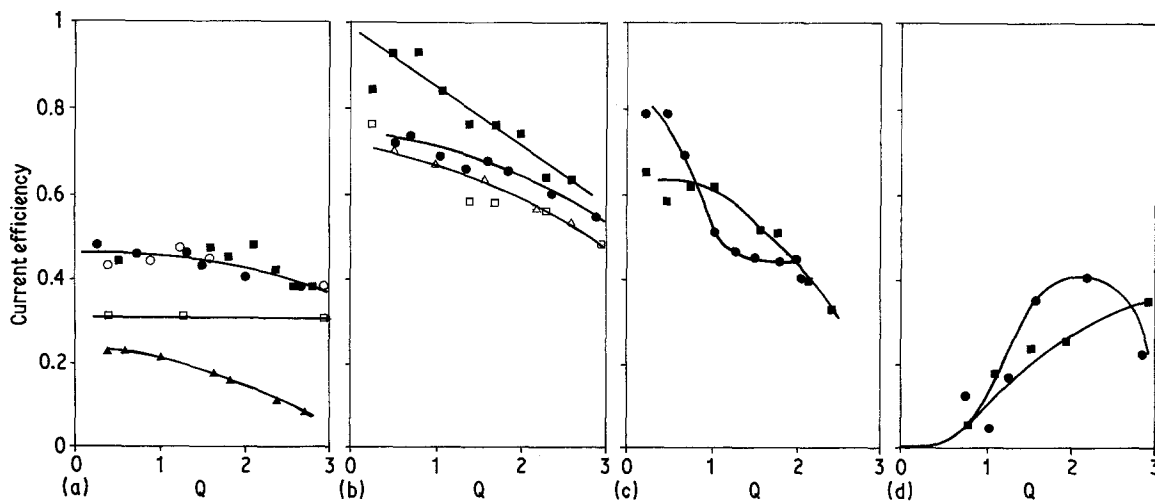At first sight, the influence of the different parameters seems to be similar to the case of

Fig. 4. Variation of current efficiencies as functions of the amount of electricity Q. Same experimental conditions and symbols as in Fig. 3.
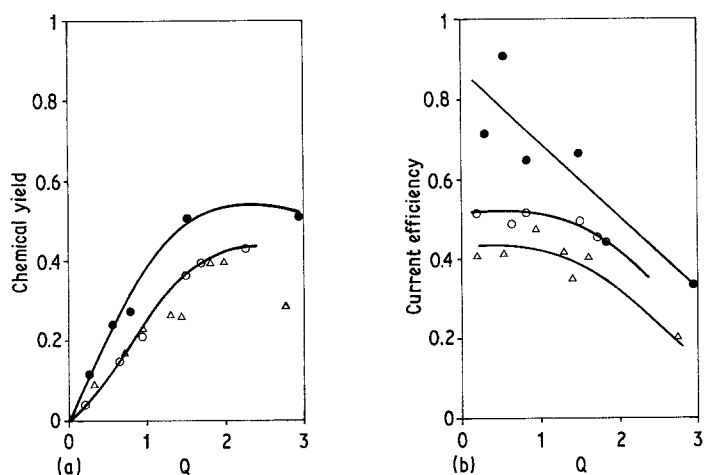
Fig. 5. Variations of chemical yields and current efficiencies as functions of the amount of electricity Q. Ionac membrane, 3×10^{-2} mol furan, graphite anode. Cell voltages and current intensities: o: 10 V, 30 mA; •: 15 V, 85–50 mA; △: 30 V, 200–85 mA.

chemical yields. In particular, the membrane sample leading to good chemical yields afforded high current efficiencies and the same comments about voltage influence can be made on Fig. 4a, b as have been made on Fig. 3a, b.

The observed variations of current efficiencies (Fig. 4a–c) as the electrolysis progresses are in agreement with the decrease of furan concentration because of its consumption. It should however be noted that slopes are more negative in Fig. 4c. This is due to the important transfer of electrolysis product; indeed, the calculated current efficiency corresponds to the amount of product present in the working compartment at the moment of the measurement and not to the amount of product which has been formed at the electrode from the beginning of the experiment. In Fig. 4d, the low initial values and positive slope of the curve can be interpreted by preferential initial transfer of product into the membrane. Differences between Fig. 4c and d also represent the different behaviour of the two membranes towards permeation by methanol and electrolysis product under the given experimental conditions.

3.2.3. Conclusions. From these data, it is evident that better chemical yields and current efficiencies were observed in the batch reactor when using the Ionac sample and applying a 15–20 V voltage. However, other aspects are of interest for practical purposes such as hourly production and energy consumption. These are indicated in Table 1 for the experiments performed with the Ionac membrane, on one hand for electrolyses using $0.5 \, F \, mol^{-1}$, on the other hand for electrolyses using $2 \, F \, mol^{-1}$ of furan. As expected, the hourly production increases with cell voltage and the corresponding current intensity.

Energy consumptions are not prohibitive, which is an additional encouragement to pursue the study of the proposed process.
N.B. Fig. 5 reports the results obtained when using an Ionac membrane sample and woven graphite as anode. The values are lower than those given earlier for the case of a platinum anode. Moreover, measurements are less regular. In this case, the product stays in the graphite fibres; so, no other run was performed with graphite.

Table 1. Dependence of hourly production and energy consumption on cell voltage

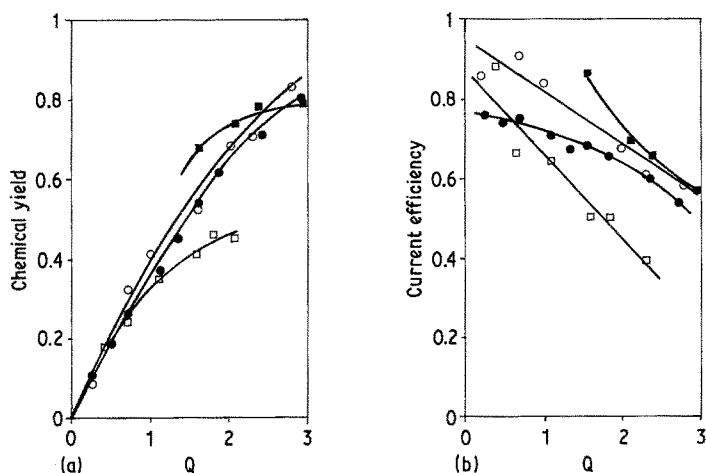| Cell voltage (V)	Production (g h⁻¹)		Energy consumption (kWh kg⁻¹)	
	$Q = 0.5 \, F \, mol^{-1}$	$Q = 2 \, F \, mol^{-1}$	$Q = 0.5 \, F \, mol^{-1}$	$Q = 2 \, F \, mol^{-1}$
8	0.12	0.9	5	6
15	0.39	0.37	8.4	9.2
20	0.65	0.54	8.8	11

Fig. 6. Variations of chemical yields and current efficiencies as functions of the amount of electricity Q. Ionac membrane, 15 V cell voltage, platinum anode. ●: (1); $c = 0.375\,\text{mol}\,l^{-1}$; $i = 280\,\text{mA}$. ■: (4); $c = 0.75\,\text{mol}\,l^{-1}$; $i = 200\,\text{mA}$. ○: (3); $c = 1.5\,\text{mol}\,l^{-1}$; $i = 150–200\,\text{mA}$. □: (2); $c = 3\,\text{mol}\,l^{-1}$; $i = 280–190\,\text{mA}$.

3.3. Influence of furan concentration (c)

Because of the conclusions of Section 3.2, this study has been limited to the use of an Ionac membrane sample and a platinum anode under a 15 V applied voltage. Results are plotted in Fig. 6.

At the beginning of the electrolyses, the curves of the chemical yield merge into one another. Afterwards, chemical yields are not basically different for the three lowest furan concentrations, whereas increasing the concentration to $3\,\text{mol}\,l^{-1}$ leads to a low yield. By comparison with the experiment performed at the lowest furan concentration, this can be explained by an increased loss of product through the membrane because the electrolysis duration is then very long, the amount of furan being large and the current intensity falling progressively from 280 to 190 mA.

Evaluations of current efficiencies lead to the same conclusions.

Another phenomenon has to be pointed out: furan concentration cannot account for current intensity values indicated in the caption of Fig. 6. In fact, electrolyses were performed on the same piece of membrane in the order specified in brackets in the caption. It is obvious that previous experiment affects the current intensity of the following one and that the membrane does not recover its initial state between two experiments, probably because organic products remain inside. A similar observation was made by Ogumi et al. in attempted applications of the SPE method to organic electro-oxidations [11, 12].

As current intensities and efficiencies are roughly of the same order of magnitude whatever the furan concentration, hourly production is not dramatically affected. As for the energy consumption, it increases to about $13\,\text{kWh}\,\text{kg}^{-1}$ for the highest furan concentration because of the electric resistance of the membrane.

4. Conclusion

The difficulties encountered have been emphasized in this paper in order to analyse the performance of the cell.

However, high chemical yields and current efficiencies can be observed, as well as energy consumptions at acceptable levels: values such as 83% for the chemical yield and 63% for the corresponding current efficiency could be reached, resulting from compromises in the choice of the different parameters that may be varied.

Comparing these values with the results previously obtained in attempted dimethoxylation of olefins [2] shows that the nature of the substrate is most important: the selectivity of the involved electrochemical reaction is similar both in classical and membrane processes.

The results presented in this paper have also to be compared with the characteristics of commercially practised electrosynthesis of 2,5-dimethoxy-2,5-dihydrofuran [7]. Yields obtained in our batch reactor are not as high as those of the commercial synthesis using soluble electrolytes (over 90%). Nevertheless, the difference is not so large that closing the gap is impossible. So, using a process

avoiding use (with recycling and loss) of conducting salt would then be of interest.

As in earlier studies on the choice of the supporting-electrolyte, ion exchange membranes other than the four tested samples have to be investigated in order to determine whether they present the required qualities to give better results. Simultaneously, experiments must be performed in a flow reactor which would work according to the same principle.

Acknowledgements

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