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Electrolytic oxidation of diacetone-L-sorbose (DAS) to diacetone-2-keto-L-gulonic acid (DAG) at a nickel foam electrode

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The paper deals with the anodic oxidation of diacetone-L-sorbose (DAS) to diacetone-2-keto-L-gulonic acid (DAG) at a peroxidized nickel foam electrode. A stirred cell and a flow cell were used at 29°–30° C and/or 60° C with 1 M aqueous KOH containing nickel ions and 0.9 to 9 wt % of pure DAS as the electrolyte. High conversions of DAS to DAG, a maximum chemical yield of 90% and a faradaic yield of about only 20% were obtained.

1. Introduction

Many tens of thousands of tons per year of vitamin-C are produced globally from glucose. One step in the process is the oxidation of DAS (diacetone-L-sorbose) to DAG (diacetone-2-keto-L-gulonic acid). By electrochemically generating hypobromide *in situ* as an oxidation agent, Borisov *et al.* [1] effected the indirect electrolytic oxidation of DAS to DAG; using platinum or graphite electrodes, they reached a 85–87% DAS chemical yield and a 32% current yield.

For the electrooxidation, authors like Meller *et al.* [2] obtained a 96% chemical yield with graphite electrodes, while Vertes *et al.* [3], who were among the first using nickel plates from Ni–Cd accumulators, obtained a 91–96% chemical yield. On a more industrial scale, Pesheva *et al.* [4] used a porous anode made of Ni–Cr steel alloy and obtained a chemical yield higher than 70%, with an energy consumption of 2 kWh kg^{-1} of DAG. More recently, Witmann *et al.* [5] and Reiff *et al.* [6] obtained a 92% chemical yield and a conversion of 77%. However, the most important work at the pre-industrial scale was that of Robertson *et al.* [7]; with Swiss-Roll cells in series, they were able to produce 2 tons of DAG daily with a conversion of 99%, a faradaic yield of 70% and an energy consumption of 1.2 kWh kg^{-1} of DAG.

As indicated by the authors in a previous paper [8], the following overall mechanism was proposed for the anodic oxidation of DAS at a nickel electrode in an alkaline medium:

$$\mathrm{NiOOH + DAS \rightleftharpoons Ni(OH)_2 + DAG} \quad (1)$$

$$\mathrm{Ni(OH)_2 + OH^- \rightleftharpoons NiOOH + H_2O + e^-} \quad (2)$$

In [8] the anode potential conditions for the nickel peroxidation (Reaction 2) and for the DAS to DAG transformation (Reaction 1) were determined in 1 M KOH alone and in 1 M aqueous KOH containing DAS and nickel ions, respectively.

As the kinetic aspects of both the above reactions are unknown, it was important, according to Robertson *et al.* [7], to use sufficiently high OH^- concentrations in order to avoid a controlling effect of Reaction 2 through the limited diffusion of OH^- to the electrode. With 1 M KOH, it was demonstrated in [8] that the overall current was proportional to the DAS concentration.

The aim of the present paper is to present and discuss the experimental results obtained in experiments for DAG production including conversion, chemical yield and faradic yield, in two types of cells.

2. Experimental details

2.1. *Cells*

The two cells used are shown in Fig. 1.

The first cell (Fig. 1a) was used previously [8]. It was a batch stirred cell in which a rectangular sheet (3 cm × 5 cm) of 0.21 cm thick nickel foam (100 p.p.i.) was submerged between two rectangular sheets of expanded stainless steel. This cell was operated at two temperatures (29° C and 60° C).

The second cell (Fig. 1b) was a two-compartment cell containing a flow-by nickel foam anode. This cell, made of Altuglas, was parallelepipedic. The anodic compartment was defined by the inner part of a nickel frame to which a rectangular sheet (0.21 cm thick; 3 cm wide and 3.7 cm high) of 100 p.p.i. nickel foam was electrically soldered. The nickel frame itself was 0.1 cm thick, with a rectangular aperture of dimensions 6 cm × 3 cm; the parts of this frame which contacted the electrolyte were painted with M-COAT D (Vischay-Micromesures). The cathodic compartment was a rectangular aperture (6 cm × 3 cm) made of Altuglas 1 cm thick, situated between the separator

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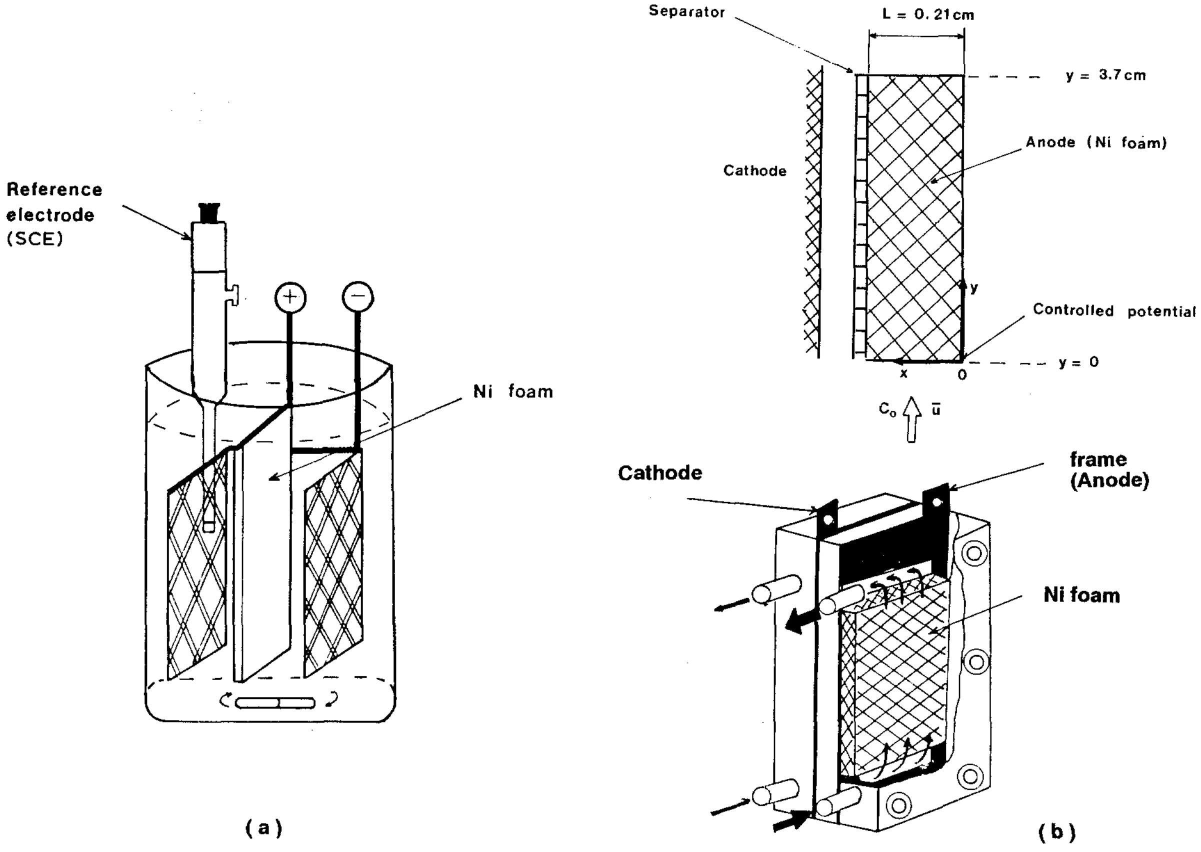

Fig. 1. Cells used: (a) batch stirred cell; (b) flow cell with a porous anode.

and a rectangular sheet of nickel acting as the cathode. The separator was a sheet of Vyon, 0.1 cm thick, with 100 μm mean pore diameter, a porosity between 33 and 40%, and an ionic conductivity factor of 6 [9].

Rubber joints were used to guarantee the water tightness between the different elements of the cell which was operated only at 30° C.

A schematic view of the cell cross-section is given in

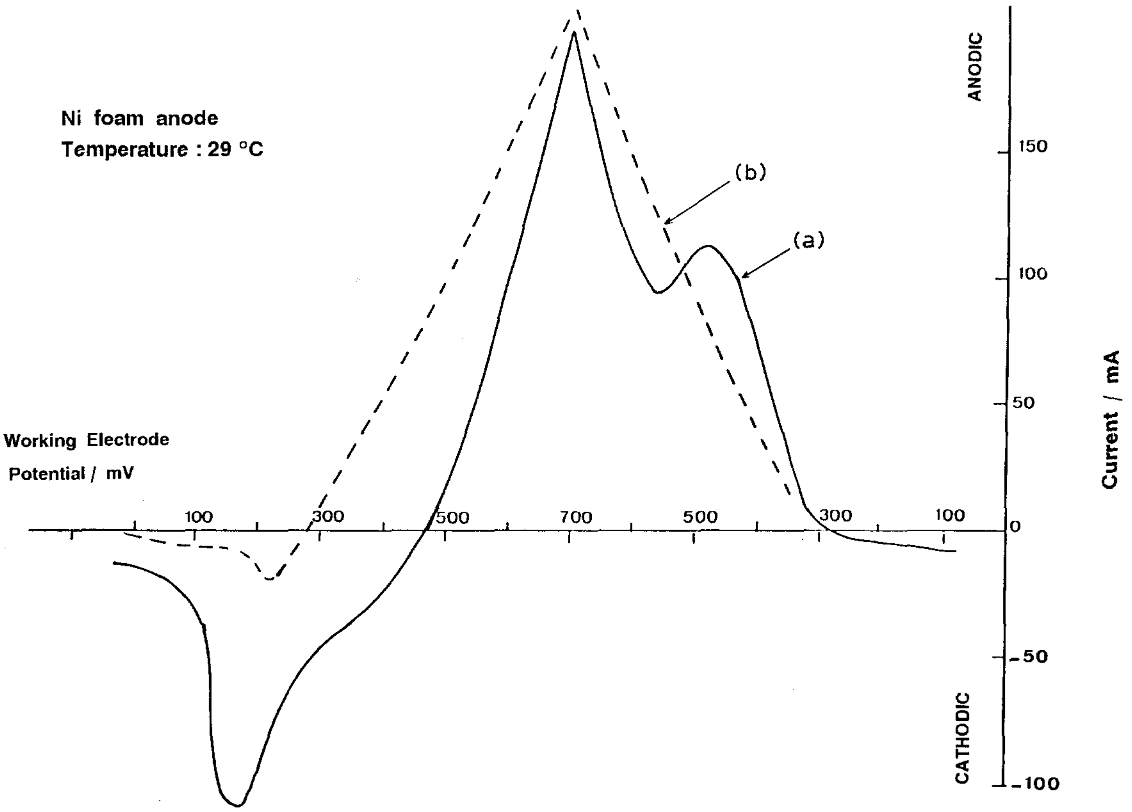

Fig. 2. Cyclic voltammograms obtained in the cell of Fig. 1(a): (a): supporting electrolyte along; (b) with DAS (9 wt %). (from [8]).

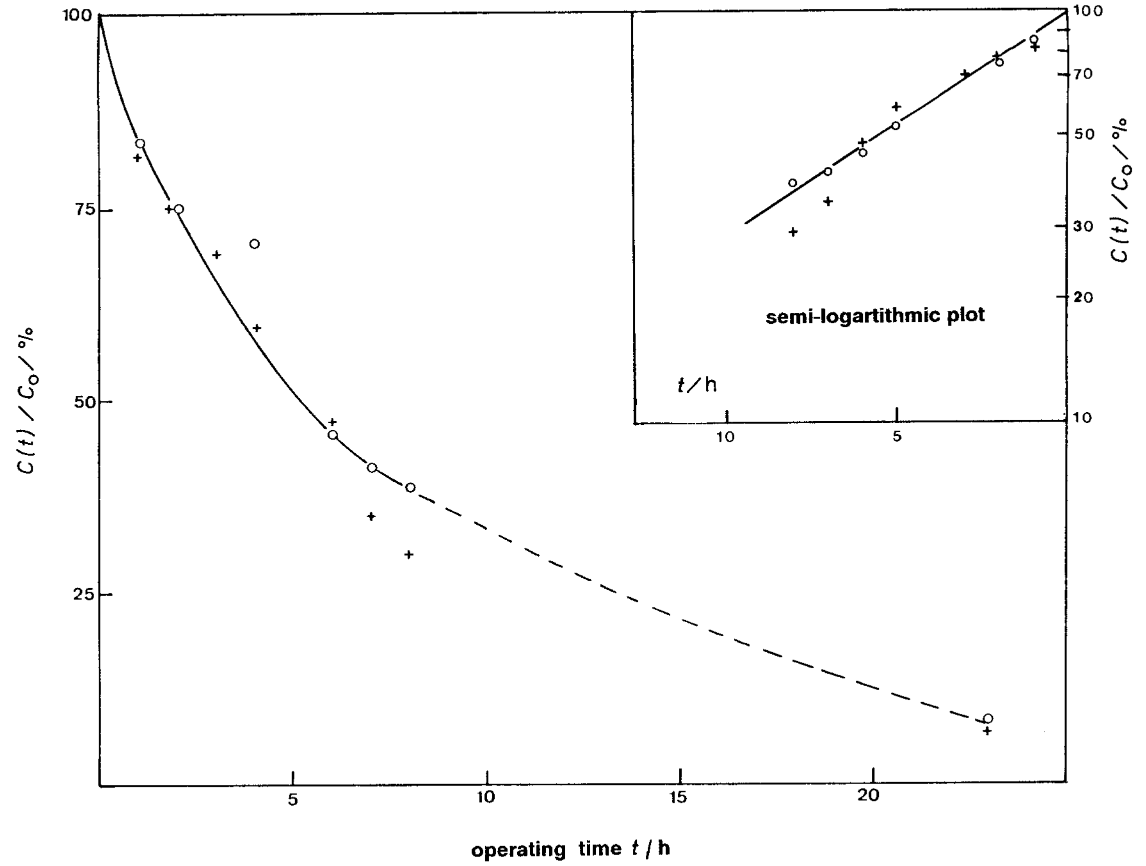

Fig. 3. Variations of the instantaneous relative DAS concentration with time in the batch stirred cell. Temperature: (○) 29° C, (+) 60° C.

Fig. 1(b). As indicated, the anodic potential was controlled at $x = 0$ in the entrance plane ($y = 0$); a glass Luggin capillary introduced through a cylindrical tap was used for this control.

The flow circuit for the cell of Fig. 1(b) was a closed loop. It included a magnetically stirred double-wall reservoir and a small pump, with a direct partial recirculating flow to the reservoir. The electrolyte entered the cell by the anodic compartment, then flowed through the cathodic compartment and returned to the reservoir. The temperature was maintained at 30° C by continuously recirculating water at 30° C through the double-wall. The flow-rate was controlled with a valve and was measured by weighing at the cell exit. The total volume of electrolyte in each experiment was $450\,\text{cm}^3$. The mean flow velocity, $\bar{u}$, across the empty cross-section ($0.21\,\text{cm} \times 3\,\text{cm}$) of the anodic compartment was varied between 0.057 and $0.13\,\text{m}\,\text{s}^{-1}$.

Table 1. Experiment results obtained for the DAS to DAG transformation in the cell of Fig. 1(b).

	Time/s	$C(t)/C_o$	$X(t)$	$I(t)$/A	$R_F(t)$
Run 1 $\bar{u} = 0.084\,\text{m}\,\text{s}^{-1}$	0	1.0	0	0	–
	3600	0.88	0.12	1.10	0.2
	7200	0.80	0.20	1.10	0.19
	10800	0.66	0.34	1.10	0.22
	14400	0.51	0.49	1.10	0.23
Run 2 $\bar{u} = 0.096\,\text{m}\,\text{s}^{-1}$	0	1.0	0	0	–
	3600	0.86	0.14	1.5	0.19
	10800	0.76	0.24	1.5	0.17
	14400	0.68	0.32	1.5	0.15

2.2. *Electrolytes, electrical circuit and DAS titration*

The anode activation, i.e. the formation of NiOOH on the nickel electrode, was performed using 1 M KOH, as in [8], and according to the technique proposed by Briggs *et al.* [10]. The DAS transformation to DAG was made using aqueous solutions containing 0.9 to 9 wt% of pure DAS (i.e. 1 to 10 wt % of the DAS 90% purity prepared as reported in [8]) in 1 m KOH; also nickel ($1.4\,\text{g}\,\text{Ni}\,\text{dm}^{-3}$) ions, which may act as catalysts [1, 7], were introduced as nickel sulphate into the solutions. The pH of the electrolyte was maintained at 14 throughout the experiments.

Each of the two cells of Fig. 1 was associated with a reference calomel electrode in a classical three-electrode potentiostatic circuit including a Tacussel PRT 20-2 potentiostat, a recorder, a voltmeter and an ammeter. The experiments were performed potentiostatically and the variation of the DAS concentration with time was monitored. All potentials are quoted with reference to SCE.

The DAS concentration was measured by u.v. spectrophotometry [11] by a technique adapted from that used in [12] for the titration of mono and diacetone-L-sorbose in a mixture of both. By measuring the absorbance as function of the wavelength, for three solutions (supporting electrolyte alone; supporting

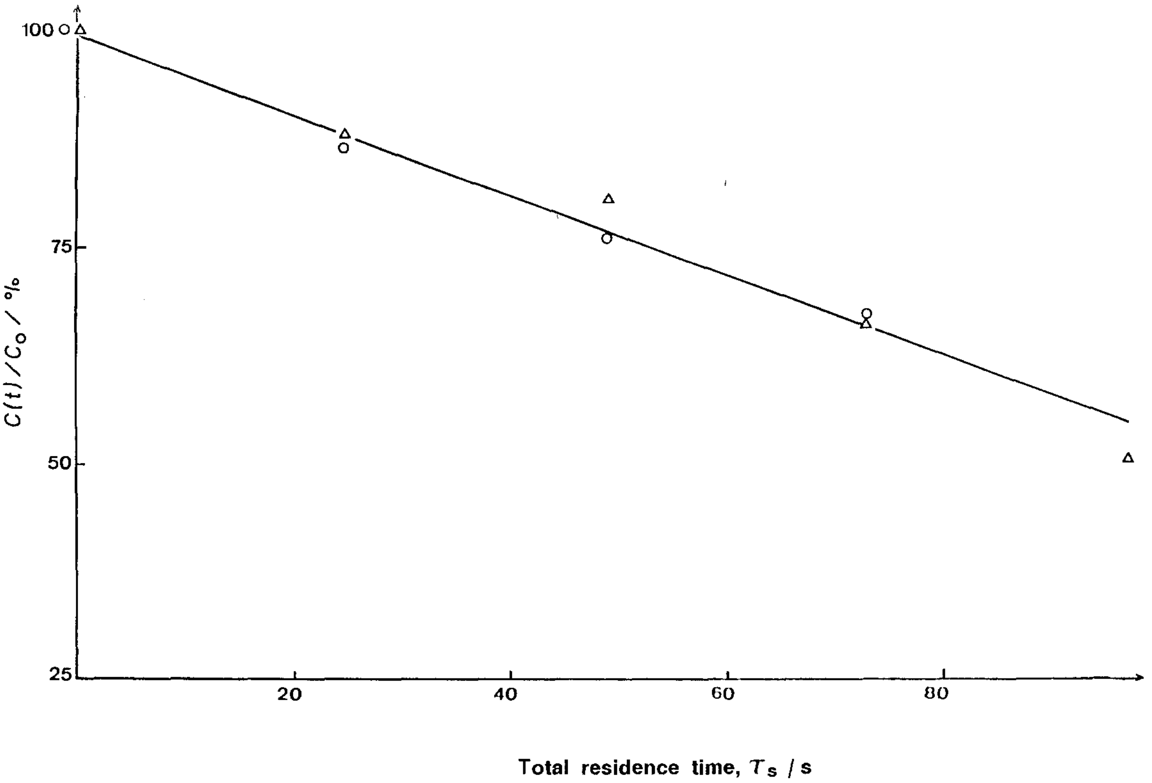

Fig. 4. Variations of the relative DAS concentration with the total residence time in the flow-by porous anode of Fig. 1(b). $\bar{u}$: (△) 0.084 m s^{-1}, (○) 0.096 m s^{-1}.

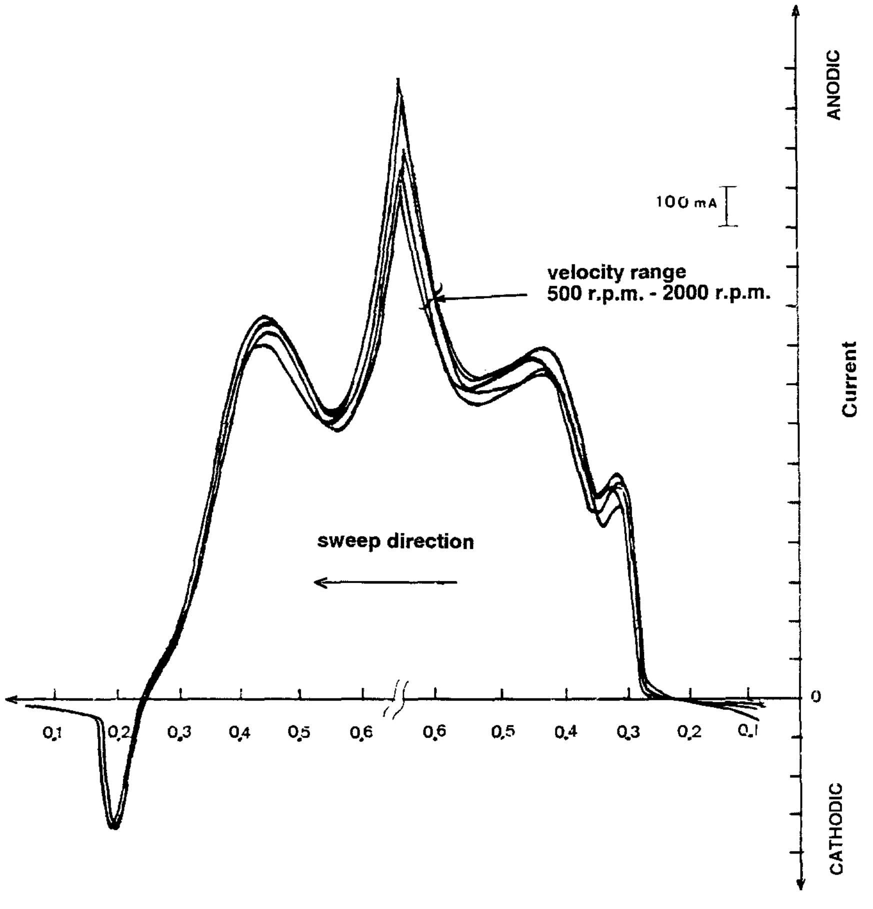

Fig. 5. Cyclic voltammograms at different rotating velocities of a disc anode, with DAS 0.2 wt %. Conditions: 1 M KOH + DAS 1.8 wt % at 30° C.

electrolyte with DAS; supporting electrolyte with DAG) it was shown that a wavelength of 490 nm corresponds to the maximum absorbance of DAS [11]. This value of 490 nm was chosen for the determination of the DAS concentration. A Pye-Unicam u.v. Philips spectrophotometer was used for the measurements. The solution samples were taken at regular intervals (generally every hour); all were titrated immediately after the end of the experiment.

3. Results

3.1. *Experiments with the stirred cell*

Current–potential sweeps, such as those of Fig. 2 and previously given in [8], were obtained using a nickel foam electrode submerged in the same stirred cell as in the present case. In [8], it was deduced that stable nickel peroxide exists at an anodic potential higher than 350 mV, while an anodic potential of 500 mV may be adequate for the transformation of DAS to DAG. For DAS concentrations higher than 5% (Fig. 2), the 'camel back' curve corresponding to the NiOOH formation (curve A of Fig. 2) is not apparent (curve B of Fig. 2). In the present experiments it was decided to apply a constant anodic potential of approximately 500 mV for the DAS to DAG transformation. It was observed that for such an anodic potential, the current intensity did not depend on the agitation intensity, as it would be in the case of a kinetically controlled process. Each electrolysis was followed for 24 h; the total disappearance of DAS was verified by thin layer chromatography [13, 14].

Figure 3 gives, for the two temperatures, the experimental variations of the relative DAS concentration with time. It is seen that high values of the conversion were obtained (around 60–65% after 8 h; 90% after 24 h). A semi-logarithmic plot of the instantaneous relative concentration against operating time gives a straight line [11] according to the theoretical behaviour of a batch electrochemical reactor in which an irreversible first order electrochemical reaction is performed potentiostatically. Such a plot is shown inset in Fig. 3. After the experiments, the DAG was precipitated from the solution; the method used [11] was similar to that used by Vertes *et al.* [3]. The values obtained for the overall chemical yield (83% at 29° C and 90% at 60° C) confirmed the influence of temperature as outlined by Amjad *et al.* [7]; indeed, if these authors observed a temperature increase during the electrolysis, they did not give details of such an increase.

The melting point of the DAG crystals obtained was 77–78° C, a value not very different from that [78–79° C] indicated in the literature for the product purified by TLC. The elementary analysis of the crystals gave [C51.64%; H6.92%] while the values corresponding to the DAG formula C_{12} H_{18} O_7 are [C52.55%; H6.57%]. Using NMR for carbon-13, the presence of 12 atoms of carbon was confirmed, together with that of a carbonyl group which results from the oxidation of the alcohol group localized on the first atom of carbon. NMR for hydrogen revealed the presence of 18 atoms of hydrogen.

3.2. *Experiments with the flow cell*

In the flow-by porous anode of Fig. 1(b), the more anodic potential is localized at ($x = 0.21$ cm; $y = 3.7$ cm) while the less anodic potential is situated at ($x = 0$; $y = 0$) where the control was made. For the DAS transformation to DAG, the anode was first activated in a batch stirred cell and then installed in the parallelepipedic cell. A control potential of 480 mV was imposed; it was hoped that such a potential at the less anodic position would be adequate for the optimum conversion, on the condition that the maximum anodic potential would be less anodic than the potential for oxygen evolution.

Table 1 summarizes the results of 2 h experiments, starting from a solution having a DAS concentration, C_0, of 173 mol m^{-3}, i.e. 4.5 wt%. The mean flow velocity, $\bar{u}$, was 0.084 m s^{-1} for run 1 and 0.096 m s^{-1} for run 2. The values of the relative DAS concentration $C(t)/C_0$ at the time t, are given as function of this operating time t; the corresponding current flowing through the cell, $I(t)$, the conversion $X(t) = 1 - C(t)/C_0$, and the mean faradic yield between $t = 0$ and t, $R_f(t)$, are also given in this Table. The conversions were approximately 49 and 32%, respectively. According to the definition:

$$R_F(t) = \frac{\text{Amount of DAS transformed at } t}{\text{Amount of DAS theoretically transformed at } t}$$

the mean faradaic yield is calculated as:

$$R_F(t) = \frac{1 - C(t)/C_0}{\int_0^t I(t)\,dt} VzFC_0 \qquad (3)$$

where V is the total volume of electrolyte ($V = 450$ cm^3), F the Faraday number, and z ($z = 1$ according to Reaction 2) the number of electrons in the reaction. As seen in Table 1, $I(t)$ does not change during the experiment [$I(t) = I$]; this allows a simplification of Equation 3 as follows:

$$R_F(t) = \frac{X(t)VzFC_0}{It} \qquad (4)$$

Table 1 shows that $R_F(t)$ varies between 15 and 25%. The latter value, which corresponds to the first hour of operation in experiment 1, agrees with the values of Borisov *et al.* [1]. However, the observed range 15–25% disagrees with the value $R_F = 70\%$ obtained by Robertson *et al.* [7] using a series of two Swiss Roll cells. In experiment 2, the current intensity was higher than in experiment 1, and the faradaic yield decreased during the operation. This last point may be explained by the fact that the 'camel back' region attributed to the DAS/DAG reaction in the current–potential curve moves towards cathodic potentials when the DAS concentration decreases, as shown in [8]. As a consequence, the relative contribution of the oxygen evolution reaction to the total current is higher as the

DAS concentration decreases, thus reducing the faradaic yield of the DAS disappearance.

4. Discussion

In Fig. 4, the data conversion of Table 1 are plotted as $C(t)/C_0$ against the total residence time, τ_s, of the liquid in the porous electrode of Fig. 1(b). This parameter τ_s, which is given by:

$$\tau_s = \frac{y_0 Q_v}{\bar{u} V_R} t$$

where Q_v is the volumetric flow rate, V_R the reservoir volume and y_0 the electrode height, is physically more easy to relate with the instantaneous conversion than the operating time t. A single straight line describes both sets of results. By extrapolating such a line to $\tau_s = 100\,\mathrm{s}$, a conversion of 50% is obtained.

It is now clear that a high DAS conversion can be obtained using a nickel foam anode, but the faradaic yield observed (approximately 20%) is between two and three times smaller than the value indicated by Robertson *et al.* [7]. A satisfactory explanation of this disagreement has not been found.

Also a doubt subsists concerning the overall kinetics of the anodic process. Fleischmann *et al.* [16], and Amjad *et al.* [15] considered that the electrooxidation of primary alcohols is kinetically controlled. By contrast, for the particular case of the direct DAS electrooxidation, Robertson *et al.* [7] concluded that the process was diffusion-controlled at small OH^- concentrations and kinetically controlled at high OH^- concentrations, a conclusion which was surprising to them.

In order to clarify this question of the reaction control, cyclic voltammetry experiments similar to those made in [8] were undertaken. These were performed using a nickel rotating disc electrode submerged in a 1 M KOH electrolyte containing 1.8 wt% of DAS and maintained at 30° C. The rotating disc velocity was between 500 and 2000 r.p.m. In Fig. 5, where the current–potential sweeps are given, it is seen that the current corresponding to the peak does not vary within the rotating velocity range. This conclusion from Fig. 5 also agrees with the observation made using the batch stirred cell (Section 3.1). This suggests that the overall reaction is not diffusion controlled, a conclusion in agreement with Robertson *et al.* [7] for a similar OH^- concentration.

5. Conclusions

The experimental conditions determined in [8] for the DAS to DAG transformation at a nickel foam electrode previously peroxidized were applied. The results showed that, in agreement with the literature, a chemical yield of about 90% can be obtained, and also a high conversion. The faradaic yield appears to be only of about 20%, a value which disagrees with the unique reference work on the question [7]. Finally this last point appears to be the unique point of disagreement with work concerned with the DAS to DAG transformation at other materials than nickel foam. This point merits further attention owing to its consequence on the energy consumption per kg of DAG.

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