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The influence of non-ionic surfactants on electrosynthesis in extended channel, narrow gap electrolysis cells

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ABSTRACT

It is demonstrated that the addition of a non-ionic surfactant (Triton X-100 or Brij L23) to the electrolyte medium leads to a significant improvement to the current efficiency for the methoxylation of *N*-formylpyrrolidine in a flow electrolysis cell with a horizontal, extended channel length and narrow interelectrode gap (the Ammonite 8). In the presence of Brij L23, the fractional current efficiency is much improved and approaches 1.0 while maintaining a fractional selectivity of 0.99 at a very high conversion in a single pass. The improvement in current efficiency is ascribed to a decrease in the bubble size of the H_2 gas evolved at the counter electrode leading to an enhancement in the mass transport regime in the flow stream through the extended channel with millimetre dimensions.

1. Introduction

Presently, there is great interest in using flow electrolysis cells in continuous organic synthesis [1,2]. A particularly attractive approach employs a flow cell with a reaction channel with an extended channel length and narrow interelectrode gap so that a very high conversion of reactant to desired product can be achieved in a single pass of the reactant through the cell; cells with productivities of multigrams/h have been described [3–9]. These cells are presently undivided and hence it is necessary to consider both anode and cathode reactions. Hydrogen evolution is a convenient cathode reaction for anodic syntheses but it leads to gas bubbles within the interelectrode gap and these will have consequences to cell performance.

Surfactants can enhance the performance of electrode reactions by a number of mechanisms and, indeed, non-ionic surfactants have an established place in electrochemical technology, for example in corrosion inhibition and electroplating [10]. Although there is a very extensive literature on electrosynthesis, non-ionic surfactants as additives to improve reaction performance have been little explored.

This paper reports a study of the influence of two non-ionic surfactants on the methoxylation of *N*-formylpyrrolidine in the Ammonite 8 cell [6–8].

2. Experimental

2.1. Equipment

The cyclic voltammetry was carried out in a three-electrode, two-compartment cell with a vitreous carbon disc (diameter 3 mm) working electrode, a Pt wire counter electrode and an aqueous SCE reference electrode mounted in a Luggin capillary. An Autolab PGStat204 potentiostat with Nova 1.9 software was used and responses were analysed using Nova 1.9 software. Syntheses were carried out in an Ammonite 8 flow cell (Cambridge Reactor Design) with a carbon/PVDF composite anode and 316L stainless steel cathode [7]. This cell has a spiral electrolyte channel, 1 m in length and 2 mm in width and the interelectrode gap is 0.5 mm. The cell current was controlled with a Rapid Electronics switching mode power supply (85–1903). A peristaltic pump (Ismatec Reglo Digital Model ISM831C) was used to flow the solutions through the electrochemical cell.

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2.2. Chemicals and analysis

Methanol (Fisher Scientific, HPLC grade), *N*-formylpyrrolidine (Sigma-Aldrich, 97%), Triton X-100 (Sigma-Aldrich) and Brij® L23 (Alfa Aesar) were used without purification. Tetraethylammonium tetrafluoroborate (Alfa Aesar, 99%) was recrystallized from hot methanol and dried at 60 °C in a vacuum oven (~10 mbar) for 24 h.

Conversion and selectivity were determined by gas chromatography using a Shimadzu GC-2014 equipped with an autosampler, FID detector and Agilent technologies HP5 column (length 30 m, I.D. 0.32 mm, film thickness 0.25 μm). The results were processed using GC Solution Lite software. Separations were carried out using He as carrier gas with a flow rate of 2.48 mL min^{-1} through the column. A split injection was conducted using a split ratio of 100:1. The injection and detector temperatures were maintained at 280 and 295 °C, respectively. The oven temperature was initially held at 60 °C and then programmed to increase at 10 °C min^{-1} to 180 °C, where it was held for 1 min. Starting material and product were observed at 5.0 and 6.0 min, respectively. The GC was calibrated using a range of solutions of known concentration of both the starting material and the product.

2.3. Modelling

Computational Fluid Dynamics (CFD) was used to clarify the influence of the electrolysis medium on bubble growth. The code used for the simulations is ANSYS Fluent (ANSYS Inc., 2018) [11]. The computation domain is oriented horizontally with dimensions 0.5 mm × 1.0 mm × 8.0 mm and a computational mesh of approximately 10 million cells is used to mesh it.

3. Results

3.1. Voltammetry

The voltammetry of two non-ionic surfactants, Triton X-100 and Brij L23 (Fig. 1), was investigated at a vitreous carbon disc electrode in methanol/0.1 M Et_4NBF_4. The voltammogram for Triton X-100 (see Fig. S1) showed a well-formed oxidation peak at $E_p = +1.51$ V vs the aqueous SCE reference electrode. The oxidation is completely irreversible but the peak current density is proportional to the square root of the potential scan rate (25–400 mV s^{-1}) confirming that the oxidation is diffusion controlled. Presumably, it is the aromatic group in the Triton X100 that is oxidised in the electrode reaction. In contrast, Brij L23 did not oxidise prior to the solvent decomposition current positive to +2.10 V (see Fig. S2). There is, however, a small positive shift in the current for solvent decomposition.

Fig. 2 reports the voltammetry of *N*-formylpyrrolidine at a vitreous carbon disc electrode in methanol/0.1 M Et_4NBF_4. In the absence of surfactant, a well-formed, irreversible oxidation peak, $E_p = +1.89$ V vs SCE is observed. Moreover, there is no significant change to the response when Brij L23 is added to the medium. In all three solutions the peak current is proportional to the square root of the potentials scan rate showing that the oxidation of *N*-formylpyrrolidine is diffusion controlled. The mechanism for the oxidation of *N*-formylpyrrolidine appears to be unchanged by the presence of the surfactant. It was also noted that at the peak potential for the oxidation of *N*-formylpyrrolidine (+1.89 V vs SCE), the current density observed in the absence of the substrate is negligible (see Fig. S2).

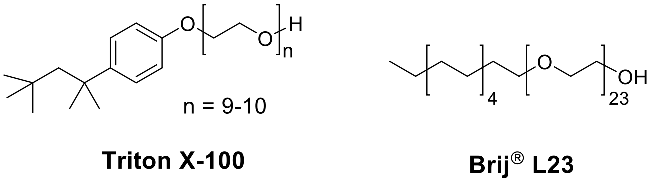


Fig. 1. Chemical structures of Triton X-100 and Brij L23.

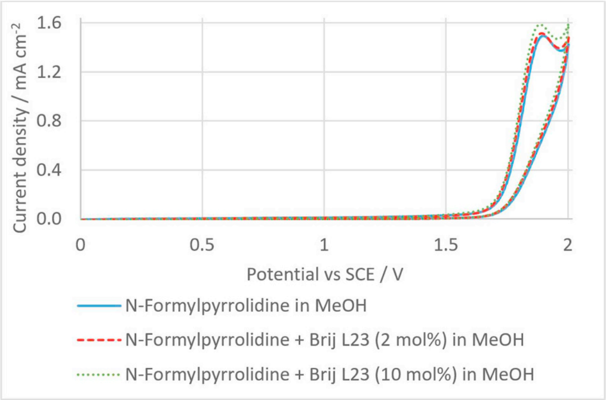


Fig. 2. Cyclic voltammograms for 5 mM *N*-formylpyrrolidine in methanol/ 0.1 M Et_4NBF_4 at a vitreous carbon disc electrode in the absence (blue —) and the presence of 0.1 mM (red - - -) and 0.5 mM (green ••••) Brij L23. Potential scan rate 25 mV s^{-1}. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

3.2. Electrosyntheses

We have reported the methoxylation of *N*-formylpyrrolidine in three different extended channel, narrow gap electrolysis cells. In the Syrris cell [1,3–5], Ammonite 8 [1,6–9] and Ammonite 15 [1,8] electrolysis cells it was possible to achieve a high selectivity and conversion in a single pass of solution through the cell but a high conversion required a cell current higher than the theoretical value and the passage of an excess of charge; the fractional current efficiency was less than 1.0, typically around 0.8.

A series of electrolyses was carried out in an Ammonite 8 cell with a carbon/polymer anode and steel cathode to define the influence of surfactants on this electrochemical reaction. Using a feed solution containing 0.05 M Et_4NBF_4 + 0.1 M *N*-formylpyrrolidine in methanol with and without the presence of 2 mM Triton X-100 or Brij L23. The flow rate selected was 0.5 cm^3 min^{-1} and the cell current was set at 100 mA, a value that would give a maximum fractional conversion of 0.63 in a single pass of the solution through the cell. The results are reported in Fig. 3. It can be seen that the reaction selectivity is always high but the presence of surfactant leads to a significant increase in the current efficiency. It can also be seen that the current efficiency is higher with Brij L23 than Triton X-100. This is to be expected since Triton X-100 (although present in much lower concentration than the *N*-formylpyrrolidine) will itself undergo mass-transfer-controlled oxidation in the conditions of the electrolysis, see Fig. S1.

In a further set of electrolyses under the same conditions, the concentration of the surfactants was varied. For example, with Triton X-100, its concentration was varied over the range 0–2 mM. The addition of 0.5 mM surfactant increased the fractional current efficiency from 0.80 to 0.89 and higher additions led to smaller benefits, the fractional current efficiency reaching 0.95 with 2 mM Triton X-100.

3.3. Modelling

In order to have more understanding of the effect of surfactant on the electrolyses, Computational Fluid Dynamics (CFD) adopting the Volume of Fluid (VOF) framework was used to study bubble growth and detachment at the surface of electrodes. The model employed considered three pre-defined nucleation sites for bubble formation on the cathode surface in a line parallel to the solution flow and dissolved gas is neglected. Consistent with the electrosyntheses, the flow through the

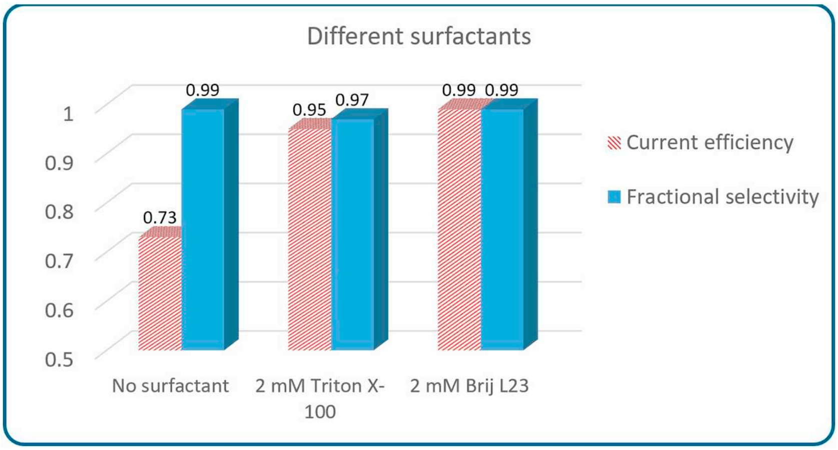


Fig. 3. Influence of 2 mM surfactant on the selectivity (blue solid bar) and current efficiency (red hash bar) for the conversion of *N*-formylpyrrolidine to 2-methoxy-*N*-formylpyrrolidine. Medium: 0.05 M Et_4NBF_4 + 0.1 M *N*-formylpyrrolidine in methanol. Solution flow rate: 0.5 mL min^{-1}. Cell current 100 mA. Fractional selectivity (estimated using calibrated GC) represents the fraction of the converted starting material resulting in the product 2-methoxy-*N*-formylpyrrolidine. Current efficiency is calculated from the theoretical conversion and the product obtained (estimated using calibrated GC). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

channel is horizontal and the interelectrode gap is 0.5 mm; the cathode is at the bottom of the channel and the solution flow rate is 0.5 mL min^{-1}. The total cell current was 4 mA so that the hydrogen generation rate estimated using Faraday's law is 4.18×10^{-11} kg s^{-1}.

The addition of surfactants reduces both the surface tension coefficient and the contact angle and three cases have been simulated. Fig. 4 shows the development of the bubbles as a function of time. Case (a) corresponds to no added surfactant. The gas bubbles remain in contact with the cathode surface for an extended period and this leads to the formation of relatively large bubbles. In addition, neighboring bubbles can slide on the surface and coalesce together to form a larger bubble. In comparison, with the lower surface tension achieved by the addition of surfactants, detachment of the bubbles from the surface occurs sooner and in consequence the bubbles are smaller. The detached bubbles then move in the bulk solution, enhancing mixing. For the case (b), a bubble was detached after 24 ms when the average bubble diameter was 197 µm. Cases (b) and (c) illustrate the influence of contact angle. The influence of contact angle can be seen to be significant. A small decrease in contact angle leads to bubble release after only 7.4 ms when the average bubble diameter is 134 µm. These conclusions are consistent with a paper that considers the influence of bubble formation from an orifice [12].

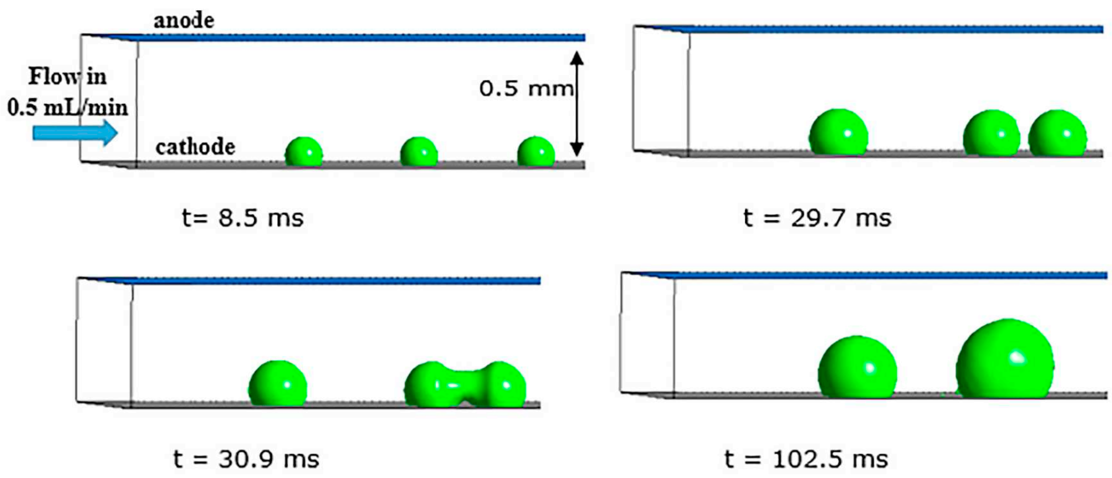
Although mixing effects in the bulk solution were not included in these simulations, they clearly show that addition of surfactants improves the efficiency of the cell by removing the bubbles more frequently from the surface, which improves mixing and brings liquid solution to the electrode surface.

4. Discussion

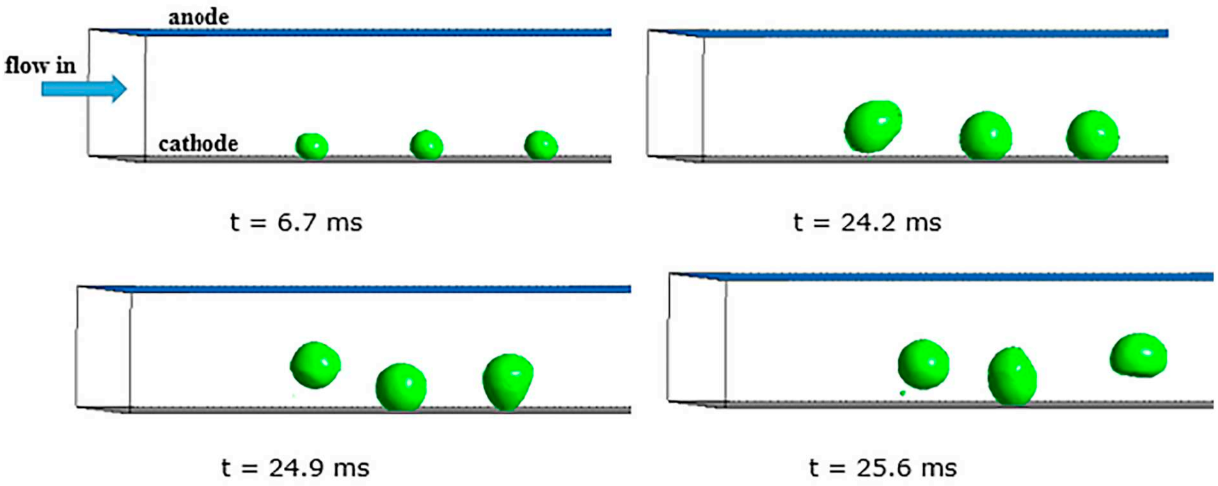
There is no evidence that the presence of a non-ionic surfactant changes the mechanism of the anodic methoxylation of *N*-formylpyrrolidine. There is no shift in the oxidation potential or change in the peak current density as determined by cyclic voltammetry (Fig. 2) and the reaction selectivity is unchanged by the presence of surfactant when the reaction is carried out to high conversion in an electrolysis cell with an extended channel. On the other hand, the presence of surfactant leads to a significant improvement in fractional current efficiency.

Two contributions to this improvement in current efficiency need to be considered. Firstly, the surfactant could adsorb on the carbon anode surface and thereby inhibit a competing reaction, most likely the oxidation of methanol. Indeed, the addition of surfactant does lead to a small positive shift in the voltammogram for the oxidation of the solvent/electrolyte (see Fig. S2) but the contribution of the current for this reaction at the potentials where *N*-formylpyrrolidine is oxidised is extremely low. Hence, the competing reaction does not appear to be the cause of the increase in current efficiency on addition of surfactants.

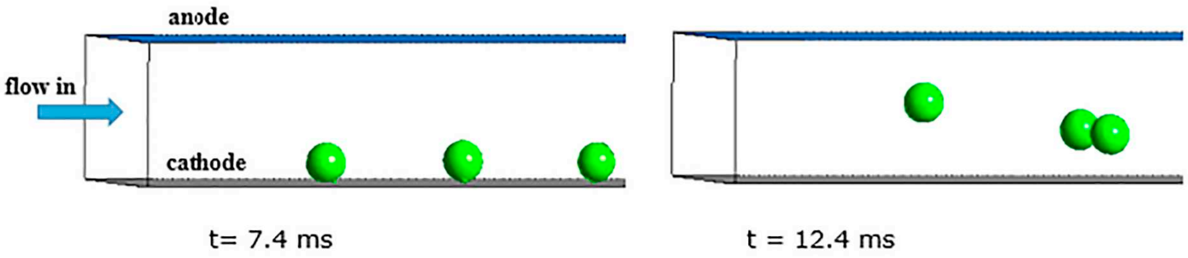
For anodic syntheses in undivided cells with an extended length of reaction channel with millimetre dimensions, H_2 evolution is a convenient cathode reaction that can be used to balance the pH in the bulk flow. Gas bubbles evolution become a significant factor. In the conditions of these electrolyses in the Ammonite 8 electrolysis cell, ~1.35 mL of hydrogen gas is produced at the cathode during the passage of the reactant solution through the cell with a channel volume of 1 mL. Hence, the gas evolution will lead to more than a doubling of solution flow rate. This will lead to an enhancement in the mass transfer conditions and a substantial increase in the limiting current for the oxidation of *N*-formylpyrrolidine. This improvement does not, however, depend on the presence of surfactant since the volume of hydrogen gas depends only on the cell current and solution flow rate, which were both kept constant in the experiments in this paper. However, the presence of surfactant is thought to decrease bubble diameter [12–14] and the simulations confirm this. The decrease in diameter is also evident visually in the solution stream exiting the cell (see Supporting Information), although much bubble amalgamation has occurred by the time the solution reaches the cell exit tube. In our simulations the flow of solution is horizontal whereas the literature on the influence of gas evolution on mass transfer [15–19] generally considers electrolysis cells where the solution flows in a vertical channel. These papers agree that the addition of surfactant reduces the average size of bubbles but the major enhancement in mass transfer regime arises from the buoyancy of the gas bubbles in the bulk flow. This will not be a factor in the Ammonite 8 cell with a horizontal channel with height 0.5 mm and width 2 mm. It is, however, expected that the gas bubbles in the solution flow will enhance turbulence and that the decrease in bubble size in the presence of surfactant will increase the number of turbulence promoters thereby being a more efficient enhancer of mass transfer prior to the bubbles merging into larger bubbles. Quantitative consideration of mass transport in the channel of Ammonite cells is hampered by both the inability to observe within the solution channel and also the very uneven distribution of current through the cell. The current and consequently H_2 evolution rate at the counter electrode is high at the inlet and decays exponentially along the channel [20].



(a) $\sigma = 0.072$ N/m , $\vartheta_w = 60°$



(b) $\sigma = 0.042$ N/m , $\vartheta_w = 35°$



(c) $\sigma = 0.042$ N/m , $\vartheta_w = 30°$

Fig. 4. The influence of surface tension coefficient for the gas/liquid interface, σ, and contact angle, θ_w, on the time for detachment of bubbles from the cathode surface and their diameter on detachment. For clarity, hydrogen formation is terminated when the first bubble leaves each nucleation site.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.elecom.2019.01.009.

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