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SHORT COMMUNICATION

Current efficiency losses in indirect electrochemical processing

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1. Introduction

At the present time there is considerable industrial interest in the indirect two-stage electrochemical process ('ex-cell' process) for the synthesis of organic compounds. In this process a carrier (M^{n+}) is electrochemically oxidized (or reduced) and then allowed to react with the organic compound in a separate vessel. When reaction is complete a separation of product takes place and the spent liquor is returned to the electrochemical cell, where the carrier is regenerated:

$$M^{n+} \longrightarrow M^{(n+m)+} + me$$

$$M^{(n+m)+} + \text{reactant} \longrightarrow M^{n+} + \text{product}$$

This method and its advantages have been described in a number of publications [1, 2], but its application on an industrial scale is limited. One reason why this process has not become common is the loss in current efficiency observed in working processes due to organic matter present in the recycled electrolyte [3–5]. In previous work [6] it has been found that the loss in current efficiency using the Mn^{2+}/Mn^{3+} system in 88% H_2SO_4 was due to the oxidation of the organic compounds (mainly to CO_2) carried over with the electrolyte back to the electrochemical cell.

In this work we extend the study in 50% w/w H_2SO_4, and a simple relation is proposed which permits the calculation of the loss in current efficiency from the total organic carbon present in the recycled electrolyte.

2. Experimental details

The electrochemical oxidation of $MnSO_4$ slurry (1.85 mol kg^{-1}) in 50% H_2SO_4 was carried out in a parallel plate cell having two lead electrodes of area 100 cm^2 each. The electrolyte was circulated through the cell with an Iwaki MD 50 R centrifugal pump; electrolysis was carried out at constant current density (400 mA cm^{-2}) and temperature (80° C).

The amount of Mn^{3+} formed during electrolysis was determined by iodometric titration, and the gas evolved was measured using a gas burette and analysed by gas chromatography. The electrogenerated electrolyte was introduced in a 1-litre agitated glass reactor. After thermostating at the required temperature the organic compound was introduced. After reaction the mixture was cooled, the organic phase was separated by decantation and the electrolyte was returned to the cell for the electrogeneration of $Mn_2(SO_4)_3$.

The total organic carbon present in the electrolyte before electrogeneration was determined using a Shimadzu Total Organic Carbon Analyzer model TOC-500, and the composition of the organic phase after reaction was estimated by gas chromatography using a Perkin Elmer gas chromatograph model 8410.

3. Results and discussion

The oxidation of toluene and its derivatives to the corresponding benzaldehydes has been carried out with electrogenerated manganic sulphate in H_2SO_4:

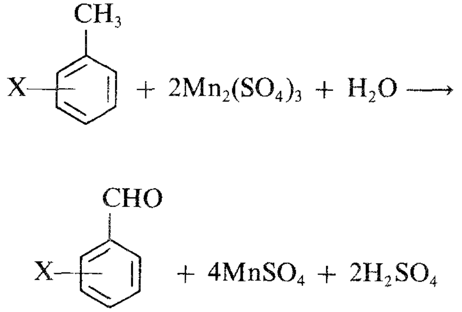

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Table 1. Oxidation of toluene and its derivatives with electrogenerated $Mn_2(SO_4)_3$ to the corresponding benzaldehydes

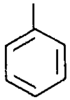
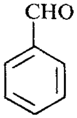
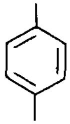
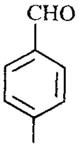
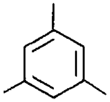
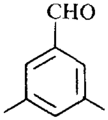
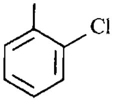
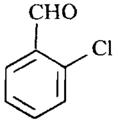
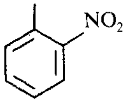
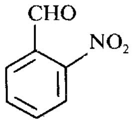
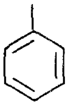
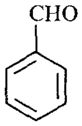
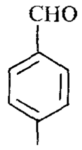
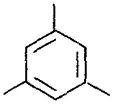
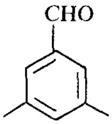
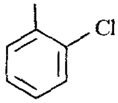
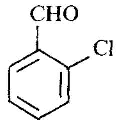
Starting material	*Reaction product*	*Temp. (° C)*	*H_2SO_4 (%)*	*Mole Mn^{3+} / Mole org.*	*Reaction time (h)*	*Conversion of organic (%)*	*Oxidation yield (%)*	*Material yield (%)*	*Main by-products (material yield)*
		80	50	0.33 0.67 1.34	1.2	7.2 11.0 15.2	42 40 30	75 62 59	benzyl benzoate (7–12%) *o*- and *p*-cresol (6–8%) benzyl alcohol (2–3%)
		50	49	0.85	1.0	20	77	83	*p*-toluic acid (3%) terephtalic acid terephtaldehyde
		40	49	0.96	3.0	16	56	71	3–5 dimethyl benzoic acid dimeric products
		90	53	1.63	3.0	38	84	83	*o*-chlorobenzoic acid (4%) *o*-chlorobenzyl alcohol (2%) *o*-chlorobenzyl chloride (1%)
		120	50	0.84	4.0	13.5	35	55	*o*-nitrobenzoic acid (30%)

Table 2. Current efficiency for the electroregeneration of $Mn_2(SO_4)_3$ in recycled electrolyte

Starting material	*Reaction product*	*TOC in electrolyte ($g\,kg^{-1}$)*	*Current efficiency for the electrogeneration of recycled electrolyte (%)*	*Current efficiency recycled electrolyte / Current efficiency fresh electrolyte*	
				Experimental	*Calculated*
		3.7	42	0.61	0.57
		3.5	44	0.64	0.59
		5.0	35	0.51	0.50
		1.2	60	0.87	0.81

The results obtained are given in Table 1, which shows that the oxidation and material yield depends strongly on the substituant present on the benzene ring.

At the end of the reaction the organic phase was separated and the electrolyte was electrogenerated:

$$2MnSO_4 + H_2SO_4 \longrightarrow Mn_2(SO_4)_3 + H_2$$

It has been found that the current efficiency for the electrogeneration of $Mn_2(SO_4)_3$ in the recycled electrolyte was much lower than that of fresh electrolyte. This decrease in current efficiency is due to oxidizable organic material carried over with the electrolyte back to the electrochemical cell where it is oxidized to CO_2 [6].

The 'carry-over' can be treated by equations for diffusion-controlled processes; thus, to estimate the current efficiency in the recycled electrolyte the following relation can be derived:

$$\frac{(\eta_c)_{\text{recycled}}}{(\eta_c)_{\text{fresh}}} = \frac{[MnSO_4]X}{[MnSO_4]X + \dfrac{Z}{BM}[TOC]} \qquad (1)$$

where η_c is the current efficiency for $MnSO_4$ oxidation, $[MnSO_4]$ is the concentration of the manganous sulphate slurry ($1.85\,mol\,kg^{-1}$), X is the conversion of $MnSO_4$ (0.97), TOC is the amount of total organic carbon in the electrolyte ($g\,kg^{-1}$), B is the amount of carbon in the organic compound, Z is the number of electrons involved in the oxidation of the organic compound to CO_2, and M is the molecular weight of the organic compound (substituted benzaldehyde).

For the organic compounds studied we can consider the following average values: B, 0.75;

Z, 35; M, 130. Equation 1 becomes

$$\frac{(\eta_c)_{\text{recycled}}}{(\eta_c)_{\text{fresh}}} = \frac{1.8}{1.8 + 0.36\text{TOC}} \quad (2)$$

The calculated values from Equation 2 are in good agreement with the experimental values, as shown in Table 2.

References

[1] R. Ramaswamy, M. S. Venkatachalapathy and H. V. K. Udupa, *J. Electrochem. Soc.* **110** (1963) 202.

[2] K. Kramer, P. M. Robertson and N. Ibl, *J. Appl. Electrochem.* **10** (1980) 29.

[3] Ch. Comninellis and E. Plattner, *ibid.* **14** (1984) 533.

[4] *Idem*, Amer. Inst. of Chem. Engineers, Summer National Meeting, Seattle, USA, 25–28 August 1985, Paper No. 14e.

[5] *Idem*, Intern. Symp. on Electro-organic Synthesis Kurashiki 1986, paper No. PI-13.

[6] Ch. Comninellis, Ch. Griessen and E. Plattner, *J. Electrochem. Soc.* **132** (1985) 72.