

Anodic substitution in emulsions under phase transfer catalysis conditions. II. Acetoxylation of dimethoxybenzenes

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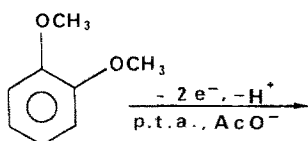
The anodic acetoxylation of 1,2-dimethoxybenzene in $H_2O-CH_2Cl_2$ emulsions with different phase transfer agents ($nBu_4N^+HSO_4^-$, $nBuP^+\phi_3Br^-$, Aliquat 336, Hyamine 1622 and CTAB) has been investigated. The conversion rates and the electrochemical efficiencies are mainly governed by two parameters: (a) the anode wetting by an organic layer which varies with the nature of the catalyst as shown by the preparative polarization curves; (b) the competitive oxidation of the counter-ions present in the organic phase (CH_2Cl_2). The latter point is very important in the case of bromide salts.

On the basis of these observations, the use of $nBu_4N^+HSO_4^-$ appears to be the best compromise for the case of anodic acetoxylation of aromatic substrates in the media studied.

1. Introduction

The use of emulsions containing a phase transfer agent (p.t.a.) allows one to overcome certain difficulties relevant to organic electrochemistry such as, low electrical conductivity and poor chemical and current yields and reaction selectivity [1]. The interest of such a technique has been shown in the case of the anodic aromatic substitutions performed in $H_2O-CH_2Cl_2$ emulsions in the presence of a p.t.a. such as $nBu_4N^+HSO_4^-$ [1-5]. In these media, the anode wetting by the organic phase governs the electrochemistry efficiency. Moreover, it depends on the nature of the catalyst as shown in our first paper on anodic cyanation of dimethoxybenzenes (DMB) [6]. The aim of this study is to determine if the same parameter is effective in the anodic acetoxylation of aromatic substrates.

A preliminary report on anodic acetoxylation of 1,2-dimethoxybenzene (Reaction 1) [7] indicates two main points:



Contrary to the results observed in anodic cyanation [6], the amount of acetate ions extracted into the organic phase varies very little with the nature of the p.t.a. Except with $nBuP^+\phi_3Br^-$, 80-90% of the catalyst Q^+ is transferred as Q^+AcO^- , $nAcOH$ in the organic phase (Table 1). This means that the hydrophobic character of the acetate-acetic acid complex is important enough to overcome the differences in the free transfer enthalpies of the different counter ions X^- [8].

The conversion rates and the product yields do not depend on acetate ion concentrations (Table 1). The low current yields (3-16%) indicate the occurrence of strong competitive oxidation phenomena. The question that arises is whether these competitive processes are due to the oxidation of the aqueous phase or that of the counter-

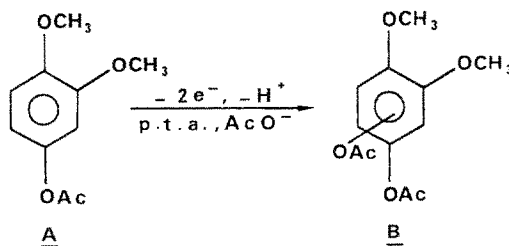


Table 1. Anodic acetoxylation of 1,2-DMB as a function of different p.t.a. Electrolyte: aqueous 1 mol dm^{-3} $\text{CH}_3\text{COONa}/\text{CH}_3\text{COOH}$ 0.09 mol dm^{-3} p.t.a., (50 ml), methylene chloride/ 0.13 mol dm^{-3} 1,2-dimethoxybenzene (50 ml), 2 F mol^{-1} of substrate, Pt at 293 K

$Q^+ X^-$ p.t.a.	Anodic* potential V vs SCE	Current densities (mA cm^{-2})		Conversion rate (%)	Yields (%)**		Organic phase		Run
		Initial	Final		Organic†	Current	$[Q^+ \text{AcO}^-] \times 10^2$ (mol dm^{-3})	(%) Q^+ ‡ Transfer	
CTAB	~ 0.8	0.70	1.10	20	16	3§	7.2	81	1
$n\text{BuP}^+\phi_3\text{Br}^-$	~ 0.9	3.40	1.60	15	18	3	5.5	61	2
A 336	~ 1.4	0.85	0.80	37	29¶	10	6.9	84	3
BzCl	~ 1.5	0.85	1.20	29	31	9	6.8	84	4
$n\text{Bu}_4\text{N}^+\text{HSO}_4^-$	~ 1.4	1.60	0.90	43	39	16	7.9	89	5

* Values estimated from the preparative $I-E$ curves plotted with a Luggin capillary.

** Product A unless otherwise indicated.

† Based on unrecovered starting material.

‡ % of Q^+ transferred as $Q^+\text{AcO}^-$.

§ Product A is accompanied with 1-bromo-3,4-dimethoxybenzene (67% chemical yield, 14% current yield).

¶ 22% A and 7% B derivative.

CTAB is cetyltrimethylammonium bromide $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Br}^-$.

BzCl is benzethonium chloride $(\text{CH}_3)_3\text{CCH}_2\text{C}(\text{CH}_3)_2-\text{C}_6\text{H}_4-(\text{OCH}_2-\text{CH}_2)_2-\text{N}^+(\text{CH}_3)_2-\text{CH}_2-\text{C}_6\text{H}_5 \text{Cl}^-$ (Hyamine 1622).

Aliquat 336 is tricapyryl methylammonium chloride $(\text{C}_8\text{H}_{17})_3\text{N}^+\text{CH}_3\text{Cl}^-$.

ions present in CH_2Cl_2 . This problem is related to the importance of the anode coverage by the organic layer. In order to elucidate these points as well as the formation of the bromine derivative (Table 1, footnote§), we have reinvestigated the anodic acetoxylation of 1,2-DMB in emulsions.

2. Experimental procedure

The apparatus and procedure for small-scale electrolysis was the same as previously described [6, 7]. All the experiments were run at 293 K.

2.1. Preparative electrolysis and potential measurements

The results reported by Ebersson and Helgee [9] led us to use emulsions formed by stirring 50 ml aqueous acetate-acetic acid buffer (1 mol dm^{-3} of each) containing 0.09 mol dm^{-3} p.t.a. (except A 336 which is dissolved in CH_2Cl_2) with 50 ml CH_2Cl_2 in which 0.13 mol dm^{-3} of 1,2-DMB is dissolved.

The substrate was electrolysed at a controlled potential. In our early experiments [7], the SCE was simply immersed near to the anode and the

potential was fixed at the values indicated in Table 2.

In order to check the ohmic drop, the real anodic potential (Table 2) was measured with a second SCE equipped with a Luggin capillary which was in contact with the platinum gauze, all the other experimental conditions remaining the same as in the previous preparative runs.

The polarization curves $I-E$ were plotted in preparative electrolysis conditions using an SCE equipped with a Luggin capillary. Two types of anode were used: a 90 cm^2 Pt gauze (the working electrode itself) and a 2.16 cm^2 Pt sheet.

2.2. Conductivity measurements of the organic phase

An emulsion of $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$ containing CH_3COOH , CH_3COONa , p.t.a. and 1,2-DMB in concentrations equal to those of the preparative runs was formed.

After separation, the CH_2Cl_2 phase was poured into a thermostated cell (293 K). The organic phase conductivity was determined by using a Tacussel CD7N conductivity meter equipped with a Tacussel CM.02/55 G ($K = 84.810^{-2}$) measuring

Table 2. Potential and conductivity measurements (293 K)

p.t.a.	Aqueous 1 mol dm ⁻³ CH ₃ COONa, CH ₃ COOH, 0.09 mol dm ⁻³ p.t.a. (50 ml) + CH ₂ Cl ₂ (50 ml) with 0.13 mol dm ⁻¹ 1,2-DMB			Conductivity × 10 ³ (Siemens cm ⁻¹)	
	Set up potential E (V vs SCE*)	Real potential E' (V vs SCE) (Luggin capillary)	Ohmic drop E - E' (V)	Aqueous phase	Organic phase
CTAB	2.5	0.80	1.70		0.15
nBuP ⁺ φ ₃ Br ⁻	1.7	0.90	0.80		2.17
nBu ₄ N ⁺ HSO ₄ ⁻	1.7	1.40	0.30	~ 40	1.25
BzCl	2.0	1.60	0.40		0.25
A 336	1.7	1.30	0.40		0.39

* Anodic potentials of electrolyses reported in our earlier paper [7].

cell. The same values of the conductivity were obtained at 250 and 1000 Hz.

2.3. Study of AcO⁻ transfer

The quantitative determination of acetate ions transferred into the organic phase was performed in the following way. Emulsions of water and dichloromethane described as in the preparative runs were maintained for 1 h. The organic layer was then separated and evaporated under vacuum. The residue was taken up with H₂O and titrated with HCl (0.1 mol dm⁻³).

2.4. Decarboxylation study in the presence of nBuP⁺φ₃Br⁻

An aqueous solution of CH₃COONa:CH₃COOH (1:1 mol dm⁻³) and nBuP⁺φ₃Br⁻ (0.1 mol dm⁻³) (100 ml) was emulsified with 100 ml of CH₂Cl₂ for 1 h. The CH₂Cl₂ phase was then separated. After the addition of 0.45 mol dm⁻³ of nBu₄N⁺BF₄⁻, the resulting organic solution was electrolysed at 1.7 V vs SCE (1150 C) under a N₂ stream. The CO₂ formed was bubbled through a saturated solution of baryte. BaCO₃ precipitate was recovered on an ashless filter paper. After calcination, 0.12 g (6 × 10⁻⁴ mol) of BaCO₃ was obtained. Bromine was reduced with an excess of aqueous KI and the I₂ obtained was titrated with Na₂S₂O₃ (0.1 mol dm⁻³). 4 × 10⁻³ mol of Br₂ was obtained.

2.5. Chemical bromation

The emulsion of 50 ml aqueous acetate buffer (1 mol dm⁻³) containing CTAB (9.9 × 10⁻² mol dm⁻³) with 50 ml CH₂Cl₂ was oxidized at an anode potential of 1.4 V vs SCE equipped with a Luggin capillary. A total of 1 F mol⁻¹ CTAB was passed. Then 1.1 g of 1,2-DMB (15.9 × 10⁻² mol dm⁻³) was added and stirred for 1 h. The usual work up procedure affords 1.46 g of crude material. After chromatography (90 g silica gel, 10% ether-90% petroleum ether), a mixture (1.11 g) was obtained. Its ¹H NMR indicated the presence of a bromine derivative and the starting material. These were separated in pure form by preparative gas-liquid chromatography (GLC) (10% diethylene glycol succinate (DEGS) packed column, 180° C).

The IR, ¹H NMR and mass spectra of the bromo-1-dimethoxy-3,4-benzene thus obtained are in agreement with those reported in the literature [10, 11]. The yield based on the total amount of charge necessary to oxidize Br⁻ is 26%.

3. Results and discussion

As evidenced in the anodic cyanation of DMB [6], the polarization curves recorded in preparative conditions can provide information about the anode wetting phenomena.

In aqueous buffer solution of acetate-acetic acid, the I-E curves are not significantly modified by the addition of different p.t.a. For example,

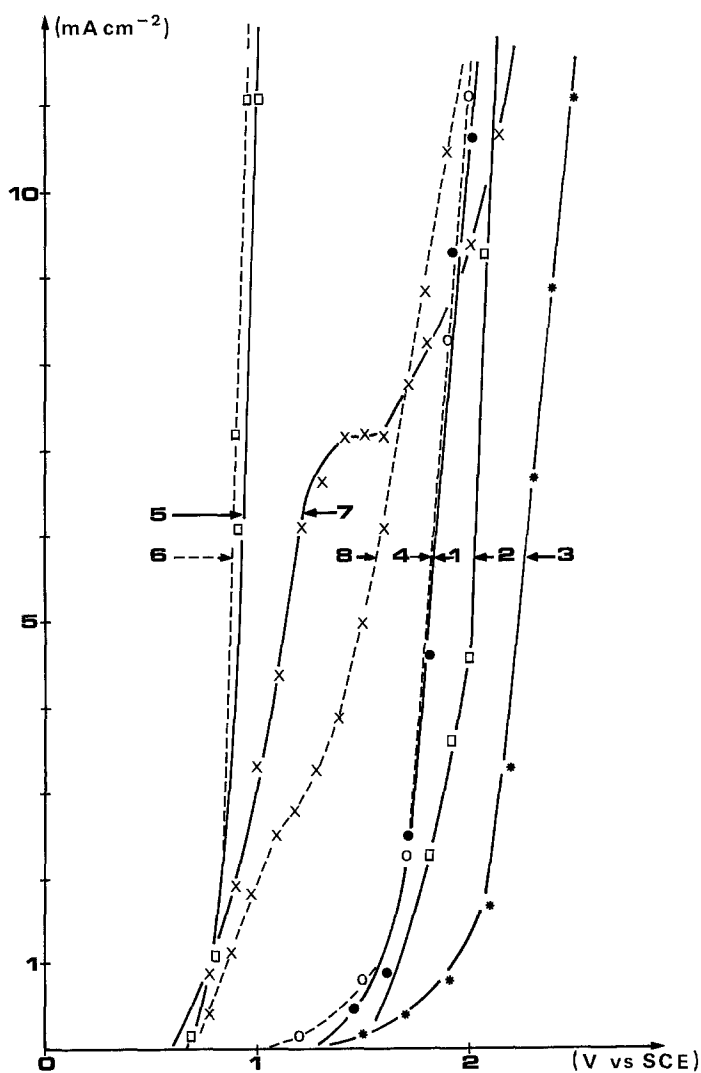


Fig. 1. Polarization curves in preparative conditions. Curve 1 —●— aqueous acetate-acetic acid buffer (1 mol dm⁻³ of each); Curve 2 —□— aqueous acetate-acetic acid buffer (1 mol dm⁻³ of each) + 0.045 mol dm⁻³ *n*BuP⁺φ₃Br⁻; Curve 3 —*— CH₃CO₂H—CH₃CO₂⁻ *n*Bu₄N⁺ (0.079 mol dm⁻³) and *n*Bu₄N⁺ClO₄⁻ (0.45 mol dm⁻³) in CH₂Cl₂; Curve 4 ---○--- emulsion of CH₂Cl₂ (50 ml) and aqueous acetate buffer (50 mol); Curve 5 —□— emulsion + 0.09 mol dm⁻³ *n*BuP⁺φ₃Br⁻; Curve 6 ---□--- emulsion + 0.09 mol dm⁻³ *n*BuP⁺φ₃Br⁻ + 0.13 mol dm⁻³ 1,2-DMB; Curve 7 —×— emulsion + 0.09 mol dm⁻³ CTAB; Curve 8 ---×--- emulsion + 0.09 mol dm⁻³ CTAB + 0.13 mol dm⁻³ 1,2-DMB.

Curve 2 (Fig. 1) plotted with *n*BuP⁺φ₃Br⁻ represents in general the type of curve obtained with the different catalysts.*

In methylene chloride containing *n*Bu₄N⁺ClO₄⁻ as a supporting electrolyte, our results are in agreement with those of Ellis *et al.* [3]; oxidation of acetate anions introduced as a *n*Bu₄N⁺ salt begins at 1.1 V vs SCE. This potential is shifted to a higher value when the acetate anion is transferred with a p.t.a. from the aqueous acetate buffer to CH₂Cl₂ (Curve 3, Fig. 1). This results

* In aqueous acetate buffer the Br⁻ oxidation seems to be inhibited by the competitive adsorption of acetate anions, the concentration of which is 10 times higher than that of Br⁻.

from the presence of acetic acid in methylene chloride [3].

Emulsions formed with CH₂Cl₂ and aqueous acetate buffer lead to the same *I*-*E* curves (Curve 4, Fig. 1) as in aqueous buffer (Curve 1, Fig. 1). This indicates an anode wetting by the aqueous phase since the organic phase does not contain any depolarizer. When a p.t.a. is added to this emulsion, two cases are to be considered:

(a) In the presence of bromide salts (*n*BuP⁺φ₃Br⁻ and CTAB), the polarization curves (Curves 5 and 7, Fig. 1) are shifted to lower potentials in comparison to those recorded in aqueous acetate buffer containing the p.t.a. (Curve 2,

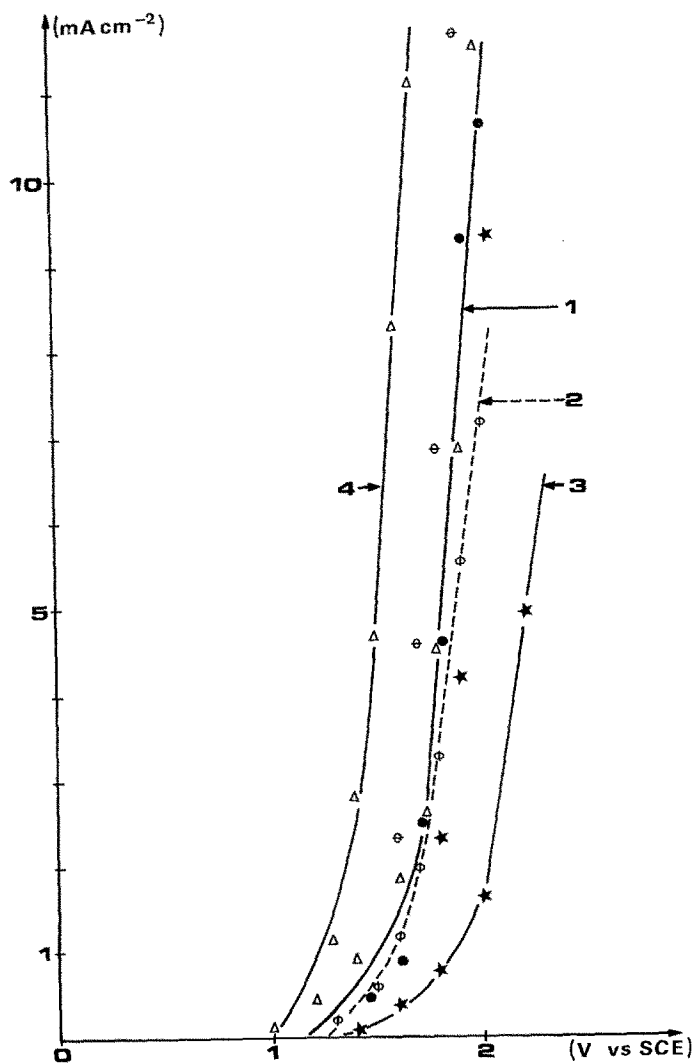


Fig. 2. Polarization curves in preparative conditions: (a) in aqueous acetate buffer (1 mol dm^{-3}) containing $0.045 \text{ mol dm}^{-3}$ p.t.a.: Curve 1 \bullet - without p.t.a.; Δ - $n\text{Bu}_4\text{N}^+\text{HSO}_4^-$; \circ - BzCl ; \star - A 336; (b) in emulsions (CH_2Cl_2 + aqueous acetate buffer) + 0.09 mol dm^{-3} p.t.a.: Curve 2 $-\circ-$ - BzCl ; Curve 3 $-\star-$ - A 336; Curve 4 $-\Delta-$ - $n\text{Bu}_4\text{N}^+\text{HSO}_4^-$.

Fig. 1 and Table 3). These results demonstrate that an oxidation process takes place in an organic layer covering the anode. As the acetic acid-acetate anion complex undergoes oxidation at a higher potential (Curve 3, Fig. 1), the current densities observed between 0.8 and 1.2 V vs SCE must result from Br^- oxidation in the organic phase. The addition of 1,2-DMB leads to similar waves (Curves 6 and 8 in broken lines, Fig. 1). Only a slight inhibition of Br^- oxidation seems to occur in the case of CTAB. In consequence, the competitive Br^- oxidation in the organic layer covering the anode may account for the low current yields obtained with these two catalysts. In fact, this conclusion is further supported by the following experiments: similar current inten-

sities are observed in CH_2Cl_2 medium obtained after separation of $\text{H}_2\text{O}-\text{CH}_2\text{Cl}_2$ emulsion and addition of $n\text{Bu}_4\text{N}^+\text{BF}_4^-$ (see Section 2). Furthermore, electrolysis of this organic phase at 1.7 V vs SCE shows that, after a run of 2 F mol^{-1} of AcO^- ions, 10% of the current is consumed in decarboxylation reaction and 67% in bromine formation.

(b) In the presence of the other p.t.a. ($n\text{Bu}_4\text{N}^+\text{HSO}_4^-$, BzCl and A 336), the $I-E$ waves are close to those plotted in aqueous buffer solutions (Curve 1, Fig. 2 and Table 3) and therefore, the relative importance of the anode wetting either by the organic or the aqueous phase cannot be determined. However, the anode wetting probably differs with these catalysts. Indeed, current den-

Table 3. Anodic potential (*V* vs SCE) corresponding to a current density of 2 mA cm⁻²

Media*	CTAB	nBuP ⁺ φ ₃ Br ⁻	nBu ₄ N ⁺ HSO ₄ ⁻	BzCl	A 336	Without p.t.a.
Acetate buffer	1.4	1.8	1.7	1.6	1.8	1.7
Emulsions CH ₂ Cl ₂ + acetate buffer	0.9	0.85	1.4	1.7	2	1.7
Emulsions + DMB	1	0.85	1.4	1.5	1.5	—

*For concentrations see Table 1.

sities observed with A 336 are similar to those obtained in CH₂Cl₂ containing acetic acid-acetate anion complex and a supporting electrolyte (Curves 3, Figs. 1 and 2) but they are lower than those observed in the presence of nBu₄N⁺HSO₄⁻ (Curve 4, Fig. 2). This difference may result from a slight increase of the anode wetting by the aqueous phase with nBu₄N⁺HSO₄⁻ and the contrary when A 336 is used. The preceding results are not greatly modified by the addition of 1,2-DMB. Therefore, it is reasonable to assume that the low current yields obtained in these cases probably result on the one hand from the competitive oxidation of the aqueous phase and on the other, to the oxidation of counter ions in CH₂Cl₂.

The experimental results reported above are confirmed by the study of the ohmic drop, the importance of which is illustrated by the differences (Table 2) between the values of the anodic potential monitored respectively by using a reference electrode simply immersed near to the anode and a second reference electrode equipped with a Luggin capillary (see Section 2). The conductivity of the aqueous phase is 20 to 300 fold higher than those of the organic phases (Table 2). Consequently, the high ohmic drop observed with the different p.t.a. indicate that the anode is essentially covered by an organic layer. Assuming an ohmic control for the *I-E* waves, the value of the organic film thickness is found to vary between 0.01 and 0.06 cm. These values are consistent with the 0.05 cm reported by Fleischmann *et al.* [12].

† In our experimental conditions (Table 1) the current densities are much lower than those used in the experiments performed at constant current [3, 9]. The polarization curves (Figs. 1 and 2) show that a slight increase in the anodic potential induces a strong variation of the current densities. Thus the differences observed between the reported and our values probably result from differences in the anodic potential.

The remaining problem is the formation of 1-bromo-3,4-dimethoxybenzene which occurs only when the p.t.a. used is CTAB (Table 1). The anode potential does not affect this formation greatly (Table 4). Indeed, when the working potential is increased from 1 to 1.7 V vs SCE, the conversion rates and the yield of acetoxyated derivative tend to be enhanced but the electrochemical efficiency of 1-bromo-3,4-dimethoxybenzene remains practically the same (~45%). This result suggests a pure chemical origin for the formation of the bromine derivative in our experimental conditions: Br₂, a primary product of the electrode reaction ($\text{Br}^- \xrightarrow{-e} 1/2\text{Br}_2$) would react with the starting material yielding the bromo compound [13].

In order to confirm this point, electrochemically formed bromine was allowed to react with 1,2-DMB in emulsified medium (see Section 2). As expected, the 1-bromo-3,4-dimethoxybenzene compound was obtained.

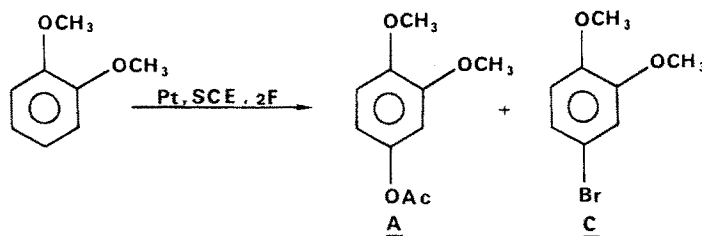
It is, however, to be mentioned that no bromine derivative was formed in the presence of nBuP⁺φ₃Br⁻ although Br₂ is also generated in this case (see Sections 2. 2-4).

4. Conclusion

We have shown in this study that anode wetting by the organic phase and counter-ion oxidation in this layer are the limiting factors in carrying out anodic acetoxylation. Thus, very poor electrochemical yields due to strong Br⁻ oxidation are obtained in the presence of nBuP⁺φ₃Br⁻ and CTAB although the concentration of Br⁻ transferred in comparison to AcO⁻ anions is very low.

Anion transfer across the interface of two immiscible electrolyte solutions (ITIES) is thus not a determining factor in anodic acetoxylation. In other words, the influence of the adsorption of

Table 4. Bromine derivative in the presence of CTAB. Electrolyte: 50 ml aqueous acetate buffer (1 mol dm^{-3} of each) containing 0.09 mol dm^{-3} of p.t.a. + 50 ml CH_2Cl_2 (0.13 mol dm^{-3} of 1,2-DMB) 293 K



Run	Anodic* potential (V vs SCE)	Current densities (mA cm^{-2})		Conversion rate (%)	Chemical yield [†] (%)		Current yield (%)	
		Initial	Final		<u>A</u>	<u>C</u>	<u>A</u>	<u>C</u>
1 [‡]	~ 0.8	0.67	1.1	20	16	67	3	14
2	1.0	1.50	2.0	58	5	82	3	47
3	1.4	4.72	4.44	64	5	70	3	45
4	1.7	7.50	4.44	80	10	55	8	43

*Potential measured with a Luggin capillary

[†]Based on unrecovered starting material

[‡]From [7]

cationic surfactants at the ITIES is negligible [14].

Among all the p.t.a. examined in this work, tetrabutylammonium hydrogen sulphate affords the best results. The electrochemical yields with this p.t.a. could be improved by increasing the AcO^- concentration in the aqueous phase as recently shown by Ellis *et al.* [3].

It is to be noted that the results obtained in acetoxylation are very similar to those reported on anodic cyanation of DMB in emulsified media [6] except that the co-oxidation of counter-ions interferes to a lower extent in the latter case for reasons which are yet unknown.

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