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Anodic substitutions in emulsions under phase transfer catalysis conditions. I. Cyanation of dimethoxybenzenes

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An emulsion electrolysis technique in the two-phase system water–dichloromethane containing NaCN and a phase transfer agent (PTA) has been examined with 1,2- and 1,3-dimethoxybenzenes as a function of various parameters (nature of Q^+, X^-, anodic potential, cyanide ion concentration in the organic phase, preparative current potential curves). The anodic cyanation results indicate that the anode wetting phenomena, the extraction of cyanide ion and the competitive oxidation of X^- are the determining factors. It is shown that the best criterion for a successful anodic cyanation is to operate under conditions of maximum coverage of the anode by the organic layer. Among all the PTA studied (cetyltrimethylammonium bromide, $n\text{Bu}_4\text{N}^+\text{HSO}_4^-$, $n\text{BuP}^+\phi_3\text{Br}^-$, benzethonium chloride and A 336), A 336, a very hydrophobic PTA, affords the best chemical (81%) and current (77%) yields with 1,2,-dimethoxybenzene.

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1. Introduction

Electrochemical conversion in aqueous electrolytes of sparsely water soluble organic substances can be performed either in micelles (and microemulsions) or in emulsions. Several reports [1–12] have emphasized the interest of Phase Transfer Catalysis (PTC) in anodic substitution reactions: the nucleophile (Nu^-) is transferred from the aqueous phase into the organic phase as a tetraalkyl ammonium salt (Q^+Nu^-) where it undergoes reaction with the electrogenerated species (radical cation).

This method presents many advantages in preparative electrochemistry: cheap nucleophile source (sodium salts), clean cathodic process (hydrogen evolution), high conductivity and in general higher product yields in comparison to anodic substitution in homogeneous organic solutions. Yet, many parameters such as the nature of the phase transfer agent (PTA) Q^+X^-, the anode wetting, the mass and charge transfer across the aqueous–organic phase boundary, play an important role and are not completely understood. In order to gain more insight concerning these problems, we have reinvestigated the electrochemical reaction studied by Eberson and Helgee [1], i.e. anodic cyanation of 1,2- and 1,3-dimethoxybenzenes (DMB) in the emulsified system ($\text{H}_2\text{O}/\text{CH}_2\text{Cl}_2$) in the presence of PTA.

2. Experimental procedure

The results of Eberson and Helgee [1] led us to use a platinum anode, emulsions formed with water and methylene chloride in equal volume, equal concentrations in DMB and in PTA, and a coulometric run of $2F\ \text{mol}^{-1}$ of the substrate. All the chemicals were of reagent grade quality.

Electrolyses were conducted at 293 K in a non-divided thermostated cell equipped with a 90 cm^2 active area Pt gauze anode, a Pt or stainless steel cathode, the nature of which reveals no effect on electrochemical results, and a saturated calomel reference electrode (see Fig. 1). Anodic potential was controlled with a Tacussel PRT 100 potentiostat and the charge was monitored with a Tacussel IG5 LN integrator.

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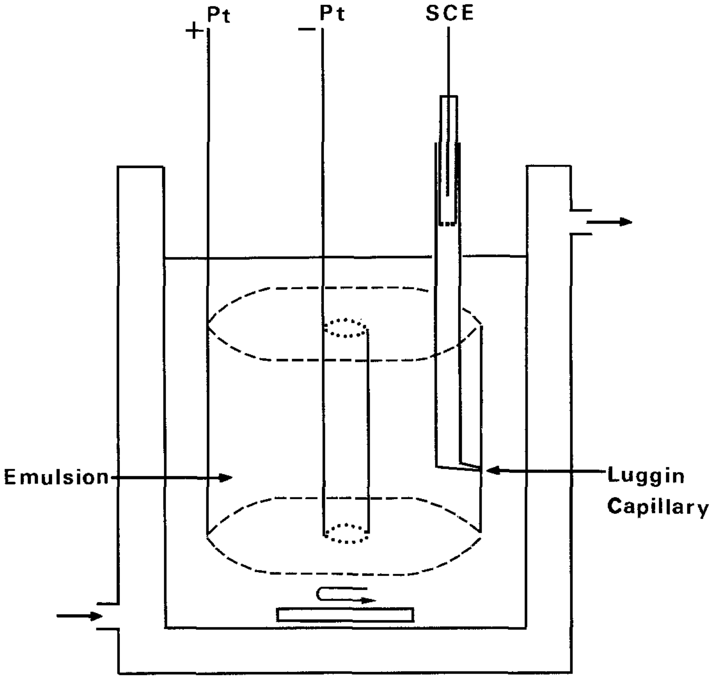


Fig. 1. Preparative scale electrolysis cell.

The emulsion was formed with 50 ml of CH_2Cl_2 (0.04 mol dm^{-3} DMB) and 50 ml of aqueous phase containing 0.4 mol dm^{-3} NaCN and 0.04 mol dm^{-1} PTA (except A 336 which was solubilized in CH_2Cl_2). Emulsification was achieved with a magnetic bar stirrer at the lowest speed (~ 600 r.p.m.) necessary to prevent the separation of the two phases. A few experiments were performed using an Ultra-Turrax stirrer (Janke and Kunkel, Typ. TP 1.8/10): this is an agitator equipped with a dispersor which functions according to the turbine principle. The liquid is sucked from the bottom to the top and then squeezed out laterally through the outlets of the stator. A very fine dispersion is thus obtained due to the high turbulent flow prevailing in the region between rotor/stator.

After electrolysis, the organic phase was separated and evaporated under vacuum. The residue was taken up with water and extracted in a continuous process with ether. The different products were separated and purified on a silica gel Merck 60 chromatography column.

Electrolyses in homogeneous organic solutions were run with 100 ml CH_3CN (or CH_2Cl_2) containing 0.45 mol dm^{-3} $nBu_4N^+ClO_4^-$, 0.05 mol dm^{-3} $nBu_4N^+CN^-$ and 0.023 mol dm^{-3} DMB. Water (50 ml) was then added to the electrolysed solution before stripping it on a rotary evaporator. The remaining aqueous phase was worked out as described previously.

All the isolated products were characterized by the usual spectroscopic techniques: IR, proton NMR and mass. The spectroscopic characteristics were in agreement with those reported in the literature [13, 14] or with those of the corresponding authentic samples.

The amount of CN^-, Br^- or Cl^- transferred in the organic phase was evaluated: emulsion of 50 ml H_2O and 50 ml CH_2Cl_2 containining NaCN and PTA in the same concentrations as in preparative runs was maintained throughout 60 min. After separation and evaporation of the organic phase, the residue was solubilized in 50 ml H_2O. The resultsing aqueous solution was titrated by potentiometry with 0.1 mol dm^{-3} $AgNO_3$ solution. The reliability of this method was tested with standard solutions of each PTA (relative error ± 5%).

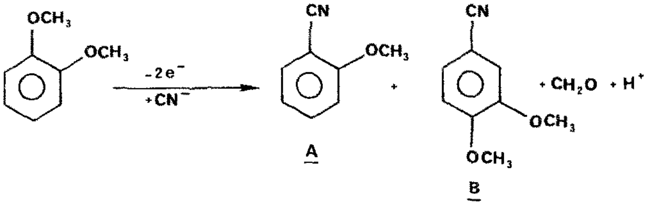
The polarization curves (*I–E*) were recorded in preparative electrolysis conditions with the 90 cm^2 Pt anode gauze. The anode potential was measured in two different ways: firstly, the reference electrode was immersed near the working electrode and, secondly, with the same reference electrode equipped with a Luggin capillary. The two methods gave similar *I–E* curves except in the case of $n\mathrm{BuP}^+\phi_3\mathrm{Br}^-$. Hence, preparative electrolyses were run without the Luggin capillary except with $n\mathrm{BuP}^+\phi_3\mathrm{Br}^-$. In the later case, the current intensities were very sensitive to the relative position of the reference electrode indicating a high ohmic drop near the anode. However, electrosynthesis carried out with and without a Luggin capillary gave the same results. This confirms the absence of the anodic potential influence as evidenced with $n\mathrm{Bu_4N^+HSO_4^-}$ (see Section 3 Table 1).

3. Results and discussion

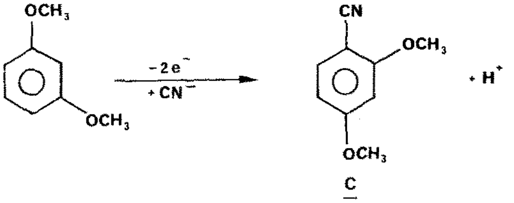
In all the experiments, 1,2- and 1,3-DMB yielded respectively 2-methoxybenzonitrile (*A*) plus 3,4-dimethoxybenzonitrile (*B*) (Reaction 1) and 2,4-dimethoxybenzonitrile (*C*) (Reaction 2) along with mixtures of unidentified polymeric products.

stirrer (Runs 5, 7) leads to lower conversion, chemical and current yields in comparison to an emulsion formed with a magnetic bar stirrer, the product distribution remaining the same in both cases.

As evidenced by Eberson and Helgee [1], a homogeneous organic system leads to a more selective anodic cyanation (replacement of methoxy, product *A*) than emulsions (replacement of hydrogen and methoxy, products *A* and *B*) (Table 2). But, contrary to Eberson's proposition, this variation in product distribution cannot be explained in terms of solvent effect alone. Indeed, all the other experimental conditions remain the same; changing CH_3CN to CH_2Cl_2 induces only a small difference in the ratio *A*/*B*. One obtains respectively 78/22 and 86/14 (Runs 2 and 3, Table 2). However, the nature and/or the concentration of the ammonium salt can modify the reaction selectivity (Runs 1 and 2, Table 2). We have thus studied the anodic cyanation of 1,2-DMB with different PTA (Tables 3 and 4).



(1)

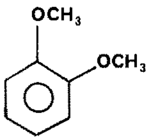
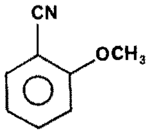
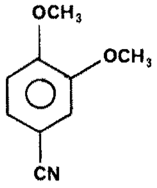
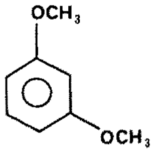
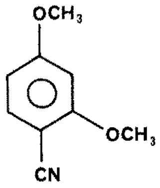


(2)

Since our experimental conditions (current density, anodic potential, dispersion of the organic phase) differ from those of Eberson and Helgee, the influence of these parameters were examined. The results obtained with $n\mathrm{Bu_4N^+HSO_4^-}$ (Table 1) indicate that neither the anodic potential nor the current density significantly affect the yields and the product distribution. Only a slight increase in polymeric yield is observed at higher potential (Run 4). On the contrary, yields of cyanated products vary remarkably with the dispersion state of the organic phase. A fine dispersion of CH_2Cl_2 in water obtained with an Ultra-Turrax

As expected from various theoretical and experimental reports in the literature [16–20], about 85% of the catalyst Q^+ is transferred into the organic phase (CH_2Cl_2) as Q^+CN^- when the PTA is a sulphate or a chloride salt (Runs 1, 2 and 8, 9). This value falls to 23–44% in the case of bromide salts (Runs 6 and 7). It is apparent from Table 3 that the amount of CN^- extracted into the organic phase increases with the lipophilic character of the cation (Q^+). The lowest value (23%) obtained in the presence of CTAB, although it is more hydrophobic than $n\mathrm{BuP}^+\phi_3\mathrm{Br}^-$, may be attributed to the micellization of the former in water.

Table 1. Effect of the anode potential and current density on the anodic cyanation of DMB–50 ml CH_2Cl_2 (0.04 mol dm^{-3} DMB)–50 ml H_2O (0.4 mol dm^{-3} NaCN, 0.04 mol dm^{-3} $nBu_4N^+HSO_4^-$); charges passed: 2F mol^{-1} DMB

Substrates	*Products*	*Stirrer*	*Anodic potential V vs SCE*	*Current* densities (mA cm^{-2})*	*Conversion (%)*	*Yields (%) chemical†*	*current*	*Product distribution (%)*		*Run*
								A	B	
	 **A**	magnetic bar	1.2 1.7 2.2 2.7	1.7–1.1 1.1–0.9 1.1–0.8 1–1.5	84 79 74 88	69 75 72 60	55 58 53 51	68 70 68 68	32 30 32 32	1 2 3 4
	 **B**	Ultra Turrax	constant‡ current	14	–	42§		70	30	5
	 **C**	magnetic bar	1.7	5–5	90	70	63	–		6
		Ultra Turrax	1.7 constant‡ current	5–5 14	48 –	54 69	24 60	– –		7 8

* Initial and final values; † based on unrecovered starting material; ‡ Eberson and Helgee [1]; § 3F mol^{-1} of substrate.

Table 2. Anodic cyanation (1.7 V vs ECS) of 1,2-DMB in different media 2F *mol*$^{-1}$ *of substrate*

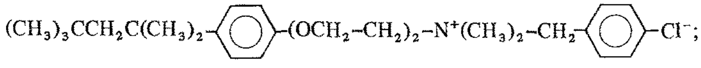
Run	*Media*		*Conversion (%)*	*Chemical yield (%)*	*Current yield (%)*	*Distribution A/B (%)*
1	CH_3CN* $Et_4N^+CN^-$:0.4 mol dm^{-3} Substrate: 0.023 mol dm^{-3}		–	94	–	100/0
2	nBu$_4$N$^+$CN$^-$:0.05 mol dm^{-3}	CH_3CN	92	72	65	78/22
3	nBu$_4$N$^+$ClO$_4^-$:0.45 mol dm^{-3}	CH_2Cl_2	63	89	55	86/14
4	$H_2O + CH_2Cl_2$† nBu$_4$N$^+$HSO$_4^-$		79	75	58	70/30

* See Andreades and Zahnov [15]; † electrolyte composition is the same as used in Table 1.

Table 3. Per cent of PTA transferred in CH_2Cl_2 *(50 ml) from an aqueous solution (50 ml) containing 0.04 mol dm*$^{-3}$ *PTA and 0.4 mol dm*$^{-3}$ *NaCN (pH 11.5)*

PTA	$[Na_2SO_4]$ (× 10^3 mol dm^{-3})	*Per cent of PTA* Q^+ *transferred in* CH_2Cl_2		$\frac{[Q^+CN^-]_{CH_2Cl_2}}{[Q^+ \text{total}]_{CH_2Cl_2}} \times 100$	*Run*
		Q^+ CN^-	Q^+ *total*		
nBu$_4$N$^+$HSO$_4^-$†	0	25	30	83	1
	2	21	–	–	2
	0	11	–	–	3
nBu$_4$N$^+$CN$^-$	0.7	23	–	–	4
	1.3	23	–	–	5
nBuP$^+\phi_3$Br$^-$	0	40	90	44	6
CTAB	0	4	17	23	7
BzCl‡	0	72	83	87	8
Aliquat 336§	0	63	75	84	9

CTAB is $C_{16}H_{33}N^+(CH_3)_3Br^-$; BzCl is



Aliquat 336 is tricaprylyl methylammonium chloride $(C_8H_{17})_3N^+CH_3Cl^-$.

* Based upon the total amount of PTA (average of two independent experiments); † neutralized to pH = 7 with (0.1 mol dm^{-3}) NaOH prior to NaCN addition; ‡ the destruction of BzCl by the basic cyanide solution [20, 22] can be avoided by operating at pH 10.5 (NaH_2PO_4/NaOH:0.1 mol dm^{-3}); § solubilized initially in CH_2Cl_2.

Table 4. Anodic cyanation of 1,2-DMB as a function of PTA electrolyte: aqueous 0.04 mol dm^{-3} *PTA – 0.4 mol dm*$^{-3}$ *NaCN (50 ml) (pH 11.5); methylene chloride (50 ml) – 0.45 mol dm*$^{-3}$ *DMB, charge passed equivalent to* 2F *mol*$^{-1}$

Run	*PTA*	*Anodic potential (V) vs SCE*	*Conversion (%)*	*Yields (%) Chemical**	*Current*	*Relative (%)*		*Organic phase*† *(× 10*^{2} *mol dm*$^{-3}$*)*	
						A	B	CN^-	Q^+ *total*
1	CTAB	1.7	32	67	21	62	38	0.18	0.7
2	nBuP$^+\phi_3$Br$^-$	1.7	72	69	48	69	31	1.6	3.6
3	nBu$_4$N$^+$HSO$_4^-$‡	1.7	79	75	58	70	30	1.0	1.2
4	Aliquat§	2.2	96	81	77	60	40	2.6	3.2
5	BzCl§¶	2.2	67	91	60	70	30	2.9	3.4

* Based on unrecovered starting material; † average of two independent experiments; ‡ neutralized with NaOH 0.1 mol dm^{-3}; § current intensity at 1.7 V drops rapidly to 0.5 mA cm^{-2} (after ~ 10 C); ¶ in the presence of NaH_2PO_4–NaOH; see ‡ of Table 3.

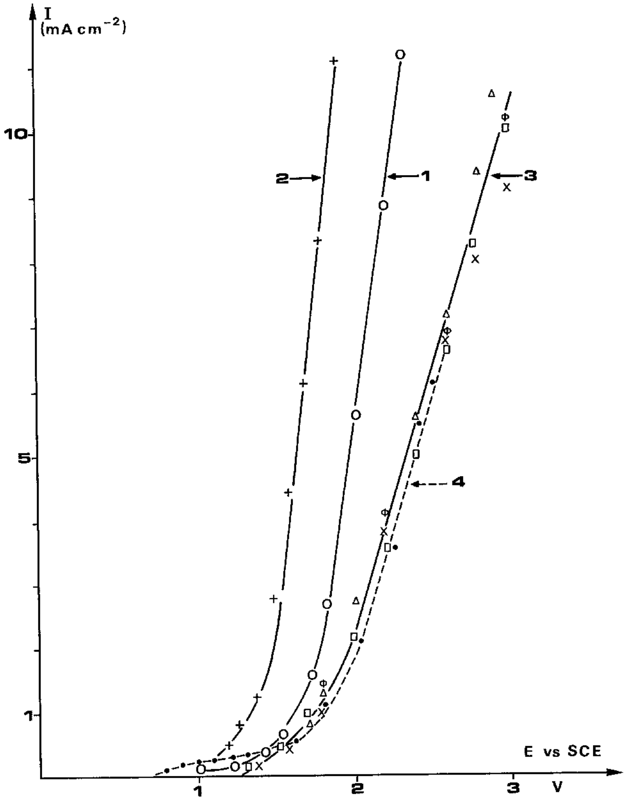


Fig. 2. Plots of electrolysis current vs anode potential in aqueous media (solid lines) and in CH_2Cl_2 (broken lines). 1. ○ – 0.2 mol dm^{-3} NaCN; 2. + – 0.02 mol dm^{-3} CTAB and 0.2 mol dm^{-3} NaCN; 3. 0.02 mol dm^{-3} PTA and 0.2 mol dm^{-3} NaCN; △ – $n\mathrm{Bu_4N^+HSO_4^-}$; ϕ – BzCl; □ – $[n\mathrm{BuP^+}]_3\mathrm{Br^-}$; × – A 336; 4. + – 0.5 mol dm^{-3} $n\mathrm{Bu_4N^+ClO_4^-}$ and 0.05 mol dm^{-3} $n\mathrm{Bu_4N^+CN^-}$ in CH_2Cl_2.

It is interesting to note that the well known salting-out effect due to Na_2SO_4 addition to $n\mathrm{Bu_4N^+CN^-}$ solution is rapidly achieved (Runs 3–5). Moreover, the salting-out factor is insignificant (compare Runs 1–5) in our experimental conditions, since $n\mathrm{Bu_4N^+HSO_4^-}$ is neutralized prior to NaCN addition. Consequently, all the experiments that follow were carried out without salt addition.

The conversion rate, yields and product distribution (*A*/*B*) of the anodic cyanation of 1,2-DMB (Reaction 1) as a function of different PTA are summarized in Table 4.

Chemical yields and the reaction selectivity are little affected by the nature of the PTA and the CN^- concentration in the organic phase. Indeed, 91% of the chemical yield (Run 5) drops to only 67% (Run 1), when the CN^- concentration is decreased by a factor 16 (2.9×10^{-2} mol dm^{-3} – 1.8×10^{-3} mol dm^{-3}). The product distribution (*A*/*B*) is *c.* 70/30 except in the cases of long chain quaternary salts (CTAB, A 336). These PTA lead to the two products *A* and *B* in the ratio *A*:*B* = 60:40, comparable to 55/45 obtained in cationic micellar aqueous medium [21].

Of further interest are the polarization curves *I*–*E* recorded in preparative electrolysis conditions. They predict that CN^- and Br^- ions undergo easy electron transfer at potential available for electrolysis experiments (for example, Curve 4, Fig. 2).

All the polarization curves plotted in aqueous media containing different PTA are similar (Curves 3, Fig. 2), except in the case of CTAB, which indicates a higher anodic current (Curves 1 and 2, Fig. 2). These curves are strongly modified when one switches to emulsified media (H_2O/CH_2Cl_2) (Curves in solid lines, Fig. 3).

In H_2O/CH_2Cl_2 emulsion and in the absence of 1,2-DMB, the anodic current results from the oxidation of anions present in the aqueous as well as in the organic phase. The relative importance of these two contributions depends mainly on the anode wetting by each phase. The low current densities obtained in the presence of A 336, $n\mathrm{Bu_4N^+HSO_4^-}$ and BzCl (Curves 4, 3, 5, Fig. 3) suggest that the anode coverage by the

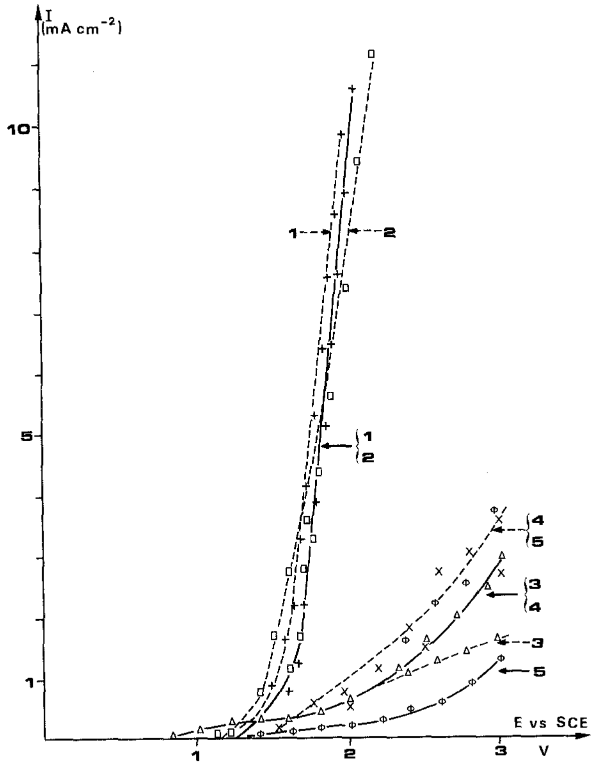


Fig. 3. Plots of electrolysis current vs anode potential for emulsions of 0.4 mol dm^{-3} NaCN–0.04 mol dm^{-3} PTA (50 ml H_2O) and 50 ml CH_2Cl_2 without (solid lines) and with 0.04 mol dm^{-3} 1,2-DMB (broken lines). 1. + – CTAB: $\tau = 32, R_i = 21$; 2. □ – nBuP$^+\phi_3$Br$^-$: $\tau = 72, R_i = 48$; 3. △ – nBu$_4$N$^+$HSO$_4^-$: $\tau = 79, R_i = 58$; 4. × – A 336: $\tau = 96, R_i = 77$; 5. ϕ – BzCl: $\tau = 67, R_i = 60$. τ and R_i indicate respectively percentage of conversion and current yield; the anodic potential was measured with a Luggin capillary.

aqueous phase is not important. Moreover, the effect of PTA is strikingly revealed by comparison of conversion rate and even more by current yields. CTAB, essentially present in the aqueous phase, gives the lowest current efficiency whereas A 336 and BzCl, soluble predominantly in the organic phase, show the best current yields (however, the low current densities require higher anodic potential in the latter two cases).

Hence we are led to conclude that the working electrode is essentially covered by the organic phase in the presence of A 336, BzCl and nBu$_4$N$^+$HSO$_4^-$. The low current densities can be attributed to the poor conductivity of the CH_2Cl_2 phase (low electrolyte concentration and dielectric constant) in which very few electroactive ions are present (Table 4), and secondly, due to unfavourable kinetics of ion transfer across the phase boundary H_2O–CH_2Cl_2 (adsorption of cationic surfactants at this interface) [23–26]. Likewise one should observe the same phenomenon with CTAB, had the anode wetting by CH_2Cl_2 been predominant. On the contrary, the high current densities observed with this PTA (Curve 1, Fig. 3) suggest that the aqueous phase is present on the anode.

These results should be treated with caution since polarization curves provide only approximate means of evaluating the anode wetting phenomena by the organic phase. For example, the I–E curve plotted in the presence of nBuP$^+\phi_3$Br$^-$ (Curve 2, Fig. 3) can be attributed to the partial aqueous phase oxidation or to the oxidation of Br$^-$, present in CH_2Cl_2. However, the second hypothesis seems to be more plausible because the I–E curve plotted with the same concentration of Br$^-$ in CH_2Cl_2 predicts a strong Br$^-$ oxidation and furthermore, the important ohmic drop observed in the vicinity of the anode in the emulsified medium can be easily interpretated if one admits the presence of the poor conducting CH_2Cl_2 phase on the anode.

The addition of 1,2-DMB to the previous emulsified solutions of NaCN and PTA leads to a slight increase in current densities and this corresponds to the aromatic substrate oxidation (curves in broken lines, Fig. 3). As is evident from the preceding discussions, the low conversion rate and current yield observed with CTAB, result from an important competitive aqueous phase oxidation. The increase in electrochemical efficiencies obtained with all the other PTA is associated with the anode coverage by the organic phase (Table 4 and Fig. 3). There is therefore reason to believe that the reaction ($ArH^{\cdot +}$ and CN^-) probably occurs in the CH_2Cl_2 phase next to the anode. This observation is supported by the fact that the best yields are obtained with big organic droplets (magnetic bar stirrer) (Table 1) as they can penetrate the hydrodynamic boundary layer and thus come in contact with the anode [27, 28].

The 48% current yield with $n\text{BuP}^+\phi_3\text{Br}^-$ is probably due to to co-oxidation of Br^- ions in the CH_2Cl_2 as explained above. Moreover, in spite of a good wetting of the anode by CH_2Cl_2 in the presence of BzCl, the current yield and the electrochemical conversion are decreased by the oxidation of this PTA, which must be strongly adsorbed on Pt via its aromatic ring.

Finally, one may note that anode wetting by CH_2Cl_2 can vary during the electrolysis, especially with A 336. In this case, current intensity drops rapidly at the beginning of the experiment and reaches the value observed with BzCl (see footnote §, Table 4).

4. Conclusion

Study of chemical and current yields as well as of the preparative I–E curves indicates that the main problems encountered in electrocyanation of aromatic substrates under PTC conditions are the type of emulsion and the choice of PTA. This choice is governed by the hydrophobic character of Q^+ (anode wetting and CN^- extraction) and by the nature of the counter ion X^- (intervenes in CN^- extraction and competitive co-oxidation phenomena).

Among all the PTA used in the present work, A 336, a very hydrophobic quaternary ammonium chloride (not soluble in water), best fulfills the above conditions. We believe that the difficulty of working at higher anodic potential with this PTA can be overcome, at least to some extent, by rendering the organic phase more conductive by the addition of an appropriate supporting electrolyte.

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