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THE ELECTRODE/ELECTROLYTE INTERFACE IN NON-AQUEOUS  
SOLVENTS: GLASSY CARBON/TETRABUTYLAMMONIUM ELECTROLYTE  
IN N,N-DIMETHYLFORMAMIDE

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ABSTRACT

The interfacial region between a glassy carbon electrode and tetrabutylammonium electrolytes (halide, perchlorate and tetrafluoroborate) in N,N-dimethylformamide has been studied using impedance techniques at varying electrolyte concentration (0.01M  $\rightarrow$  0.20M) in the potential range 0.0  $\rightarrow$  -2.0V vs. SCE. The spectra can be divided into a concentration independent low frequency part ( $\ll$ 100Hz) which is the same for all these electrolytes and a high frequency part depending on electrolyte and its concentration but not dc potential. Comparison is made with spectra obtained in aqueous solution. The results are discussed in terms of the physical properties of the solvent, electrolyte, glassy carbon, and the structure of the interfacial region. The low frequency feature is ascribed to electrolyte/electrode interactions and electrode porosity, and the high frequency feature to processes involving the electrolyte anion.

**KEYWORDS:** glassy carbon electrode, electrode/electrolyte interface, DMF, impedance, tetrabutylammonium salts.

INTRODUCTION

Many electrode reactions in non-aqueous media are carried out using alkylammonium salts as supporting electrolytes [1]. The large negative potential range on mercury electrodes can be increased in the positive direction by the use of solid electrodes such as glassy carbon. As in

aqueous media, the structure of the double layer can have an important effect on electrode kinetics and the electrolyte can even take part in the reaction of electroactive species. The interfacial region between mercury and alkylammonium electrolytes has been the subject of a number of studies in aqueous media [2], and in *N,N*-dimethylformamide (DMF) with respect to the formation of sodium amalgam [3]. At solid electrodes in DMF a few kinetic studies have been carried out [4], but the interfacial region has been little studied.

Our interest in the interface glassy carbon/alkylammonium electrolyte in DMF stemmed from work carried out on the electrochemical reduction of porphyrin free bases in tetraalkylammonium electrolytes in DMF at glassy carbon electrodes [5]. In these electrode reactions the identity of the electrolyte cation was found to have little effect on porphyrin reduction, but the anion identity (halide or perchlorate) affected the voltammetric profile significantly. A study of this interface using impedance techniques for a number of different tetra-butylammonium salts, namely halides, perchlorate and tetrafluoroborate, was initiated in order to probe the role of the supporting electrolyte, for varying electrolyte concentration (0.01M → 0.20M) and dc potential (0.0 → -2.0V vs. SCE). Owing to the surface condition of glassy carbon [6], a purely capacitative behaviour of the interface is not to be expected and a full impedance spectrum is necessary. Cyclic voltammograms in electrolyte show a significant background current ( $\approx -30\mu\text{A}$  at -1.5V vs. SCE) passing through zero at about -0.8V in thoroughly deoxygenated solution and which does not diminish with time elapsed after starting the experiment. Some preliminary results for chloride, bromide and perchlorate have already been presented [7].

#### EXPERIMENTAL

The solvent, *N,N*-dimethylformamide (DMF) (Merck pro analysi), and the tetrabutylammonium salts: perchlorate (TBAP), iodide (TBAI), bromide (TBAB), chloride (TBAC) and tetrafluoroborate (TBATFB) (Fluka purissimum - purum in the case of TBAC) were purified as described elsewhere [5] and according to standard procedures [8], and dried under vacuum. DMF was

stored over Linde 4A molecular sieves in the dark and used within 24h. of distillation.

A glassy carbon (Plessey) disc working electrode of area  $0.38\text{cm}^2$ , enclosed in a Kel-F sheath was polished with diamond aerosol (Hyprez Diamond Spray, Engis) down to  $1\mu\text{m}$  on a polishing table. It was polished regularly with  $0.3\mu\text{m}$  alumina in a slurry and then cleaned carefully with triply distilled water, dried and rinsed in DMF before being introduced into the cell. A platinum counter electrode and a Radiometer K401 SCE reference electrode inserted into a Luggin capillary were employed. The cell was painted black to avoid photochemical degradation of the solvent, and thermostatted at  $25.0^\circ\text{C}$ . Solutions were deoxygenated by bubbling with DMF-saturated oxy-free nitrogen for 1h. prior to initiating experiments; during experiments nitrogen was passed over the solution.

Impedance spectra were recorded over the range  $0.1\text{Hz} \rightarrow 65\text{kHz}$  with a Solartron 1250 Frequency Response Analyser coupled to a Solartron 1286 Electrochemical Interface and controlled by a HP9816 microcomputer. A 5mV rms sinusoidal perturbation was used and the response recorded by means of the auto integration facility (max. 1% standard deviation).

#### RESULTS AND DISCUSSION

##### General remarks

A typical example of the impedance spectra obtained is shown in Fig.1. In all cases, regardless of the electrolyte, concentration or dc potential a "low" frequency and a "high" frequency feature were encountered. For comparative purposes, and in order to test whether these results depend on electrode material, electrolyte or solvent, some experiments were undertaken in aqueous solution with the same electrolytes and with other electrolytes. Fig.2 shows typical spectra for 0.01M TBAI and 1.0M KCl. It can be deduced that the form of the low frequency feature is not solvent dependent - this will be discussed further below.

##### Low frequency

Low frequency in this context signifies up to about 100Hz. The form of the spectrum is always the same, being a line with a slight, but

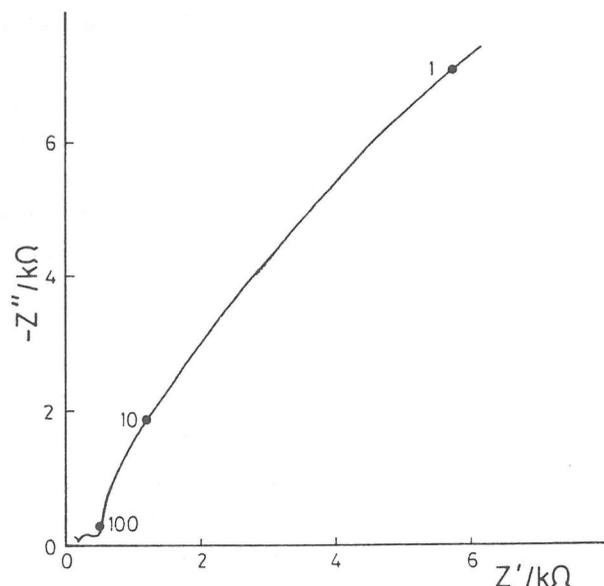


Fig.1 A typical impedance spectrum: 0.05M TBAB in DMF at glassy carbon electrode. Frequencies in Hz.

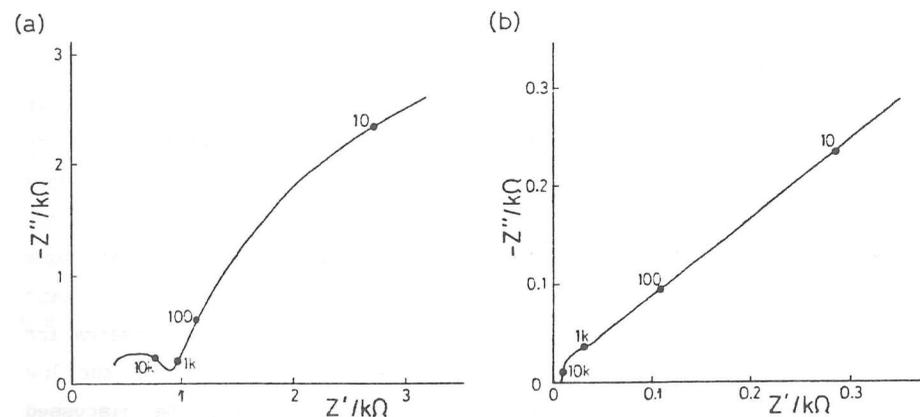


Fig.2 Impedance spectra in water at glassy carbon electrode; frequencies in Hz (a) 0.01M TBAI; (b) 1.0M KCl.

moreless constant, curvature, independent of the electrolyte and its concentration, the only dependence being in the intercept on the real axis by extrapolation. As this is a measure of solution resistivity, differences between electrolytes can be explained by dissociation of ion pairs occurring to different extents and the consequent effect on the electrolyte ion activity. Assuming a simple charge transfer process, a resistance of around  $8k\Omega\text{ cm}^2$  and a capacity of  $15\text{-}20\mu\text{F cm}^{-2}$  are obtained for a parallel RC circuit. No dependence on dc potential was found in the range studied, despite the fact that negative of  $-0.8\text{V}$  vs SCE currents are cathodic, and positive they are anodic.

The low frequency features of Figs.1 and 2a are of a very similar form, and thus we deduce that the low frequency part of the spectrum is a function of electrolyte and electrode material. Fig.2b gives a straight line diffusional impedance (of slope  $\approx 35^\circ$ ) and shows that the electrolyte is important, but also suggests that surface roughness of the electrode should be considered, and possibly its structure and surface groups.

Glassy carbon is an isotropic electrode material with two important characteristics relative to other solid electrodes. Firstly, its ability to affect the rate of electrochemical reactions is very pronounced owing to the ease with which surface links can be formed, particularly with oxygen and hydrogen, a property used to good effect in electrode modification [9], and in electrochemical pretreatment of glassy carbon to improve the kinetics [10], and to reduce adsorption [11]. Secondly, it exhibits significant porosity [12,13]: it has been found [13] that the pores of glassy carbon are sufficiently large to accommodate  $\text{TEA}^+$ , but it is unlikely that  $\text{TBA}^+$  can enter.

The roughness of the electrode can be considered following the expression

$$Y_{\text{exp}} = bY^{1/\alpha} \quad (1)$$

according to the de Levie criteria [14,15], where  $Y_{\text{exp}}$  is the observed admittance of a rough interface that when smooth has admittance  $Y$ ,  $\alpha$  is an exponent that varies between  $\frac{1}{2}$  for a fully porous electrode and 1 for a smooth electrode and  $b$  includes all the frequency independent parts. Applying the expression in reverse i.e. raising the impedance modulus to the power of  $1/\alpha$  and multiplying the phase angle by  $1/\alpha$  leads to values for  $\alpha$ . Doing this gives a minimum value of  $\alpha=0.8$  (lower values transform

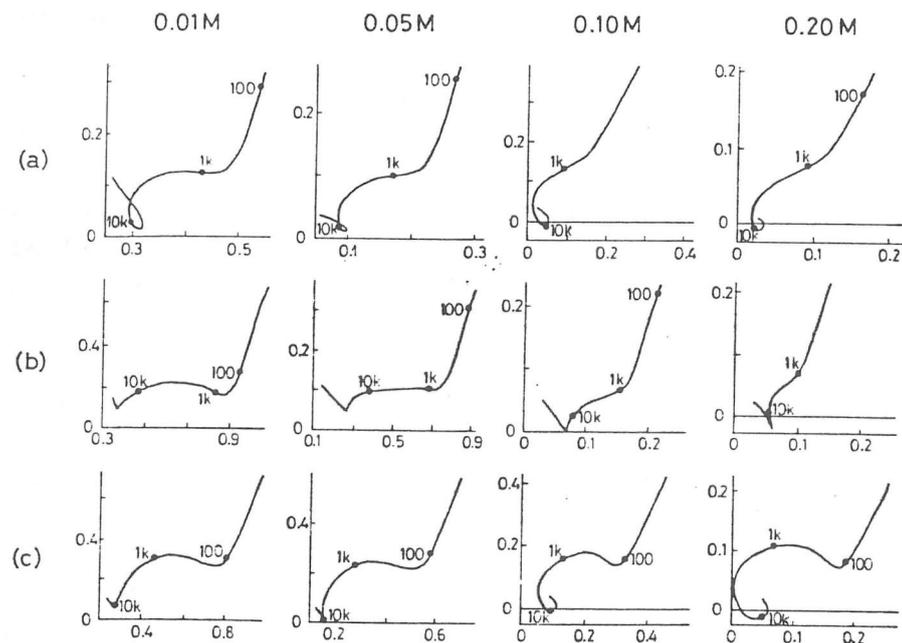


Fig.3 High frequency features of the impedance spectra at varying concentration for: (a) TBAC; (b) TBAB; (c) TBAI. Frequencies in Hz. x-axis:  $Z'/k\Omega$ ; y-axis:  $-Z''/k\Omega$ .

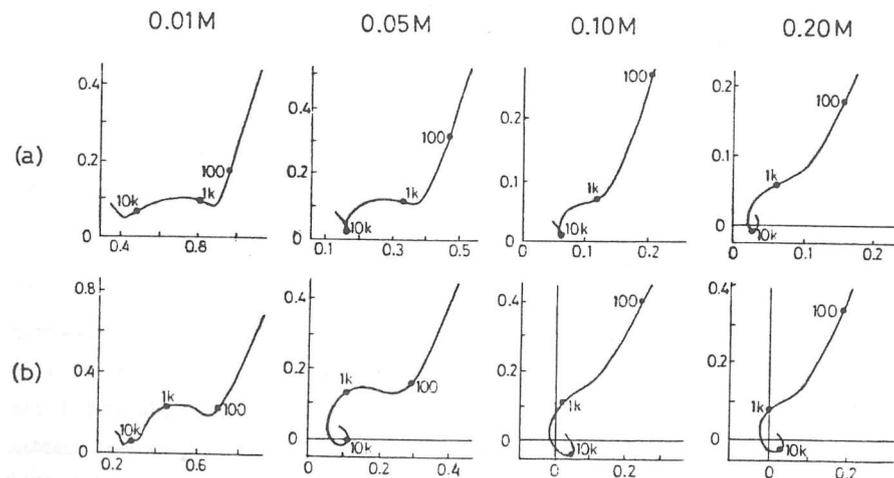


Fig.4 High frequency features of the impedance spectra at varying concentration for: (a) TBAP; (b) TBATFB. Frequencies in Hz. x-axis:  $Z'/k\Omega$ ; y-axis:  $-Z''/k\Omega$ .

the initial slope to a negative value), the centre of the semicircle moving up to the real axis. Applying (1) to the KCl spectra, in order to obtain a line of  $45^\circ$  slope corresponding to a diffusional impedance also leads to a value of  $\alpha=0.8$ . The agreement between the values in the different media confirms the importance of surface roughness.

We can thus conclude that the shape of this feature is caused by the porosity of the glassy carbon and by the electrolyte identity.

#### High frequency

In contrast to the low frequency part, at frequencies higher than 100Hz another feature appears whose form varies with anion identity and concentration, but is essentially based on a semicircular shape. Fig.3 shows results for halide electrolytes and Fig.4 for the other two electrolytes. Once again there is little dependence on applied dc potential, except a small difference between zero volts (anodic current) and the other values (see Fig.5). At very high frequency, i.e.  $\geq 10\text{kHz}$ , there are inductive aspects in some cases: since this may be due to cell geometry or external connections and leads etc., this part of the spectra will not be used for quantitative analysis.

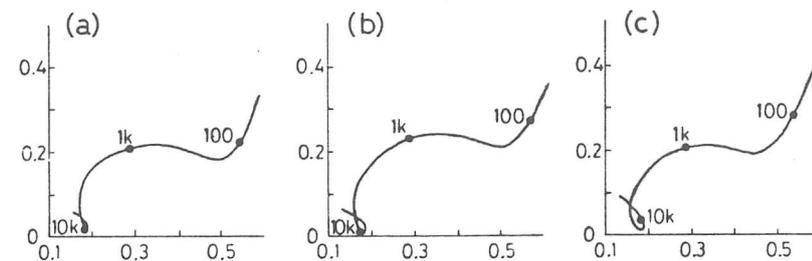


Fig.5 Effect of dc potential on high frequency feature for 0.05M TBAI in DMF at (a) -2.0V (b) -1.0V (c) 0.0V vs. SCE. Frequencies in Hz. x-axis:  $Z'/k\Omega$ ; y-axis:  $-Z''/k\Omega$ .

The appearance of a semicircle suggests that a rough calculation of the double layer capacity due to this electrode process can be made for a parallel RC circuit. Values obtained are of the order expected for this type of interface i.e. electrolyte solution in aprotic solvent.

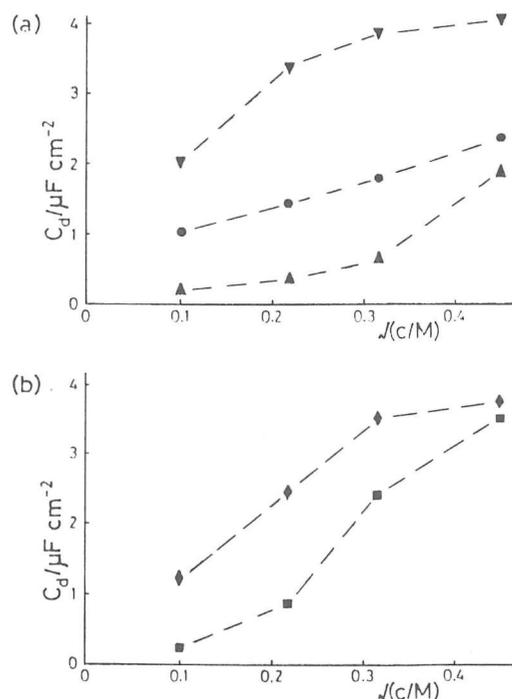


Fig.6 Plots of double layer capacity,  $C_d$ , from high frequency feature vs.  $c^{1/2}$ . (a) Halide electrolytes:  $\nabla$  TBAC,  $\bullet$  TBAI,  $\blacktriangle$  TBAB; (b) Other electrolytes:  $\blacklozenge$  TBATFB,  $\blacksquare$  TBAP.

Fig.6 displays the results obtained in plots done supposing a Gouy-Chapman type dependence on electrolyte concentration. As can be seen, this is not a very satisfactory approximation. Chloride gives the highest values and appears to reach a maximum value at 0.10M. The order of calculated capacities is



whereas ion size is in the order (Table 1)



since solvation numbers seem to be approximately the same (see Table 1 and next section). Thus, as  $\text{BF}_4^-$  and  $\text{ClO}_4^-$  have moreless the same radius, it is  $\text{Cl}^-$  that is clearly out of order. This anion must therefore have a different type of interaction at the electrode surface than the others. We also note that inductive loops occur mostly with  $\text{ClO}_4^-$  and  $\text{BF}_4^-$ , so it may be that charge distribution within the anion is a factor

to be taken into account. Indeed, as Fig.6b shows, these two anions show a higher dependence of  $C_d$  on concentration than the halide ions.

TABLE 1 Crystal radii [16] and solvation numbers [17] for selected ions in DMF

	Crystal radius/nm	Solvation number
$(\text{Me})_4\text{N}^+$	0.347	1.5
$(\text{Et})_4\text{N}^+$	0.400	1.7
$(n\text{-Pr})_4\text{N}^+$	0.452	- <sup>a</sup>
$(n\text{-Bu})_4\text{N}^+$	0.494	- <sup>a</sup>
$\text{Cl}^-$	0.181	1.6
$\text{Br}^-$	0.195	1.5
$\text{I}^-$	0.216	1.4
$\text{ClO}_4^-$	0.292	1.4
$\text{BF}_4^-$	0.275 <sup>b</sup>	- <sup>a</sup>

<sup>a</sup> Not available

<sup>b</sup> From Ref.18, equal to mean B-F bond distance in crystalline  $\text{NaBF}_4$  + 0.136nm.

#### Final Remarks

It is useful to consider the role played by the solvent. DMF is an aprotic solvent of bulk relative permittivity  $\epsilon_r=36.7$ , roughly half that of water, Table 2. X-ray studies of the pure liquid have demonstrated only a weak intermolecular interaction [19]. The way in which the molecules align themselves is important and which is highly dependent on the other species present. It is useful for modelling purposes to define a spherical radius: one value suggested is 0.34nm [3], in reasonable agreement with the structural data, taking as the size a sphere encompassing an entire molecule; from the molar volume, assuming ccp or hcp packing, one obtains a radius of 0.28nm [20]. The solvent molecules are of a similar size to the electrolyte anions, but smaller than the  $\approx 0.5\text{nm}$  of  $\text{TBA}^+$ .

Solvation can be discussed in terms of the Gutmann donor number DN (nucleophilicity) and acceptor number AN (electrophilicity). Values for DMF and for several other often-employed non-aqueous solvents plus water,

together with the Dimroth-Reichardt  $E_T$  values [23] that like the acceptor numbers measure acidic character, are shown in Table 2. It can be seen that DMF, DMSO and AcN present very similar values.

TABLE 2 Physical properties of selected solvents. Gutmann donor number (DN) and acceptor number (AN), Dimroth-Reichardt parameter  $E_T$ , and relative permittivity,  $\epsilon_r$ .

Solvent	DN <sup>a</sup>	AN <sup>b</sup>	$E_T$ <sup>c</sup>	$\epsilon_r$
Dimethylformamide (DMF)	26.6	16.0	43.8	36.7
Dimethylsulphoxide (DMSO)	29.8	19.3	45.0	48.9
Acetonitrile (AcN)	14.1	18.9	46.0	38.0
Water	33.0	54.8	63.1	80.4

<sup>a</sup> Units in kcal mol<sup>-1</sup>, equal to the negative of the enthalpy change for reaction of the solvent with SbCl<sub>5</sub> to form a 1:1 adduct [21].

<sup>b</sup> From <sup>31</sup>P nmr measurements of triphenylphosphine oxide dissolved in the solvent [22].

<sup>c</sup> Units in kcal mol<sup>-1</sup>, energy of  $\pi + \pi^*$  transition, dependent on the solvent [23].

With respect to ion-solvent interactions, Krygowski and Fawcett [24] did some calculations for solvent activity coefficients for several cations and anions in a number of solvents based on DN and  $E_T$  values: for halide ions they obtained the order Br<sup>-</sup>>Cl<sup>-</sup>>I<sup>-</sup> for DN coefficients ("small" and positive) and I<sup>-</sup>>Br<sup>-</sup>>Cl<sup>-</sup> for  $E_T$  coefficients ("large" and negative) - the latter therefore being predominant and showing the stabilisation effect of anion solvation. These calculations are essentially enthalpic; however, solvation can be highly dependent on entropic considerations. Based purely on the entropic criterion ion solvation numbers have been calculated [17], and are shown in Table 1 for several ions: the value is around 1.5 for a wide variety of ions in DMF.

It is clear from Table 2 that although most of the properties of DMF with respect to intermolecular interactions, as indeed of other common non-aqueous solvents, are substantially different from those of water, the DN values are similar. This agrees with the impedance results for TBA electrolytes' "low frequency" feature being very similar in DMF and in H<sub>2</sub>O, as the DN refers to cation solvation.

Research on mercury electrodes in aqueous solution found that the adsorption of symmetric tetraalkylammonium ions occurred with three alkyl chains directed towards the electrode, presumably displacing solvent and giving an ionic radius of 0.50nm [25] (cf. crystal radius 0.494nm - Table 1). In a further study [26], the influence of the anion on the adsorption of the TBA<sup>+</sup> cation was demonstrated, attributed to the formation of non-paired and paired ions [27] in the interfacial region, the ion pairs resulting partly from the fact that near the interface the solution is effectively more concentrated. Saturation could therefore be reached as found in this work for chloride ions.

The results suggest that it is legitimate to consider an interfacial region with a structure similar to that in aqueous solution, depending more on electrolyte identity than solvent or solvation, at least between DMF and water. In explaining the differences observed between TBA electrolyte and KCl, it should be remembered that the anions will be no closer than the second layer, perhaps as ion pairs in the former case as described above for mercury, and the high frequency loop corresponds to processes involving this layer of species on the electrode surface.

## CONCLUSIONS

This study has demonstrated the influence of the electrolyte anion on the structure of the interfacial region at glassy carbon electrodes in DMF and the influence of electrode surface roughness on the impedance spectra. A more complete elucidation of the interface will require a deeper knowledge of ionic solvation and liquid structure close to the electrode in these media.

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CURRENT REVERSAL CHRONOPOTENTIOMETRY AT SPHERICAL ELECTRODES

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ABSTRACT

A general study on current reversal chronopotentiometry at spherical electrodes (as are the hanging mercury drop electrode or the static mercury drop electrode) is carried out. The effects of amalgam formation, insolubility of reaction product and electrode curvature on the potential time functions are presented. The value of the ratio  $\tau'/t_2$  (where  $\tau'$  is the transition time in the reverse step and  $t_2$  is the previous electrolysis time) can be used as diagnostic criterion to detect amalgamation or insoluble product formation. Methods to determine kinetic parameters and the formal standard potential of the electroactive couple in all the possible behaviours of the reduced species are proposed.

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