

ELECTROCHEMICAL CHARACTERISTICS OF A CARBON PASTE ELECTRODE WITH DIAMINODURENE AND PEAT

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ABSTRACT. The electrochemical behaviour of diaminodurene in the solid state, at a carbon paste electrode, was studied. Chronocoulometric and cyclic voltammetric experiments were carried out. Under the experimental conditions diaminodurene behaved reversibly.

INTRODUCTION

The use of a carbon paste electrode (CPE) in electrochemical studies has already been described elsewhere [1-3]. The electrochemical stability and energetic properties of organic compounds, mixed with carbon, were investigated [3-8].

In this paper we describe the electrochemical properties of the diaminodurene (1)/diaminodurene radical couple, which is known to act as a reversible redox system [6]. Carbon black was used in our experiments and was partially substituted by peat, a carbon widely available in Senegal [9-11].

EXPERIMENTAL

Current-potential curves were recorded using a Tacussel PJT 120-1 potentiostat-galvanostat coupled to a pilot Tacussel type GSTP 4 and a SEFRAM X-Y recorder (Tacussel électronique, Lyon, France). A saturated calomel reference electrode (SCE), and Pt auxiliary electrode were used. The working electrode [8, 12] is shown in Figure 1.

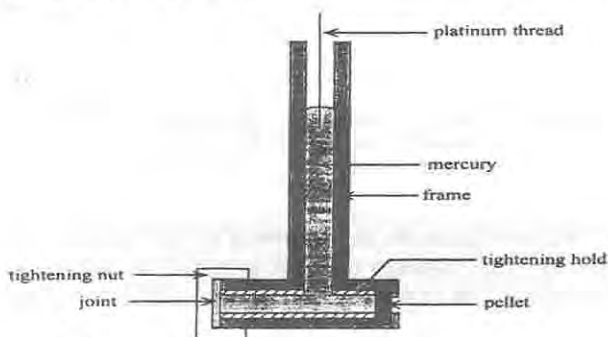
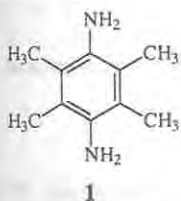


Figure 1. Transverse section of the T-tube working electrode.

The CPE was prepared by mixing 100 mg of diaminodurene, 45 mg of carbon black, 4 mg of peat and 10 mg of Teflon. The mixture was pressed in a mortar under a pressure of 6. t/cm^2 to form a pellet. Measurements were performed in a 4 M KCl solution using scan rates in the range between 1 and 6 mV/s. Britton and Robinson buffer solutions were used in chronocoulometry to determine the formal potential

RESULTS AND DISCUSSION

Figure 2 and Table 1 show that the values of $(E_p^{red} + E_p^{ox})/2$ are close to constant and give the equilibrium potential of the diaminodurene/diaminodurene radical couple [3, 5, 6].

Table 1. Variation of peak currents and peak potentials with scan rates (4 M KCl).

V (mV/s)	$I_p(ox)$ (mA)	$I_p(red)$ (mA)	$E_p(ox)$ (mV)	$E_p(red)$ (mV)	$[E_p(ox) + E_p(red)]/2$ (mV)
1	6.0	-6.4	100	-270	-85
2	7.6	-9.0	100	-280	-90
4	10.8	-12.0	110	-290	-90
6	12.6	-14.0	140	-300	-80

The dependences of the peak currents on sweep rate are shown in Figure 3. Since the active matter is in the solid state, it remains always within the carbon paste electrode. Since adsorption occurs at the surface of the electrode, one expects a linear dependence of I on the scan rate [13].

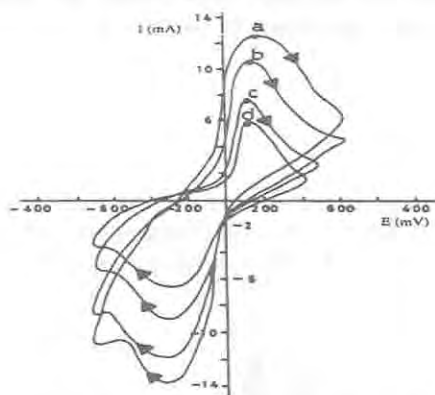


Figure 2. Variation of peak current with scan rates (4 M KCl). a) 6 mV/s; b) 4 mV/s; c) 2 mV/s; d) 1 mV/s.

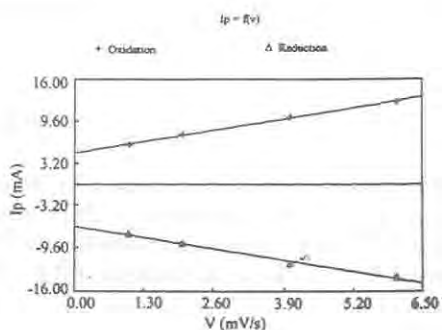


Figure 3. Variation of peak current with scan rate.

Figure 4 shows the dependence of the peak potential on electrolyte concentration. We note that the gaps between the peak potentials in oxidation and in reduction decrease and the absolute values of peak current increase with concentration.

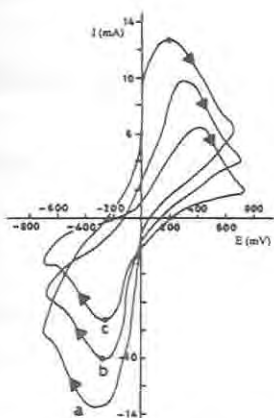


Figure 4. Variation of peak current and peak potential with electrolyte concentration. a) 4 M; b) 2 M; c) 0.5 M KCl (scan rate 6 mV/s).

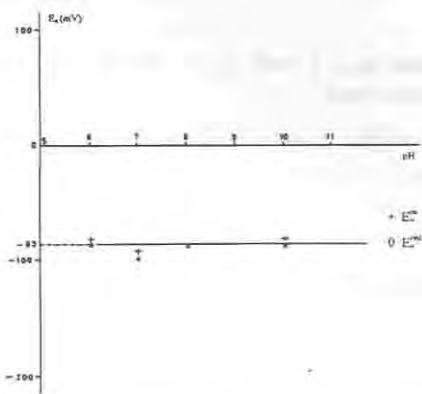


Figure 5. Determination of E_0 by extrapolation of the $E = f(\text{pH})$ curve.

Formal potential of the system. The formal potential of the system (E_0^*) is determined by extrapolation of the curves $E_{i=0}^{red} = f(\text{pH})$ and $E_{i=0}^{ox} = f(\text{pH})$. Here $E_{i=0}^{red}$ and $E_{i=0}^{ox}$ are the equilibrium reduction and oxidation potentials, respectively. We observed that the values obtained are very close and independent of the pH (Table 2). Figure 5 gives the value of the formal potential, $E_0^* = -83$ mV (vs SCE). According to this value diaminodurene should be used as an anode. The value obtained at about pH 7 confirms that there is no participation of protons in the electrochemical reaction.

Table 2. Influence of pH on the potential of the electrochemical reaction.

pH	6	7	8	10
E^{ox} (mV)	-81	-86	-84	-82
E^{red} (mV)	-82	-87	-85	-85

Influence of the chloride ions concentration. Figure 6 gives the variation of potentials with concentration of chloride ions. This was obtained from cyclic voltammograms. We observed that the potentials increased with the Cl^- concentrations. A slope of -61 mV/decade was obtained from the experimental values.

The initial electron transfer in our system can be depicted as shown in equation 1 following the proposal made by Dufeu [6].



where, $\widehat{\text{DD}}$ and DD^+ symbolize the diaminodurene molecule and the diaminodurene radical cation, respectively. This radical cation is in equilibrium between the liquid and the solid phases. As the diaminodurene is essentially in the solid state, the potential of the system at open circuit is given by:

$$E = E_0 + (RT/F) \cdot \ln(a_{\text{DD}^+})$$

$$E = E'_o (RT/F) \cdot \ln(a_{DD^+})_{aq}$$

where $(a_{DD^+})_s$ and $(a_{DD^+})_{aq}$ are the cation radical activities in the solid phase and in solution, respectively.

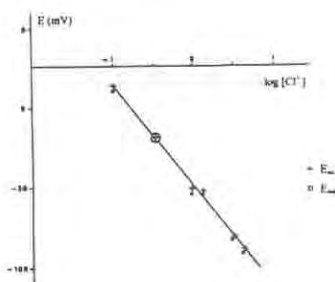
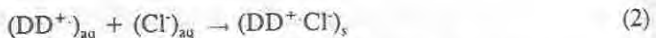


Figure 6. Effect of chloride ion concentration on the potential of the electrochemical reaction.

The electrochemical reaction of diaminodurene in KCl solution leads to the formation of diaminodurene chloride [6]:



Thus, assuming that activity is equal to concentration in solution, the potential is given by:

$$E = E'_o + (RT/F) \cdot \ln(Cl^-)$$

The theoretical slope is -59 mV/decade and is comparable to that found experimentally. The dependence of the potential on the logarithm of the chloride ions concentration proves the existence of a stable cation radical in the form of diaminodurene chloride. The electrode can therefore be considered as a chloride ion indicator electrode.

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