

## FORMATION OF A NEW ELECTROACTIVE FILM BY POTENTIAL SWEEP ELECTROLYSIS OF 4-AMINOQUINALDINE

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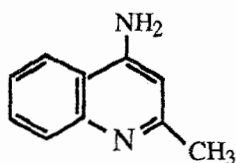
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### ABSTRACT

*Cyclic voltammetry of 4-aminoquinoldine in acidic aqueous and acetonitrile solution were studied. Only in acidic aqueous solution, polymeric film was formed on glassy carbon electrode when the potential was cycled between 0.0 and 1200 mV vs Ag / AgCl at 100 mV / sec in 1N HCl solution. The poly (4-aminoquinoldine) film coated glassy carbon electrode showed a reversible oxidation-reduction response in acidic medium. Based on IR absorption spectroscopic characterization of the film, a polymerization mechanism was proposed.*

### INTRODUCTION

The attractiveness of the electropolymerization reaction as an approach for preparing polymers of the polyaniline with electroactive properties and variable conductivity<sup>(1)</sup> promotes us to study the reactions of heterocyclic amines which undergo facile oxidation such as 4-aminoquinoldine. Previous reports on the biological activities of amino quinolines encouraged us to investigate this system.



4-Aminoquinoldine

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## EXPERIMENTAL

### Materials

4-Aminoquinaldine, lithium perchlorate and acetonitrile were obtained from Aldrich Co. and used without further purification. Aqueous solutions were prepared from distilled water.

### Apparatus

Cyclic voltammetry (CV) was carried out using a Cypress computer measuring system for electroanalytical model CYSY-IB. Current-voltage curves were recorded on Hewlett-Packard model 7440A. Analytical cell model C-IA (Bioanalytical) was used together with a glassy carbon electrode (3.0 mm dia.) as working electrode, a platinum counter electrode and an Ag / AgCl reference electrode. IR spectra were recorded on Perkin-Elmer 598 spectrometer.

### Poly (4-aminoquinaldine) film Formation

Poly (4-aminoquinaldine) (PAQ) films were prepared on glassy carbon electrode by potential-sweep electrolysis using the analytical cell used for CV. The PAQ film was produced by sweeping continuously between 0.0 and +1200 mV vs Ag / AgCl at mV / sec in 1N HCl solution containing 0.05 M 4-aminoquinaldine. The film coated electrodes are subsequently rinsed with 1N HCl and then with distilled water and used for further electrochemical measurements.

## RESULTS AND DISCUSSION

### Cyclic Voltammetry of 4-aminoquinaldine

#### a) In Acidic Aqueous Solution

Typical cyclic Voltammograms of 0.05 M 4- aminoquinaldine at glassy carbon in 1N HCl are shown in Fig. 1. The electrode potential was swept continuously at a rate 100 mV / sec. between 0 mV and 1200 mV vs Ag / AgCl. The monomer electrooxidized irreversibly in one anodic peak at 996 mV (from the first potential scan). As the current decreased gradually due to blocking the electrode surface by a growing barrier film.

#### b) In Non -Aqueous Medium

Fig. 2 show a series of cyclic voltammograms that are recorded for the electrooxidation of 0.05 M 4-aminoquinaldine at glassy carbon electrode in acetonitrile containing 0.1 M LiClO<sub>4</sub> and 0.05 M pyridine. The initial oxidation scan showed an irreversible wave at 1238 mV Ag / AgCl. On subsequent scans, this anodic wave shifted to more positive potential and the current decreased in magnitude gradually due to the film formation.

### Polymeric Film Formation and IR Spectroscopic Characterization

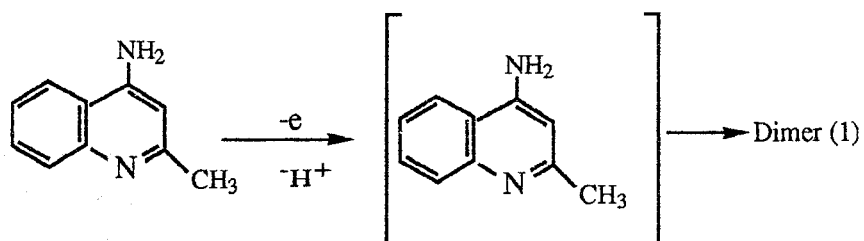
In non-aqueous medium and in the presence of pyridine, the formation of soluble products predominated and no polymeric film was detected. PAQ were prepared by potential sweep electrolysis (cf. Experimental). Ir spectrum of the obtained film has absorption peaks at 3300- 3500 cm<sup>-1</sup> (NH stretching), 1670- 1680 cm<sup>-1</sup> (C=N bonds)

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and 1300, 1270  $\text{cm}^{-1}$  (secondary aromatic amines). This agrees with the polymerization occurs via the formation of C-N=C and C-NH-C bonds (2-6).

#### 4- Aminoquinaldine Oxidation Mechanism

On the basis of the experimental results, it appeared that the anodic oxidation of 4-aminoquinaldine (AQ) follows the polymerization mechanism proposed for the primary aromatic amines<sup>(7-12)</sup>. The AQ is oxidized to a cation radical (AQ)<sup>\*+</sup> which suffered a fast irreversible chemical reaction to give the dimer D as shown in Eq. 1.



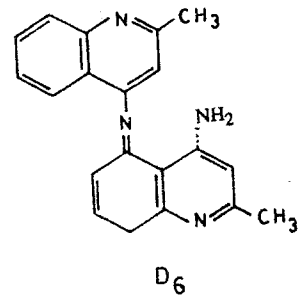
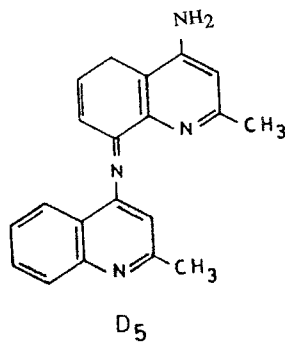
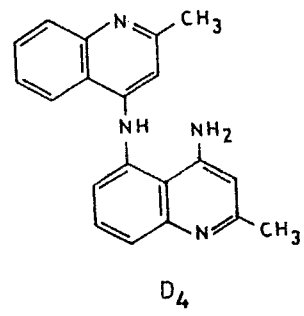
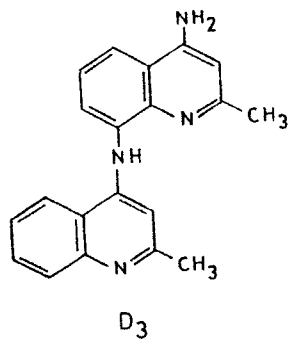
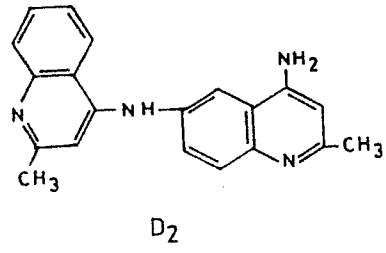
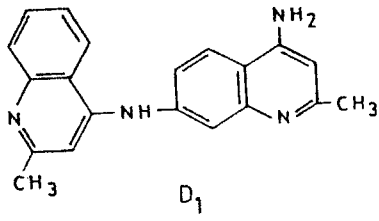
The most probable structure of the dimer are D<sub>1</sub> to D<sub>6</sub> as shown below.

The formed dimer D is electrooxidized to different trimers and tetramers. As the polymerization proceed, a polymer of a complicated structure is formed and cross-linking occurs.

#### Cyclic Voltammetric Response of PAQ film.

The PAQ film was found to be electroinactive in non-aqueous media (eg. CH<sub>3</sub> CN / LiClO<sub>4</sub>) but it is electroactive in aqueous

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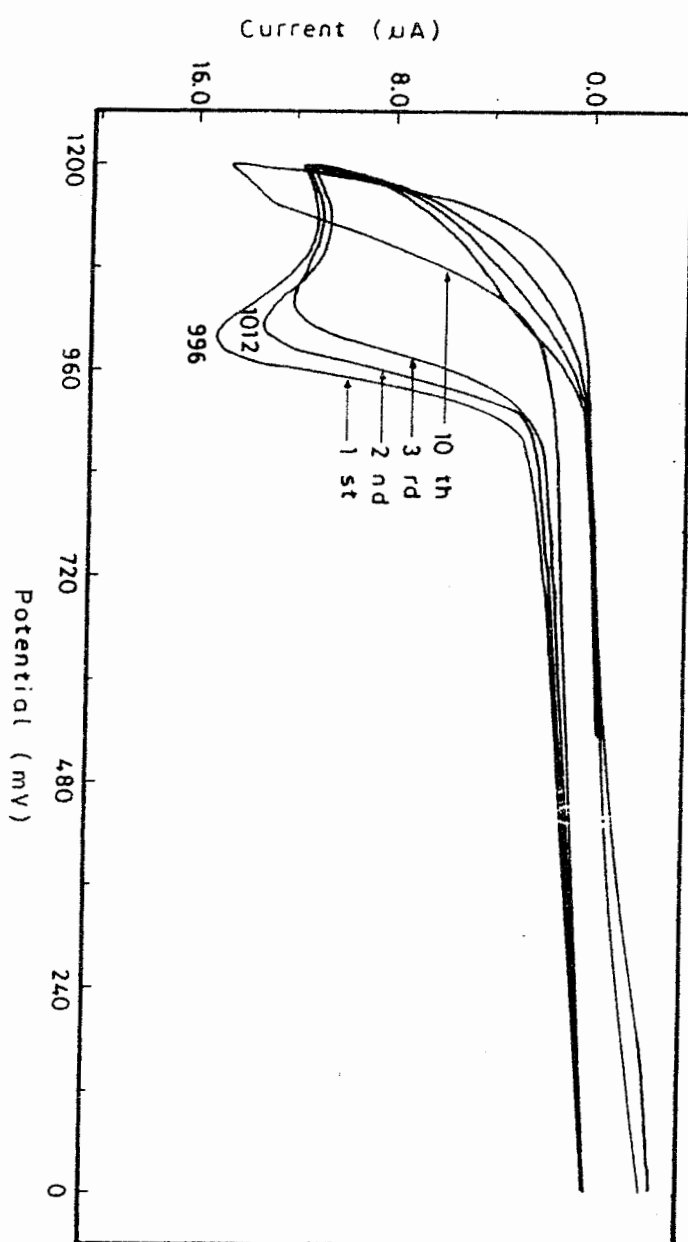


Fig. 1. Cyclic voltammograms of 0.05 M 4-aminquinoline at glassy carbon electrode in 1.0 M HCl solution. scan rate = 100 mV/s.

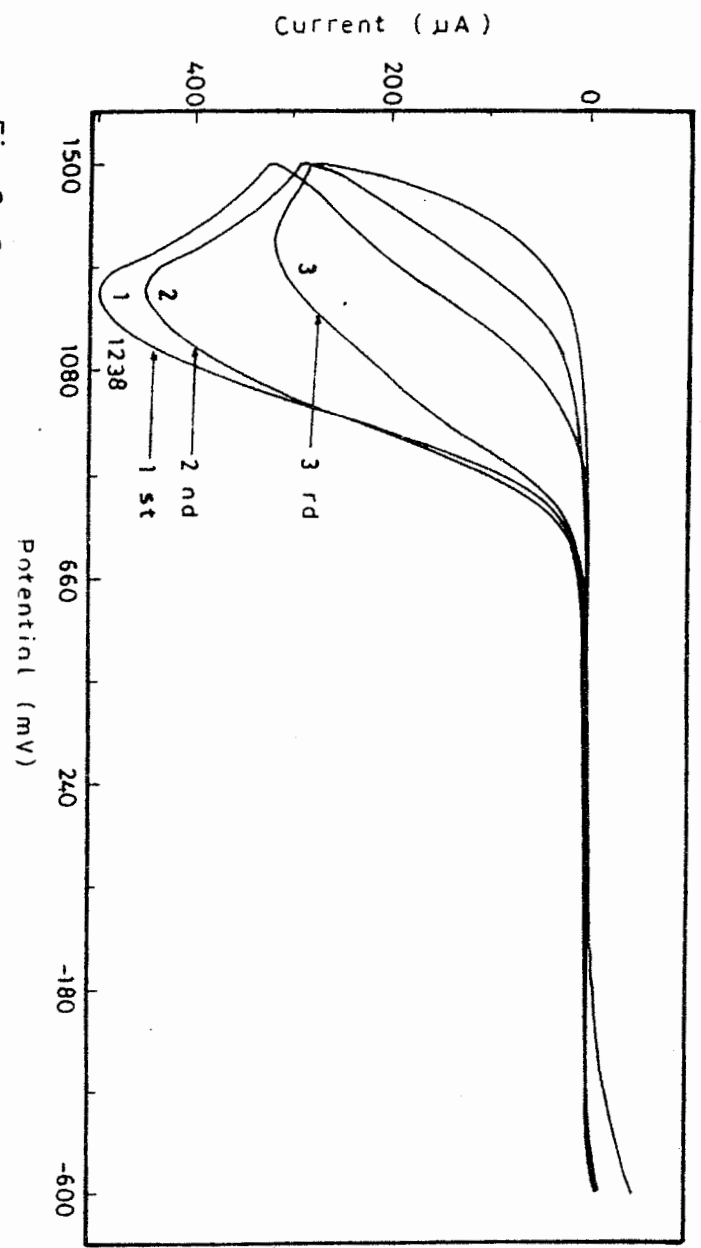
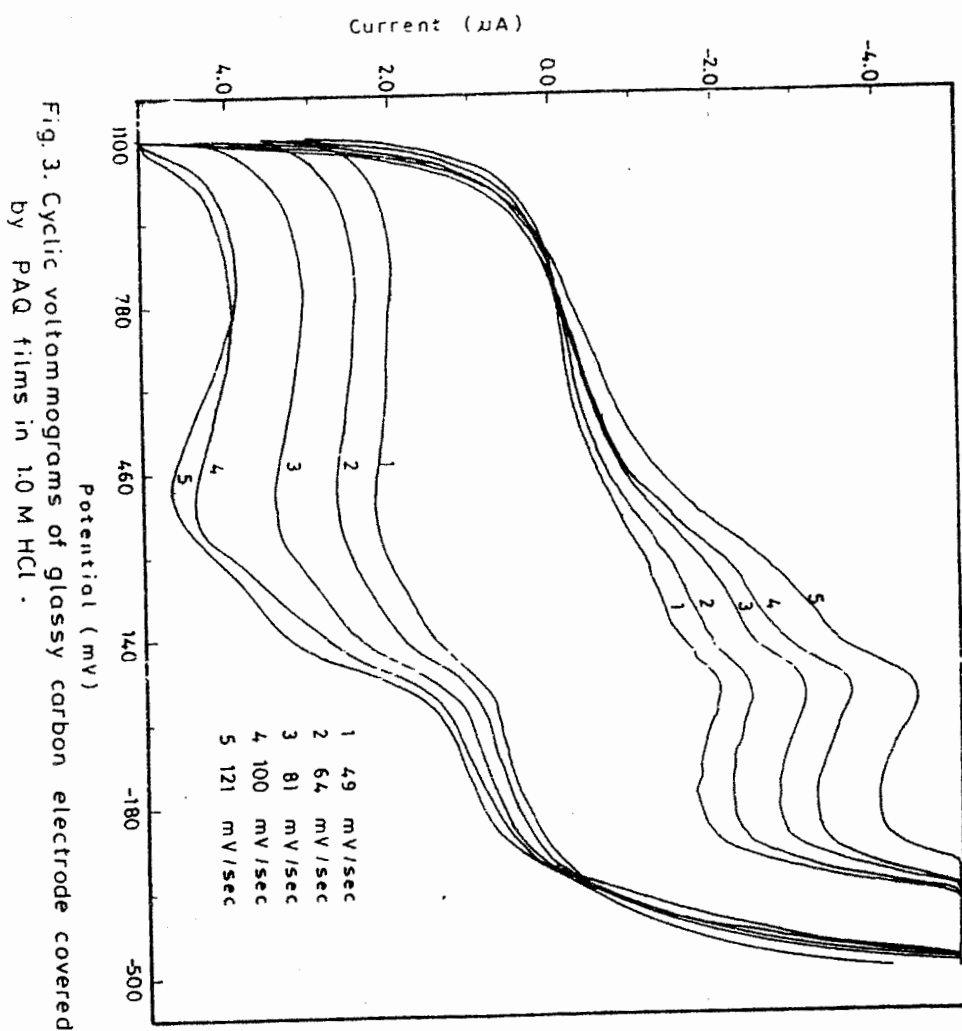


Fig. 2. Cyclic voltammograms of 0.05 M 4-aminquinidine at glassy carbon electrode in acetonitrile containing 0.1 M LiClO<sub>4</sub> and 0.05 M pyridine .

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solution containing protons. Figure 3 shows a series of cyclic voltammograms of PAQ film in 1N HCl at different scan rates. A typical redox reversible system is obtained. The anodic peaks appeared between 364-430 mV while the cathodic peak appeared between 28 and 16 mV vs Ag / AgCl. These redox peaks are attributed to a proton + electron addition / elimination process at - NH sites (3, 8, 13, 14.).

#### ACKNOWLEDGEMENTS

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