PRELIMINARY INVESTIGATION OF ANILINE OXIDATION IN NITROBENZENE AT DIFFERENT ELECTRODE MATERIALS

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By
Assefa Sergawie
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LIST OF ABBREVIATIONS

$AnClO_4$	Anilinium perchlorate
GC	Glassy Carbon
NB	Nitro benzene
PAN	Polyaniline
TBuACl	Tetra-n-butlyl ammonium chloride
$TBuAClO_4$	Tetra-n-butyl ammonium perchlorate

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ABSTRACT

The voltammetric behavior of aniline and anilinium ion has been studied in nitrobenzene as a solvent. Tetrabutyl ammonium perchlorate served as a supporting electrolyte in all experiments.

In the presence of anilinium ion a cathodic current is observed at about zero Volt, which we believe is due to the reduction of the proton of the anilinium cation. The anodic oxidation of aniline is indicated by a sharp increase in current at about 1 V. The current peak obtained in the first cycle decreases in intensity and at the same time shifts to more positive potentials in the course of successive cycles. At negative potential scans several reduction peaks are observed. A deposit is formed at the electrode which exhibits electrochromic behavior (blue in the oxidized state and colorless in the reduced state.

The deposit has been investigated in sulfuric acid and exhibits a voltammetric behavior similar to polyaniline obtained from aqueous acidic solutions.

The results of our investigation show the possibility to obtain polyaniline using aprotic solvent like nitrobenzene.

CHAPTER 1

INTRODUCTION

The electrochemical oxidation of aniline to polyaniline has been investigated in nonaqueous [1,2,3] and aqueous solvents [4,5,6,7]. The nonaqueous solvents utilized so far are dimethyl sulfoxide, propylene carbonate, and acetonitrile [1,2,3].

The formation of electroactive polyaniline has been observed only in acidic solutions, while in neutral and basic solutions no electroactive polymer was formed [2,3]. The formation of polymers by electro-oxidation is supposed to take place when the polymer is easier to oxidize than the monomer [8]. In acidic solutions the monomer will exist mainly as anilinium ion which will be oxidized at more negative potentials than aniline. Thus the requirement for polymer formation seems to be met at lower pH [9]. On the other hand the polymer formation includes the abstraction of protons in one or more steps of the reaction sequence which in turn requires the presence of a proton acceptor in the reaction system [1]. In aqueous solutions we may suppose that water acts as proton acceptor in this reaction.

Although the properties of nitrobenzene makes it a promising solvent for the investigation of anodic oxidations [10], it has hardly been utilized in electrochemical investigations [11]. No report about the anodic oxidation of aniline in nitrobenzene is known to us.

The anodic limit of the potential window in nitrobenzene is at about 2 V and thus positive enough for the investigation of the anodic aniline oxidation. On the other hand nitrobenzene may act as a proton acceptor to due its high electron density at the oxygen atom.

It was the aim of this investigation to study the voltammetric behavior of aniline in nitrobenzene and the possibility to obtain polyaniline from neutral solutions. The deposits at the electrodes have been characterized by their voltammetric behavior in different acids. The voltammetric behavior of the anilinium ion in nitrobenzene has been investigated.

CHAPTER 2

LITERATURE REVIEW

2.1 THE CHEMISTRY OF ANILINE

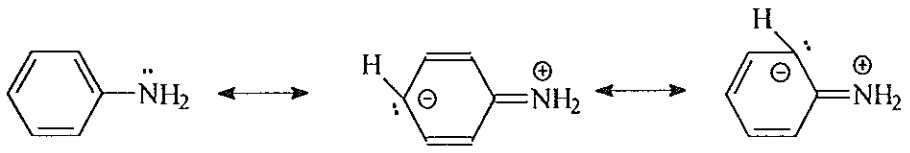
The chemistry of aniline, like all other amines, is dominated by the presence of a lone pair of electrons at the nitrogen atom. Because of the lone pair, aniline is both basic and nucleophilic. Table 2.1 compares the basicity of aniline with other aliphatic amines.

Table 2.1 pK_a values for some amines [12].

AMINE	pKa
ammonia	9.2
methylamine	10.6
dimethylamine	10.7
trimethylamine	9.8
aniline	4.6

As can be seen from the table, aniline is less basic than the aliphatic amines. The lone pair of electrons of aniline is not readily available for reactions with acids for two reasons.

1. The nitrogen atom is bonded to an sp^2 hybridized carbon atom of the aromatic ring which is more electronegative than the sp^3 hybridized carbon atom of the alkyl amines.
2. The lone pair is delocalized due to resonance as shown below.



One important reaction of aniline is oxidation. The chemical or the electrochemical oxidation of aniline produces polyaniline [13,14,15].

2.2. FORMATION OF POLYANILINE BY ELECTROPOLYMERIZATION IN AQUEOUS SOLUTIONS

The electropolymerization of aniline can be carried out by different electrochemical techniques . A cyclic voltammogram of aniline in 1M H_2SO_4 at a Pt electrode is shown in Fig. 2.2.1. It is a result of our experiment which is similar to the voltammogram obtained by Stillwell et. al. [16]).

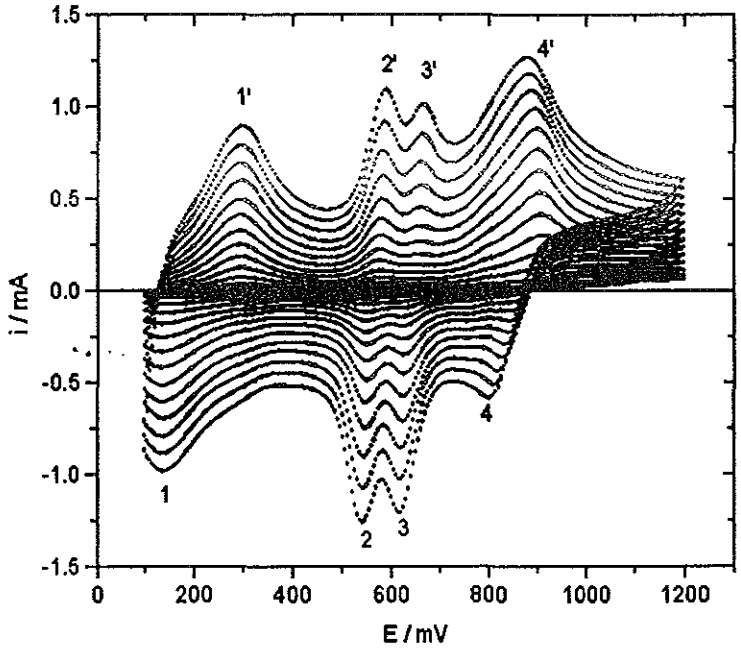


Fig. 2.2.1: Cyclic voltammogram of aniline in 1M H_2SO_4.

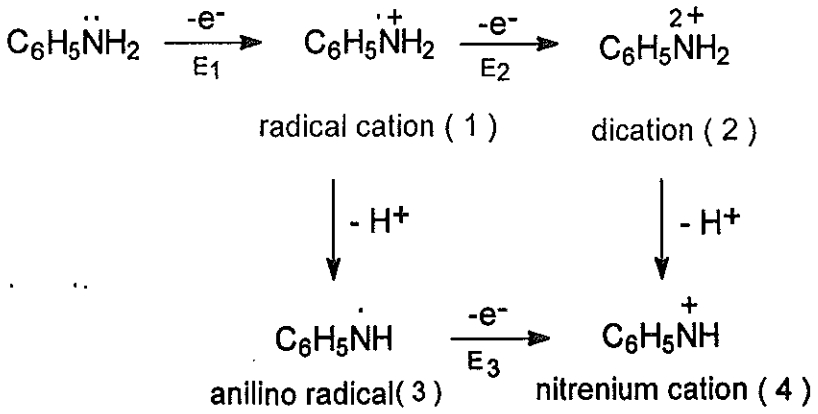
Electrode: stationary Au, C = 0.1M, v = 50 mV / sec.

The aniline oxidation at the bare electrode is indicated by an anodic current peak which starts at about 1V. This current peak diminishes after the first cycle and a set of cathodic and anodic current peaks, increasing in intensity on continuous cycling are observed. The peak potentials of these current peaks are given below where primed numbers and unprimed numbers represent reduction and oxidation respectively.

Table 2.2. Peak and Peak potentials observed in Fig. 2.2.1

Peak No.	Peak Potential (V)
1,1'	0.30, 0.13
2,2'	0.59, 0.58
3,3'	0.67, 0.62
4,4'	0.87, 0.80

It has been suggested that in the first step of the electrochemical aniline oxidation, the following intermediates might be formed [17].

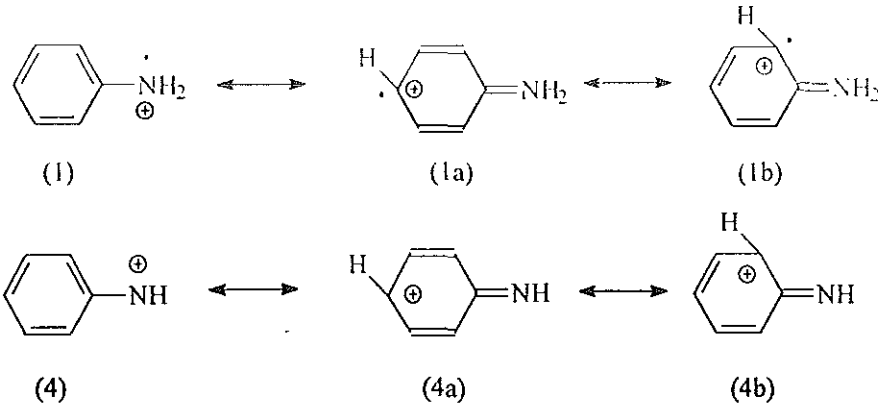


Scheme 2.2.1. Schematic representation of the possible intermediates formed in the course of the anodic aniline oxidation

The radical cation (1) is supposed to be the major intermediate at low potentials, but there is experimental evidence for the formation of the nitrenium cation (4) at more positive potentials than required for the formation of the radical cation (1) [17]. The nitrenium cation (4) is obtained by deprotonation of the dication (2).

The electropolymerization of aniline can be carried out in basic [5] or acidic media [4,18,19,20]. The polymer formed in basic media has been reported to be electroinactive [5]. It has been suggested that the formation of PAN in basic media may proceed through the anilino radical (3) [5]. In aqueous acidic solutions polymerization may take place either through the nitrenium cation (4) or the radical cation (1), depending on the potential applied. The position of bond formation or radical coupling is determined by the contribution of the different resonating structures to

the ground states as shown below for the radical cation (1) and the nitrenium cation (4) respectively.



(1) (1a) (1b)

(4) (4a) (4b)

Polymerization via the nitrenium cation (4) may involve two types of reactions as shown by eqn.(2.2.1) and eqn. (2.2.2).

$$C_6H_5NH^+ + C_6H_5\ddot{N}H_2 + H^+ \longrightarrow 2\,C_6H_5NH_2^{\cdot+} \longrightarrow PAN \qquad (2.2.1)$$

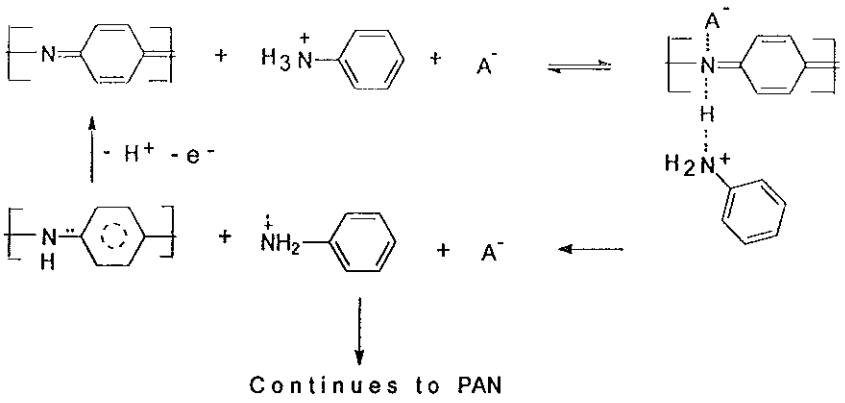
$$C_6H_5\dot{N}H^+ + C_6H_5\ddot{N}H_2 \longrightarrow C_6H_5NHC_6H_5NH + H^+ \qquad (2.2.2)$$

$$\downarrow$$

$$PAN$$

The bonding results in two nonequivalent PAN structures linked either in ortho or in para position which is independent whether the radical cation (1) or the nitrenium ion (4) is considered as starting intermediate. At pH less than 4, benzidine formation has also been observed [20,21].

Kinetic studies have shown that polymerization during the first scan is diffusion controlled [1]. The disappearance of the current peak due to the oxidation of aniline at the bare electrode and the growth of the other peaks on continuos cycling has lead to the suggestion that the direct electron transfer from the monomer to the electrode is important to prepare the initial amount of the polymer (nucleation) followed by film growth. An autocatalytic mechanism has been suggested which is mediated by an electron transfer process according to scheme 2.2.2 [22].

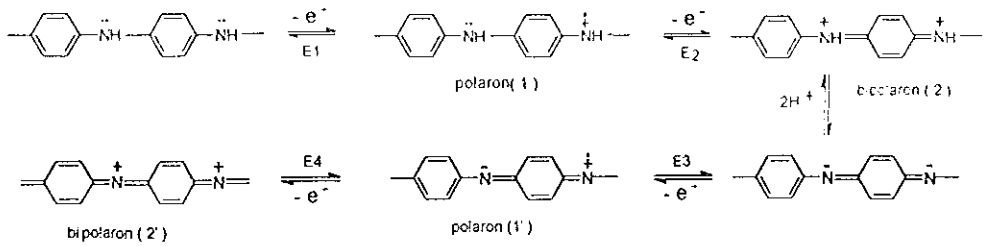


Scheme 2.2.2 Autocatalytic deposition of PAN

The potential for the catalytic deposition of polyaniline (peak 4 in Fig. 2.2.1) corresponds with the potential of the most positive oxidation peak obtained in the cyclic voltammogram of PAN [22].

Empirical relationships between current, thickness of the film and nature of the anion have been derived [22].

Different attempts have been made to interpret the voltammograms of polyaniline [1,9,25,,27,28,29]. One of the difficulties in the analysis is the inconsistency in the number of redox systems observed. All reports agree that there are two main redox couples involved (indicated by the current peaks 1,1' and 4,4' in Fig. 2.2.1) which are the responses of polyaniline itself. The interpretation of the current peaks has been based on the investigation of the effect of pH and switching potentials as well as on spectroscopic studies, and electron paramagnetic resonance spectroscopy (EPR). Thus, the formation of two polaron - bipolaron states at different potentials has been proofed by EPR studies and the following mechanism has been suggested [30].



Scheme 2.2.3 Representation of the electroactive sites in PAN and their redox mechanism.

Reaction step E_1 and E_2 correspond to peak 1 while step E_3 and E_4 correspond to peak 4.

Huang et al [13] in accordance with other groups [15,13,20] interpreted the current peaks obtained in aqueous acidic solutions as follows.

i) Peaks 1,1'

Although Genies and Tsintavis [7] reported the peak potential to be dependent on the pH, they did not indicate the pH range. Taking the pH range into consideration, Huang and coworkers reported that the peaks are independent of pH in the range 1-4 but observed a change in peak potential by 58 mV pH^{-1} for the reduction process [14]. They interpreted the peaks in the following way.

Peak 1 is suggested to be the conversion of the pale yellow leucoemeraldine base to the light green protonated form of protoemeraldine and the dark green protonated emeraldine as shown below.

$$(C_6H_4NHC_6H_4NH)_{4x} + 2xA^- \longrightarrow \underset{\text{Protoemeraldine Salt}}{(C_6H_4NHC_6H_4NH)_{3x}(C_6H_4\overset{+}{N}HA^- = C_6H_4 = \overset{+}{N}HA^-)_x} + 2xe^-$$

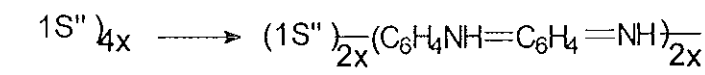
Leucoemeraldine Base

$$\downarrow 2xA^-$$

$$\underset{\text{Emeraldine Salt}}{(C_6H_4NHC_6H_4NH)_{2x}(C_6H_4\overset{+}{N}HA^- = C_6H_4\overset{+}{N}HA^-)_{2x}} + 2xe^- \quad \ldots\ldots\ldots\ldots\ldots\ldots . 2.2.3$$

The protonated emeraldine base can also be formed by the proton doping of the emeraldine base.

In the pH range -0.2 to -2.12 1A is probably in a form of 1S' or 1S" (see below). Peak 1 in this pH range can be due to the following electrode reaction.



$$(1S'')_{4x} \longrightarrow (1S'')_{2x}(C_6H_4NH{=}C_6H_4{=}NH)_{2x} + 4x\,H^+ + 4x\,e^- \quad \text{..... 2.2.}$$

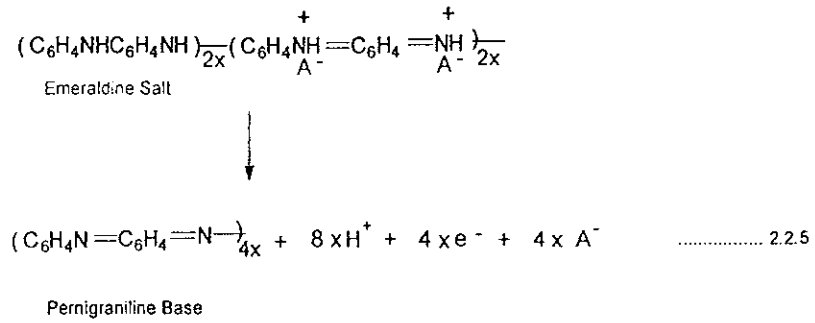
The observation that E_{red} for the first peak becomes less positive by 58 mV / pH is consistent with the above reaction.

Oxidation reactions between pH -0.2 to +1 could be the combination of the above two reactions.

The reaction for the reduction peak 1' is just the reverse of reaction described above. $E_{1/2}$ for the first peak has been observed around 0.3 V vs. SCE. In addition to pH and anion effect, its position also changes with scan rate.

ii) Peak 3,3'

Between pH -0.2 to 4 the peak shifts to lower values by 120 mV / pH. The following reaction has been suggested for peak 3.



$$(C_6H_4NHC_6H_4NH)_{2x}(C_6H_4\overset{+}{N}H\,A^-{=}C_6H_4{=}\overset{+}{N}H\,A^-)_{2x}$$

Emeraldine Salt

$$(C_6H_4N{=}C_6H_4{=}N{-})_{4x} + 8\,xH^+ + 4\,xe^- + 4\,x\,A^- \quad \text{..... 2.2.5}$$

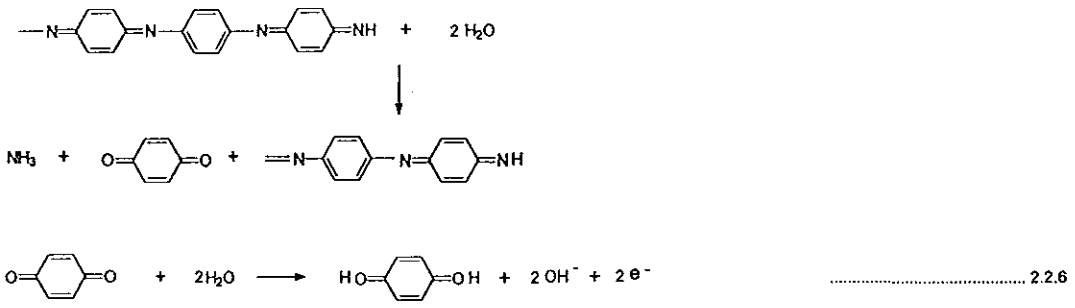
Pernigraniline Base

The reverse reaction holds for the reduction peak 3'. The average of the peak potential for the system 3.3' is scan rate independent for lower scan rates.

iii) Peak 2.2'

This peak appears during the polymerization of aniline or the oxidation of the polymer at high potentials. Its presence deteriorates the electrical properties of

PAN. There are different opinions about its origin. Genies and coworkers [8] attributed the peak to the formation of phenazine rings through the nitrenium ion intermediates of aniline and the polymer. Others [20,21,22,51] have suggested that the peak is due to the hydrolysis of the polymer to form benzoquinone or quinoneimine and represents the benzoquinone / hydroquinone couple, as shown in eqn. 2.2.6.



..... 2.2.6

I_{p1} has been used as a measure of PAN growth while I_{p2} has been used as a measure of degradation. The ratio Ip_2 / Ip_1 should be kept to a minimum for the best quality films. The following factors have been suggested to affect the ratio [23].

a. *Number of cycles:* Deposition charge is proportional to the number of cycles. The formation of PAN promotes further film growth by reacting with aniline which is a stronger nucleophile than water. As a result, the ratio Ip_2 / Ip_1 decreases as the number of cycles increases.

b. *Rotation speed of the electrode*: While using a rotating disc electrode, increasing the speed of the electrode on which PAN is deposited retards the growth of the film. Therefore, the ratio Ip_2 / Ip_1 increases.

c. *Scan rate:* At lower scan rates, PAN growth has been found to be favored. Therefore the ratio goes to a minimum.

d. *Aniline concentration* : The ratio has been found to decrease as the aniline concentration increases. This, could be due to the domination of autocatalysis over hydrolysis.

e. *Type of anion*: Certain anions decease the ratio by decreasing the degree of degradation [12]. Sulphate anions have been found to favour degradation when compared with Cl^- and sulphamate ion [12,20].

f. *pH :* Low pH has been found to decrease the degradation rate. In the degradation process water acts as a nucleophile or as a proton acceptor. At low pH, it can act as a proton acceptor. As a result, degradation rate and hence the ratio Ip_2/ Ip_1 decreases [20].

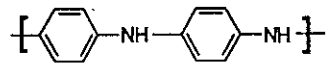
2.3 DIFFERENT FORMS OF POLYANILINE

The basic structural unit of polyaniline has been suggested to be the octamer. The dimers could be either the completely reduced form (1 A) or the completely oxidized form (2A) [7].

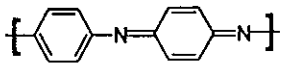
Each of these could be partly (S') or fully (S") protonated.

The different structural forms of PAN uggested are the following [29].

a)

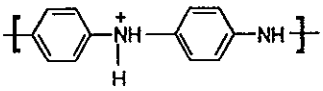


1 A

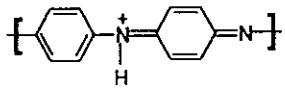


2 A

b.1)

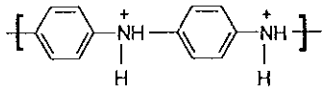


1S'

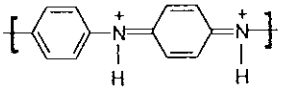


2S'

b.2)



1S"



2S"

c) I. leucoemeraldine base $(1A)_{4x}$

II. Protoemeraldine base $(1A)_{3x}(2A)_x$

III. Emeraldine base $(1A)_{2x}(2A)_{2x}$

IV. Nigraniline base $(1A)_x(2A)_{3x}$

V. Pernigraniline base $(2A)_{4x}$

The units may occur in a variety of combinations and in different ratios depending on the oxidation state of the polymer.

2.4 FACTORS AFFECTING THE MORPHOLOGY OF PAN

The morphology of polyaniline depends on the type of anion present in the supporting electrolyte and on the conditions under which electropolymerisation is carried out .

It has been observed [22] that in the presence of large anions with low charge compact fibrous structure of PAN are obtained. The films strongly adhere to the electrode.

Less compact fibrous structures which poorly adhere to the electrode have been observed in the presence of small anions. It has been suggested that the difference in the solubility of the salts produced is responsible for this behavior. The variation in the solubility of doped polymer upon the dopant in polar solvents(like dimethylsulphoxide) was studied by Dhawna and Trivedi [14]. They suggested that there is a possibility of interaction of a dopant with the polymer which may induce interaction of the polymer with the polar solvents.

It has been observed that PAN formed under potentiostatic condition [17,23], at high scan rates [24], at high temperature or using high aniline concentration [1] is less compact. The nature of the electrode may also affect the morphology [25].

2.5 PROPERTIES OF PAN

2.5.1 CONDUCTIVITY:

At the most negative potentials PAN, which is in leucoemeraldine form has been observed to be an insulator because of the absence of charge carriers. At the most positive potentials, PAN, in its fully oxidized pernigraniline form is also an insulator. In the intermediate oxidation states, PAN can act as an electrical conductor [9,25].

In view of the complexity of the material, it has been difficult to assign a particular mechanism for conduction process in PAN. It has however been suggested that it is a combination of both ionic and electronic conductivity [17]. PAN is unusual in having p-doped and proton doped conductivity. p-doping is changing the oxidation state of a substance through an electron transfer while proton doping is changing the state through proton transfer. Protonation occurs preferably at the imine

nitrogen resulting in high conductivity because of extensive conjugation in the polymer chain [25].

p-doping results in the formation of radical cations (polarons) and dications (bipolarons). Their relative stability has been observed to depend on pH and on type of the electrode [7,9]. It has been observed that there is an increase in the stability of the polaron at lower pH. Platinum electrodes have been found to favour polaron formation while gold does not. The conductivity of polyaniline therefore depends on the oxidation state of the polymer and on the protonation level. The type of the dopant anion may also contribute to the value of conductivity especially if it favours charge delocalization [9,14].

2.5.2 ELECTROCHROMIC BEHAVIOR

Polyaniline shows different colors at different oxidation states and protonation level. There are some variations in the reports about color changes [7,16,20,25,26]. Macdiarmid [25] has reported the following colors at different states of polyaniline

Table 2.3. Electrochromic behavior of PAN

Form of PAN	Protonated	Unprotonated
leucoemeraldine	pale yellow	pale yellow
protoemeraldine	light green	blue
emeraldine	green	dark blue
nigraniline	blue	blue dark
pernigranilie	violet	violet

CHAPTER 3

3.1 EXPERIMENTAL

Aniline was purified by distilling at reduced pressure. The colorless liquid was stored under nitrogen atmosphere in the dark.

Nitrobenzene (NB) was purified by two methods.

i. Nitrobenzene was washed three times with 10% (v / v) H_2SO_4, then three times with 10% (w / v) KOH and finally with distilled water until it became neutral. It was stored over anhydrous Na_2CO_3.

ii. The washed NB was distilled under reduced pressure. The middle fraction of the distillate has been used for the experiments. No difference due to the purification method was noticed in the electrochemical experiments.

Anilinium perchlorate ($AnClO_4$) was prepared by mixing equimolar amounts of aniline and aqueous $HClO_4$. It was crystallized from boiling water. Tetrabutylammonium perchlorate ($TBuAClO_4$) served as a supporting electrolyte. It was prepared by mixing equimolar amounts of tetrabutyl ammonium iodide with $NaClO_4$ both dissolved in acetone. The $TBuAClO_4$ was precipitated by addition of water and filtered off. The crude product was recrystallized from boiling water and dried in vacuum at 50° C.

All other chemicals were used as received. Aqueous solutions were prepared from double distilled water.

The electrochemical cell used was a three electrode cell. The working electrodes were Pt, Au and glassy carbon disc electrodes in PTFE (Metron) with a geometrical area of about 0.07 cm^2. The electrodes were polished with alumina, rinsed with double distilled water and dried before each set of experiments. A silver-silver chloride electrode in 10 mM TBuACl in NB served as a reference electrode in NB. A saturated calomel electrode (SCE) was used as reference electrode in the aqueous solutions. A platinum foil was employed as counter electrode. The electrolyte solutions were purged with nitrogen for 10 minutes prior to the experiments.

All electrochemical investigations were carried out with the BAS 100W electrochemical analyzer at laboratory temperature (20±1°C).

3.2 RESULTS AND DISCUSSION

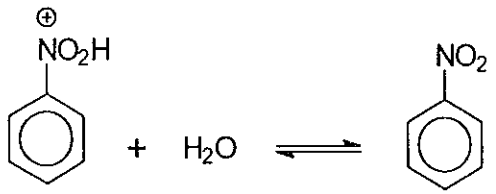
3.2.1 NITROBENZENE AS A SOLVENT

Despite the fact that nitrobenzene has been used as the preferred organic phase for the investigation of charge transfer reactions across the interface of immiscible electrolyte solutions, its application as non-aqueous solvent in metal electrolyte solution electrochemistry is rather rare [11]. Nevertheless, the physical and chemical properties on nitrobenzene makes it a promising nonaqueous solvent. Some of the physical properties together with solvent parameters are compiled in Table 3.2.1.

Table 3.2.1 Properties of nitrobenzene [10]

Property	Value	Unit	Remark
Poiling Point, t_b	210.8	°C	
Melting Point, t_m	5.8	°C	
Density, d	1.2	g cm^{-3}	
Viscosity Coefficient, η	1.8	10^{-3} Pa s	
Surface Tension, γ	4.28	10^{-2} N m^{-1}	
Refractive Index, n_D	1.55		
Dielectric Constant, ε	34.82		
Dipole Moment, μ	4.03	D	D=3.33564 x 10^{-30}C m

Resulting from the resonating structures of nitrobenzene, a rather high electron density is expected at the oxygen atom making it a possible proton acceptor. The dissociation constant of nitrobenzene in water



.....3.2.1

is reported to be 1.05 x 10^{-4} [34].This shows that there is a certain tendency of nitrobenzene to act as proton acceptor. In addition, a higher stability of radical cations in nitrobenzene is expected [11]. As compared with other non-aqueous

solvents like acetonitrile, nitrobenzene can stabilize cation radicals but being chemically inert [11].

The solubility of tetra alkylammonium salts in nitrobenzene is good due to the rather high dielectric constant.

Because of the above mentioned properties, nitrobenzene seems a promising solvent to study the anodic oxidation of aniline. It may stabilize, to some extent, the radical cation formed in the primary electrochemical reaction step and act simultaneously as a base in the successive chemical reactions.

3.2.2 ELECTRODE CHARACTERIZATION

The cyclic voltammograms obtained at stationary Au, Pt and glassy carbon in nitrobenzene with tetrabutyl ammonium perchlorate as supporting electrolyte are shown in Figure 3.2.1.

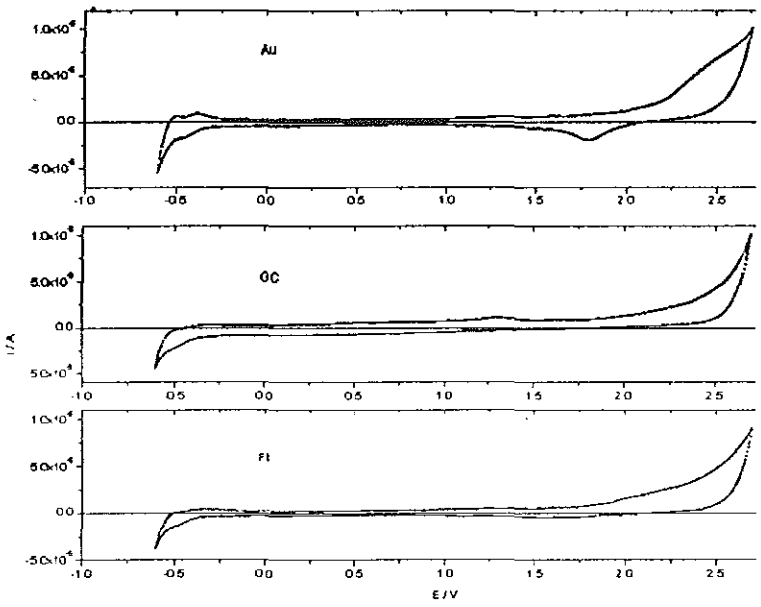


Fig. 3.2.1 The cyclic voltammograms of 0.01 M $TBuAClO_4$ in NB at different electrode materials, V = 50 mV / sec.

The results show a fairly wide potential window (- 0.4 V to + 2 V) useful for electrochemical investigation at all three electrode materials. Current peaks at about 0.5 V (reduction) and 0.9 V (oxidation) as obtained by Adams [21] and

attributed by him to the presence of impurities were not observed in our voltammograms.

3.2.3 VOLTAMMETRIC BEHAVIOR OF ANILINIUM PERCHLORATE IN NITROBENZENE

In acidic solutions, aniline will exist as anilinium ion. To check whether the aniline polymerization proceeds via the anilinium ion electrochemical investigations on anilinium perchlorate were carried out.

Figure 3.2.2a and 3.2.2b show the voltammogram of anilinium perchlorate at a stationary and a rotating glassy carbon electrode respectively.

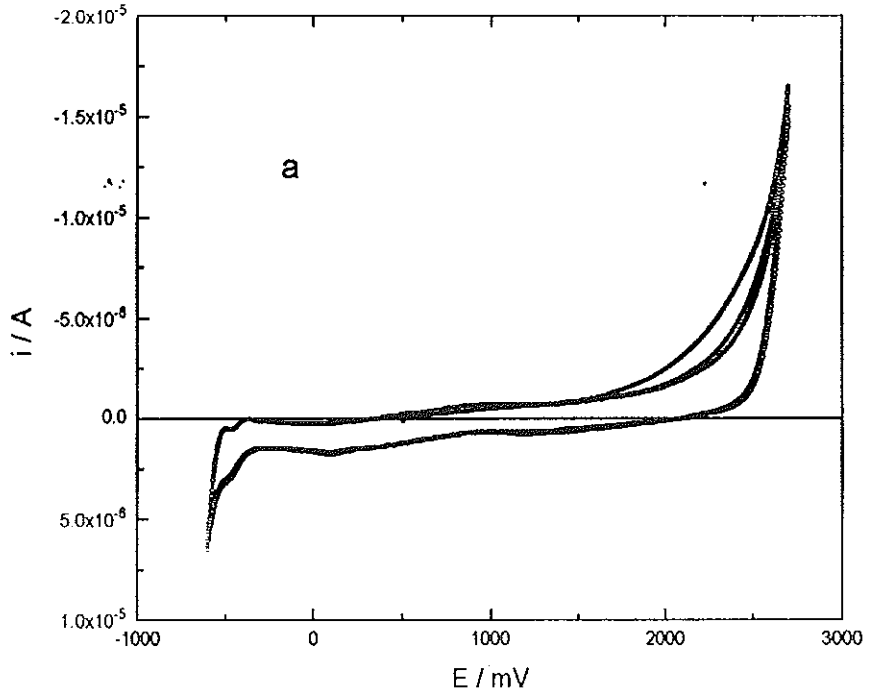


Fig. 3.2.2a The cyclic voltammogram of AnClO4 at stationary GC electrode, C = 2 x 10^{-4} M in NB, v = 50 mV / sec.

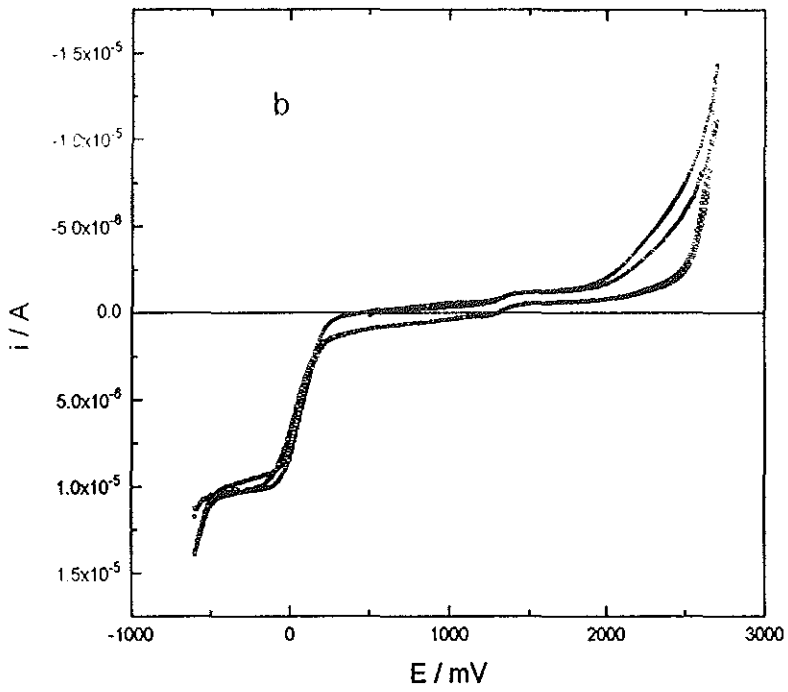


Fig. 3.2.2b Same as Fig. 3.2.2a at a rotating electrode (3000 rev / min.).

Although there was no indication of an electrochemical oxidation a reduction wave is observed at rotating electrode. The dependence of the reduction wave on the angular frequency of rotation is shown in (Fig.3.2.3a).

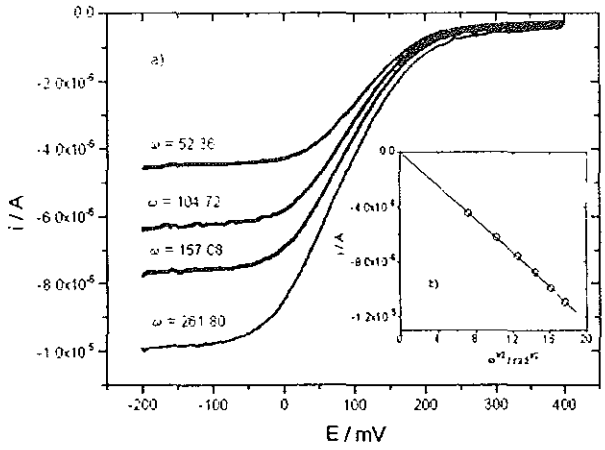


Fig. 3.2.3 a)The hydrodynamic voltammogram of $AnClO_4$ b)The dependence of i_l on angular frequency ($\omega^{1/2}$); Electrode GC, C = 2 x 10^{-4} M.

Evaluation of the limiting current ($E_{app} << E^{o'}$) according to the Levich equation [21],

$$i_l = 0.62nFAD_O^{\frac{2}{3}}\omega^{\frac{1}{2}}\nu^{-\frac{1}{6}}C_O \qquad \text{.....3.2.2}$$

where i_l is the limiting current in A, A is the electrode area in cm^2, D_O the Diffusion coefficient in cm^2sec^{-1}, ω the angular frequency of the electrode in rad sec^{-1}, ν the kinematic viscosity in cm^2sec^{-1}, and C_O the concentration in moles cm^{-3} is shown in Fig. 3.2.3.2b. The slope was found to be 5.1829×10^{-5} A $sec^{1/2}$. Taking the geometrical area of the electrode (A = 0.072cm^2) and an estimated value for the diffusion coefficient 4.5×10^{-5} cm^2sec^{-1} n = 1 is obtained from eqn.(3.2.2). We assume that the wave is due to the reduction of the proton from the anilinium ion. This assumption seems to be justified since a similar wave is obtained in the presence of acids in nitrobenzene.. On the other hand it can be seen from the hydrodynamic voltammograms that the half-wave potential shifts with increasing frequency to negative potentials. Logarithmic analysis of the wave according to

$$E = E' + \frac{RT}{\alpha nF}\ln\left[\frac{i_l - i}{i}\right] \qquad \text{.....} \quad 3.2.3$$

which holds for a charge transfer controlled reaction we get a linear dependence with a slope of 129 mV from which α = 0.46 is obtained.

The sweep rate dependence of the current peak due to the proton reduction is shown in Fig.3.2.4.

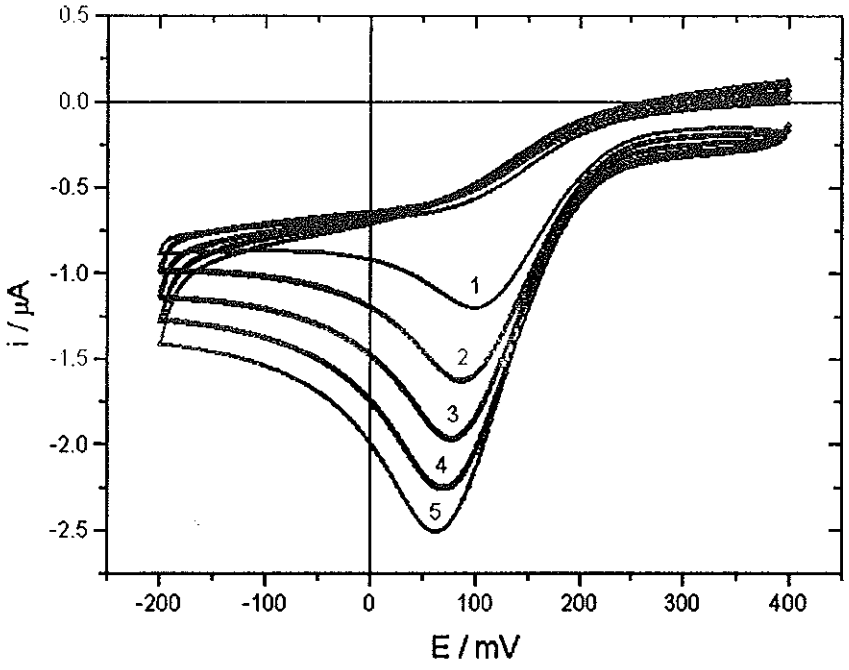


Fig.3.2.4 The sweep rate dependence of $AnClO_4$ reduction 1,2,3,4,5 refer to scan rates of 10,20,30,40 and 50 mV / sec respectively. Electrode GC, C = 2 x 10^{-4}.

The shift in the peak potential is another indication for an electrochemical irreversible reaction.

3.2.4 THE VOLTAMMETRIC BEHAVIOUR OF ANILINE IN NITROBENZENE

The voltammetric behavior of aniline in nitrobenzene has been investigated at Pt, Au and Glassy carbon electrodes. The cyclic voltammograms for a 0.01M aniline solution in the presence of 0.01M tetrabutyl ammonium perchlorate as supporting electrolyte are shown in Fig 3.2.5.

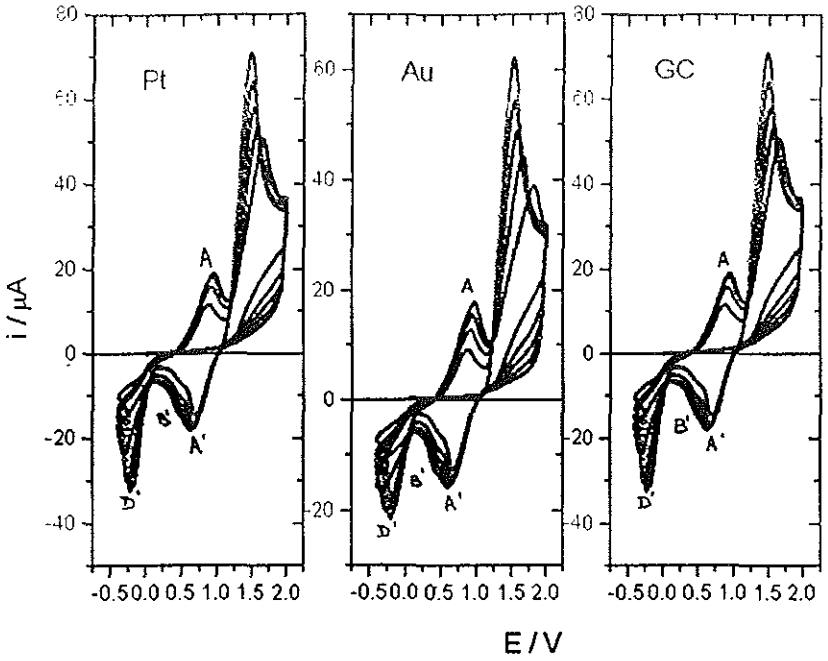


Fig.3.2.5. The voltammograms of aniline at stationary Pt, Au and GC electrodes, V = 50mV/sec. , C = 0.01M in NB.

As can be seen from Fig 3.2.5, there is no significant difference in the voltammetric behavior at the three electrodes. Aniline oxidation is indicated in the first cycle by an increasing anodic current at about 1.2 V resulting in a current peak with a peak potential at around 1.5 V. The reaction is expected to be a one electron transfer to form the radical cation. If the aniline oxidation at a bare electrode is diffusion controlled, the Randels-Sevick equation(eq. 3.2) should hold [35].

$$i_p = 2.69 \times 10^5 n^{\frac{3}{2}} A D^{\frac{1}{2}} \upsilon^{\frac{1}{2}} C \qquad (3.2)$$

Taking n = 1, D =5x10^{-6}cm^{2}sec^{-1} [36] and A = 0.072cm^2 i_p is expected to be 96.34 μA under the experimental conditions. The peak current obtained is between 63 μA and 70 μA at the electrodes investigated. This is some what less

than expected for a diffusion controlled electrode reaction. After the first scan, three reduction peaks, and one oxidation peak have been observed. The results are shown in Table 3.2.2.

Table 3.2.2. Peak and peak potentials observed in Fig. 3.2.5.

Peak	Peak Potential (V) at the 5^{th} cycle
A, A'	0.97, 0.73
B'	0.47
D'	- 0.19

Primed letters represent reduction peaks while letters without prime represent the corresponding oxidation peaks.

Peak A, A' and B' increased in intensity from cycle to cycle and the change in intensity continues to decrease. This observation indicates a continual formation of the species responsible for the peaks but with decreasing amount upon subsequent cycling. The reduction peak, B' is expected to have a corresponding oxidation peak superimposed with peak A, since peak B' would not have increased if it were a result of an electron transfer resulting in irreversible chemical reaction.
Peak D' has been observed to decrease in intensity from cycle to cycle, indicating that the reaction responsible for the peak is influenced by the potential change at the electrode solution interface due to adsorbed substances. All reduction peaks shift to more cathodic potentials with time while the oxidation peaks shift to more anodic potentials. This may indicate increased electrode resistance due to foreign deposit. The shift of peak D' was more pronounced while using Pt electrode which has a surface catalytic activity. The current peak for aniline oxidation has been observed to decrease continuously with a potential shift in the anodic direction.

From the above results we may conclude that :

1) There are two electroactive redox systems A, A' and B, B'.

2) Aniline oxidation takes place only at the electrode surface and therefore the current decreases because of foreign deposit .

3. The electroactive redox systems strongly adhere to the electrode.

The same solution has been run for 25 cycles using stationary Au electrode. The voltammogram is shown in Figure 3.2.6. The results are similar at the other electrodes.

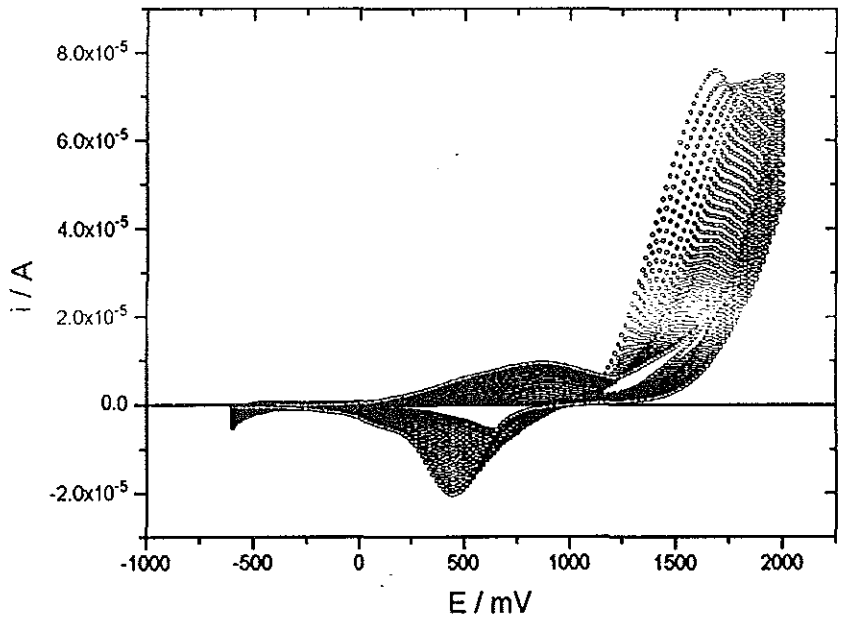


Fig.3.2.6. The cyclic voltammogram of aniline oxidation; C = 0.01M in NB, v = 50 mV /sec.

A polymer which adheres strongly to the electrode has been obtained. The polymer exhibits electrochromic behavior. It becomes blue at potentials more anodic than 0.6 V and dark blue around 2V. At potentials less than 0.6 V it becomes transparent. The electrochromic behavior of the polymer obtained in nitrobenzene is in agreement with that reported by Stillwell and Park for polyaniline prepared in sulfuric acid [20].

The aniline oxidation peak shifted to more anodic potentials as the number of cycles increased. The current peak also decreased for the first few cycles and remained almost constant afterwards. The decrease in the current peak as a function of cycle number was not reproducible in different experiments. This may be caused by variation of the electrode surface due to the pretreatment.

Two oxidation peaks and three reduction peaks have been observed. The results are compiled in Table 3.2.3.

Table 3.2.3. Peak and peak potentials observed in Fig. 3.2.6.

Peak	Peak Potential (V)
A, A'	0.9, 0.7
B, B'	0.5, 0.5
D'	0.1

From the figure it can be seen that for higher number of cycles the redox peak A, A' and B, B' remain almost constant both in intensity and peak potential. This may indicate the completion of the coverage of the electrode with polyaniline. This is in agreement with the suggestion that aniline oxidation takes place only at the bare electrode. The reduction peak D' vanished after about 10 cycles. Therefore, this peak seems to follow a side reaction while the other two systems are results of the redox behavior of the polymer.

The behavior of aniline oxidation has also been studied by chronoamperometry. A chronoamperogram obtained at 2 V at stationary Pt electrode is shown in Fig. 3.2.7. Similar results are obtained at the other electrode materials.

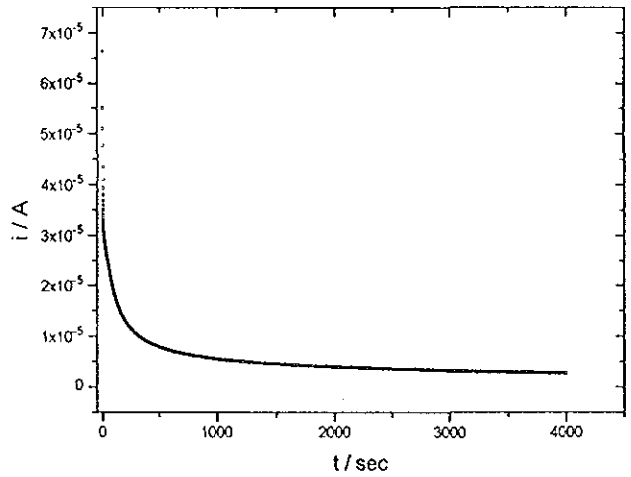


Fig.3.2.7. The chronoamperogram of aniline oxidation at 2 V;
C = 0.01M, v = 50 mV / sec

The current decreased sharply within the first 15 seconds, became constant for the next 5 seconds and then went on decreasing slowly. A dark deposit was observed which poorly adhered to the electrode. After removing the dark deposit a blue film deposited at the electrode remained.

Fig 3.2.8 shows aniline oxidation at a rotating Pt electrode (3000 rev / min).

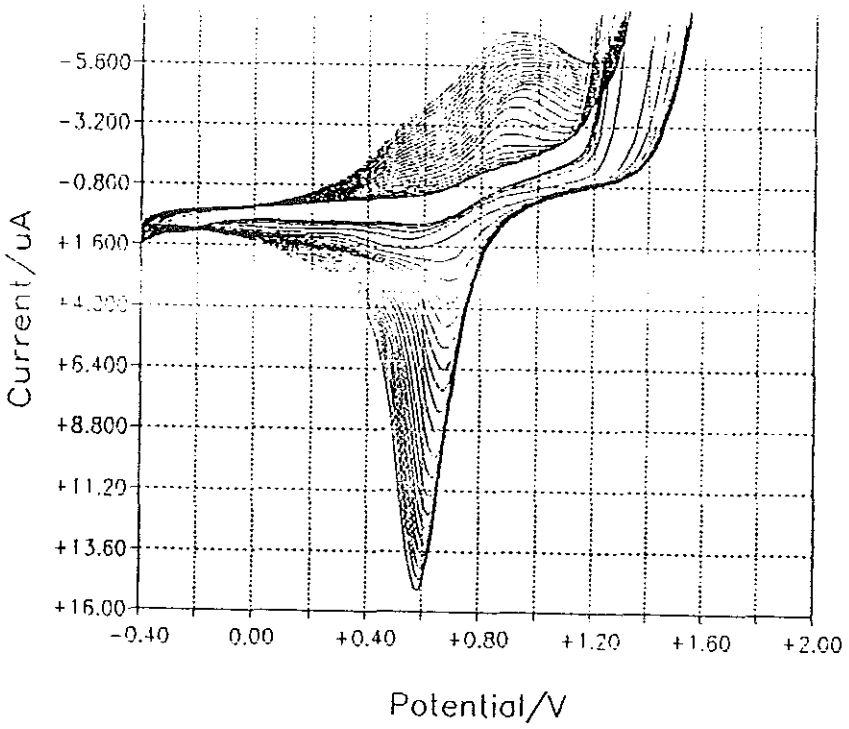


Fig. 3.2.8. The voltammogram of aniline oxidation at a rotating Au electrode (3000 rev / min), v = 50 mV /sec., C = 0.01M in NB.

No current peak was observed for aniline oxidation. The current at the anodic switching potential was much higher than at a stationary electrode. Following the first scan, one reduction peak around 0.5 V and one oxidation peak around 0.85 V of low intensity were observed. Eventhough deposition is disturbed upon rotation, the peaks observed should be the results of a deposit which undergoes electrochemical changes.

Fig 3.2.9 shows scan rate dependence of the peak current due to the aniline oxidation at a Pt electrode. As the scan rate was increased, the oxidation peaks shifted to more positive potentials while the reduction peaks shifted to more negative potentials. The plot of i vs $v^{1/2}$ for aniline oxidation is shown in fig 3.2.9.

The experimental slope value has been found to be 1.93 x 10^{-4} A $sec^{+1/2}$ $V^{-1/2}$ while the theoretical value according to equation 3.4.2 is 4.33 x 10^{-4} A $sec^{1/2}$ $V^{-1/2}$. Therefore the reaction seems to be diffusion controlled.

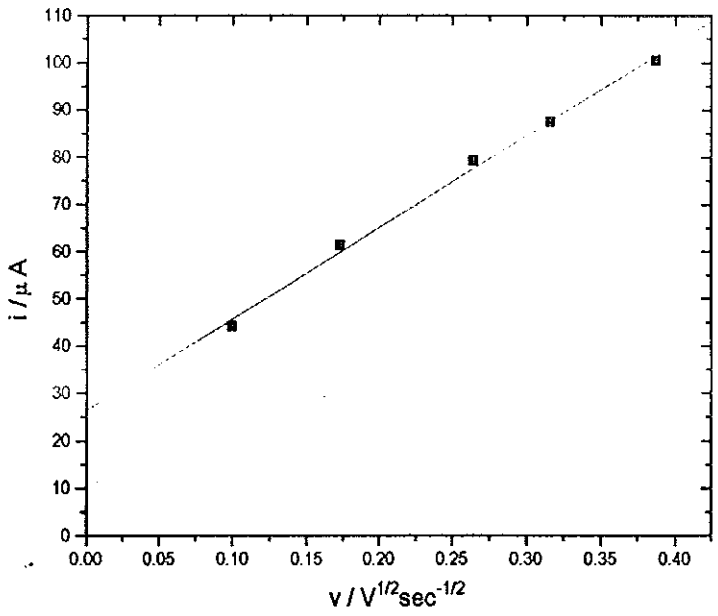


Fig.3.2.9. The dependence of aniline oxidation on scan rate; plot of i vs $v^{1/2}$, Electrode Pt, C = 0.01M in NB.

3.2.5. CHARACTERIZATION OF POLYANILINE PREPARED IN NITROBEZENE IN DIFFERENT ACIDS

A 0.1M aniline solution was run for 250 cycles in the range -0.4 V to +2 V at 1V/sec. The electrode was rinsed with water and then transferred to 1M H_2SO_4. The potential was cycled between 0.1 V and +1.2 V at 50 mV/sec. The results were compared with polyaniline formed in H_2SO_4 . HCl and $HClO_4$ were also used for the characterization.

As a result of the aniline oxidation in NB, two oxidation peaks at 0.8 V and 0.25 V and one reduction peak at 0.4 V were observed. The peak at 0.25 V diminished soon. The current at 0.4 V went on decreasing. The peak at 0.8 V shifts to positive potentials during the first 25 cycles. The reduction peak shifted to negative potentials. Comparison of this result with that of a 0.1M aniline solution run at

50 mV/sec shows that at high scan rates the side reactions have become insignificant. Peak currents for both oxidation and reduction after 250 cycles were in the order of 10^{-4} A. The color of the deposit changed rapidly between blue and transparent following the rather high scan rate. No outward growth of a poorly adsorbed substance was observed. The voltammogram of the polymer in H_2SO_4 is shown in Fig. 3.2.10.

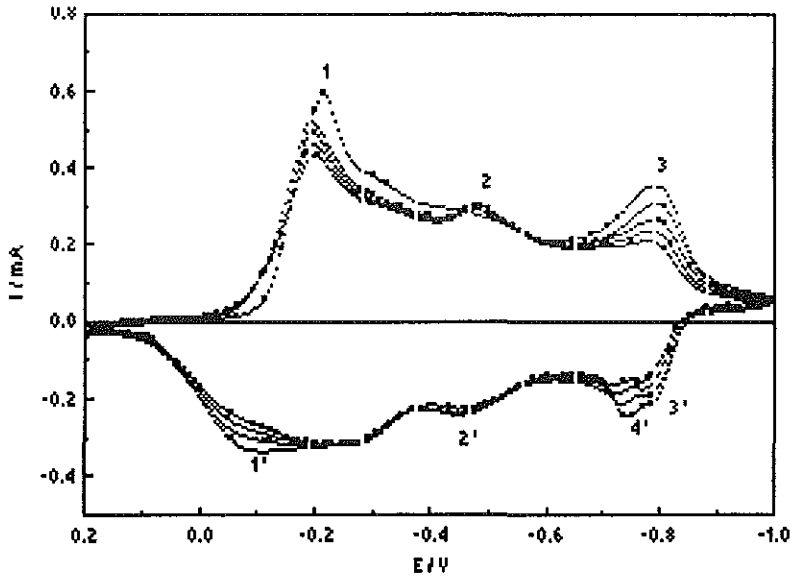


Fig.3.2.10. The cyclic voltammogram of PAN prepared in NB and run in 1M H_2SO_4 , Electrode Pt, v = 50 mV / sec.

Three oxidation peaks (unprimed numbers) and four reduction peaks (primed numbers) were observed. 1, 1', 2,2', 3,3' are redox pairs. The results are compiled in Table 3.2.4.

Table 3.2.4. Peak and peak potentials observed in Fig. 3.2.10.

Peak	Peak Potentials (V)
1, 1'	0.20, 0.10
2, 2'	0.49, 0.45
3, 3'	0.80, 0.79
4'	0.75

Peak 2 was observed as a shoulder while going to the anodic direction on the first cycle. It developed to a peak on the next cycle. It increased slightly on the third cycle and then went on decreasing very slightly. All other peaks decreased on continued cycling. For lower number of cycles (100 and 200), only one peak at 0.79V was observed instead of the double peaks 3' and 4'. The polymer showed electrochromic behavior (Table 3.2.5).

Table 3.2.5. Electrochromic behavior of the polymer prepared in NB and run in H_2SO_4 .

potential range (V)	colour
- 0.2 to + 0.1	yellow
+ 0.1 to + 0.4	greenish yellow
+ 0.4 to + 0.6	light blue
+ 0.6 to + 0.7	blue
+ 0.7 to + 1.2	dark blue

Comparison was made with polyaniline prepared and run in H_2SO_4. The voltammogram is shown in Fig. 3.2.11.

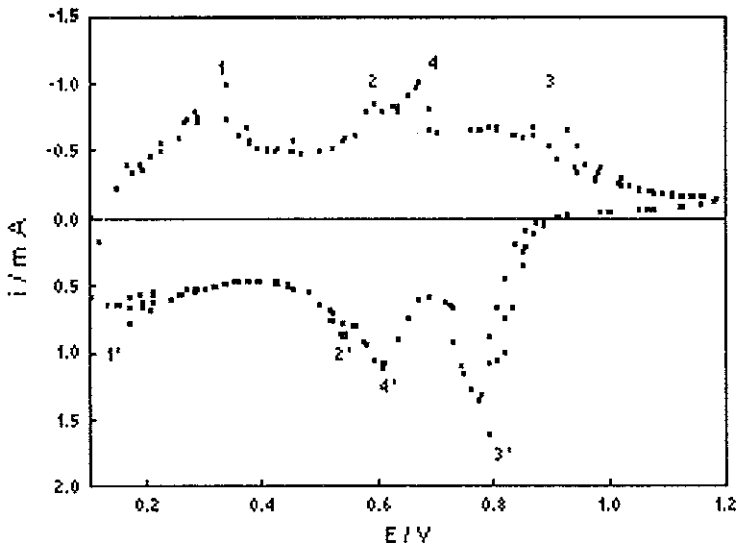


Fig.3.2.11. The cyclic voltammogram of PAN prepared and run in H_2SO_4 at Pt, v = 50 mV / sec.

Four redox systems were observed (Table 3.2.6).

Table 3.2.6. Peaks and peak potentials observed in Fig.3.2.11.

Peak	Peak Potential (V)
1, 1'	0.32, 0.17
2, 2'	0.60, 0.53
3, 3'	0.85, 0.79
4, 4'	0.68, 0.60

The behavior of the systems with time was observed to be the same as the polymer formed in nitrobenzene solution. The following color changes as a function of potential were observed (Table 3.2.7).

Table 3.2.7. Electrochromic behavior of PAN prepared and run in H_2SO_4 .

potential range (V)	colour
0.10 to 0.3	yellow
0.30 to 0.60	green
0.60 to 0.75	blue
0.75 to 1.20	dark blue

In a similar experiment, the polymer formed in nitrobenzene under the same condition was run in $HClO_4$, H_2SO_4 and HCl. The voltammograms are shown in Fig.3.2.12.

It can be seen that the system 1,1' and 2,2' exist at similar potential as 1,1' and 2,2' in figure 3.2.11, but with different relative intensities. Peak 3 was seen only during the first cycle. The reason why the system 3,3' was quenched and why the system 2,2' was more pronounced is unclear. The electrochromic behavior, however, remained the same as before.

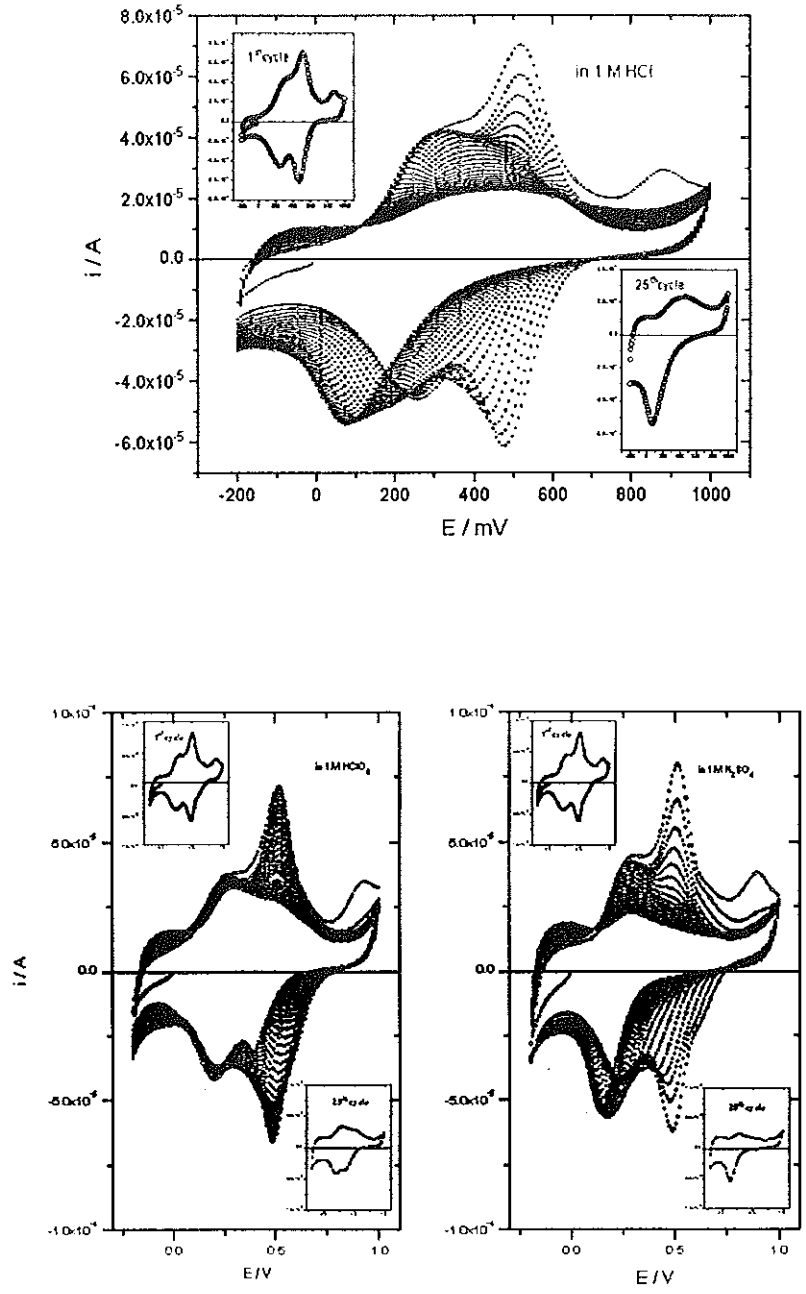


Fig.3.2.12. The cyclic voltammograms of the polymer produced in NB and run in 1M HCl, $HClO_4$ and H_2SO_4 at Pt electrode

CHAPTER 4

CONCLUSION

The results of the experiments on $AnClO_4$ may indicate that polymerization of aniline in acidic media proceeds mainly through the oxidation of aniline not anilinium ion.

Based on the close similarity between the voltammograms of the polymers formed in acidic aqueous solutions and in nitrobenzene and on the similar electrochromic behaviors of PAN prepared in nitrobenzene and in acidic solution, it can be concluded that a conducting polyaniline was formed.

The proposed mechanism of the electrochemical oxidation of aniline supposes the formation of a radical cation as the initial step followed by a sequence of chemical reactions. The final products obtained are determined by the possible recombination of the radicals and the further oxidation of the intermediates.

The positive charge at the nitrogen of the radical cation increases the acidity of one proton in the radical cation in comparison to aniline. Thus deprotonation of the radical cation to form the anilino radical (scheme 2.2.1) in the presence of a proton acceptor such as nitrobenzene has to be taken into consideration. The radical cation can further be oxidized if the anodic switching potential is higher than that required for aniline oxidation to form the dication (scheme 2.2.1).

Because of the increased acidity of the proton at the nitrogen, it will deprotonate quickly to form the nitrenium cation (scheme 2.2.1).

The anilino radical can also be further oxidized at a sufficiently high anodic potential forming the nitrenium cation.

Since the radical cations are reported to be stable in nitrobenzene [11], it can be propose that polymerization of aniline in nitrobenzene proceeds through the para coupling of the radical cation.

Suggestions for the redox systems of the polymer in nitrobenzene (Fig.3.2.

1. System B, B'

Since the solution is neutral, the completely reduced form of PAN, leucoemeraldine, may be present in an unprotonated state. Therefore, peak B should correspond to the conversion of the unprotonated leucoemeraldine salt to the emeraldine salt (eq.2.2.3).

The hydrogen atoms on the positively charged nitrogen atoms tend to be discharged because of their increased acidity and the aprotic solvent. At the same time the anions (ClO_4^-) may enter the polymer matrix as charge neutralizers suppressing H^+ expulsion. Because of these competing reactions, the peak appears only as a shoulder. Peak B' is the reverse of the above reaction which is relatively favored since only the expulsion of the anions and acceptance of the electrons are the processes involved.

2. System A,A'

Peak A can be suggested to be caused by the conversion of the emeraldine salt form of PAN to the protonated nigraniline and pernigraniline salt form of PAN (2.3) through oxidation and anion insersion. A' is due to the reverse reaction.

The suggestion for the system A, A' is different from that suggested in acidic solutions. In acidic media, peak A, A' has been suggested to be the conversion of the emeraldine salt to pernigraniline base (eq.2.2.5) through the expulsion of H^+ and A^-. If the mechanism is accepted, the reverse reaction would not have been possible because the nitrobenzene solution is aprotic. But since the corresponding reduction peak has been observed, the conversion of the emeradine salt to protonated nigraniline and pernigraniline is a possible reaction. The blue to violet deposit which has been observed could be explained by the suggested reaction [26].

It has been observed in the cyclic voltammograms that the peak attributed to aniline oxidation did not disappear, but decreased continuously while the deposition of PAN increased continuously. In potentiostatic experiments at 2 V, the current decreased continuously. Based on the above results, it is believed that there is no autocatalytic process taking place in NB. Aniline oxidation takes place only at the electrode surface. Even if the pernigraniline form of PAN is suggested to be produced in NB, the reason why there is no autocatalysis may be due to the absence of protons. The suggestion that autocatalysis proceeds through the protonated form of aniline [23] is reasonable.

Eventhough aniline oxidation is favored at a rotating electrode, deposition of PAN is difficult. This is obvious since the intermediates responsible for polymer formation can easily be swept away from the electrode.

The different electrodes used showed similar behavior but with some changes in the position of the peak potentials and peak currents. It is thus proposed that the polymerization and deposition process is independent of the electrode materials under the experimental conditions.

As the scan rate increases, the peak potential for aniline oxidation was observed to shift to the more anodic side.

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