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**ELECTROCHEMICAL BEHAVIOR OF AMINOBENZIMIDAZOLES IN
NONAQUEOUS ACETONITRILE**

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84788

Submitted to Institute of Sciences of
Hacettepe University as a partial fulfillment
to the requirements for the award of the degree of
MASTER OF SCIENCE
in
CHEMISTRY

84788

1999

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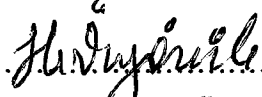
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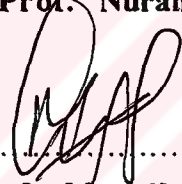
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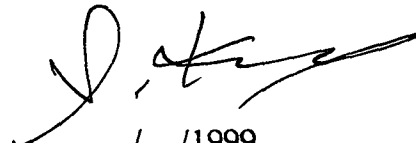
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ABSTRACT

The electroreduction and electrooxidation behavior of 2-aminobenzothiazole, 2-aminobenzimidazole and 5-aminobenzimidazole in acetonitrile/TBABF₄ in the presence and absence of anhydrous acid revealed that 2-aminobenzimidazole and 5-aminobenzimidazole forms intermolecular hydrogen bonded clusters as was the case for imidazole and benzimidazole whereas 2-aminobenzothiazole does not form such clusters.

Aniline oxidation peak is not observable in the presence of 5-aminobenzimidazole due to the formation of intermolecular hydrogen bonding between 5-aminobenzimidazole and aniline which are broken if anhydrous HBF₄ acid is added to the medium. Such behavior was not observed for 2-aminobenzothiazole, imidazole and benzimidazole, indicating that no hydrogen bonding is formed between aniline and these molecules.

The polyaniline formation from aniline is also affected by the presence of 5-aminobenzimidazole and 2-aminobenzothiazole. The amount of the polymer film decreases when these compounds coexist in solutions of aniline. If the protonated forms of these compounds are used the amount of the film electrodeposited and the dry conductivity values increase and the electroactivity loss of the film decreases.

ÖZET

2-aminobenzotiazole, 2-aminobenzimidazole ve 5-aminobenzimidazol'ün susuz HBF_4 varlığında ve HBF_4 kullanılmadan asetonitril/TBABF₄ ortamında elektrokimyasal davranışı incelenmiştir. Buna göre 2-aminobenzimidazole ve 5-aminobenzimidazol'ün moleküller arası hidrojen bağı yaparak clusterlar şeklinde bulunduğu, 2-aminobenzotiazole'ün ise moleküller arası hidrojen bağı yapmadığı saptanmıştır.

5-aminobenzimidazol varlığında anilinın yükseltgenme pikinin olmadığı, ancak susuz HBF_4 eklendiğinde, moleküller arası hidrojen bağının kırılması sonucu anilinın yükseltgenme pikinin ortaya çıktığı gözlenmiştir. 2-aminobenzimidazole, 2-aminobenzotiazol, imidazol ve benzimidazol varlığında ise, anilin ile bu bileşikler arasında hidrojen bağı oluşmadığından bu bileşiklerin varlığının anilinın yükseltgenmesini etkilemediği anlaşılmıştır.

Son olarak 5-aminobenzimidazol ve 2-aminobenzotiazol'ün polianilin filminin oluşumuna etkisi incelenmiştir. Bu bileşiklerin varlığında biriktirilen polianilin filminin miktarı azalmakta, bu bileşiklerin türlerinin kullanılması halinde ise biriktirilen filmin miktarının ve iletkenlik değerlerinin arttığı ve filmin elektroaktivite kaybının azaldığı ortaya çıkmıştır.

ACKNOWLEDGEMENT

I would like to express my gratitude to **Prof. Dr. ATTİLA YILDIZ** for his everending guidance for his help in building up of this thesis.

I would like to thank Anadolu University, Head of Chemistry Department **Prof. Dr. LALE ZOR** for her support during my study.

I am greatly indepted to **Assoc. Prof. Dr. NURAN PEKMEZ** for her help and encouragement throughout my thesis.

I am grateful to **Assoc. Prof. Dr. KADİR PEKMEZ** for his help.

I would like to express my sincere thanks to my parents and my husband for their undeniable support and encouragement.

In addition, I also wish to thank every members of Electroanalytical Chemistry group.



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1. INTRODUCTION

Polymer systems with special properties are a field of increasing scientific and technical interest, offering the opportunity to polymer and synthetic organic chemists to synthesize a broad variety of promising new materials, with a wide range of electrical and magnetic reproducible control of the molecular and supramolecular architecture of the macromolecule via a simple methodology of organic synthesis.

The electrooxidation of aniline is the usual production method for polyaniline which is one of the most widely studied conducting polymers. Electropolymerization of aniline and derivatives of aniline is usually carried out in aqueous acid solutions. Aqueous sulphuric acid is the preferred medium, although perchloric acid and hydrochloric acid are also used (Syed et al, 1991). The major disadvantage of these media is the decomposition of polyaniline to form quinone and hydroquinone type products (Hand et al, 1974 and Kobayashi et al, 1984). It has been found that polyaniline can hold water in its structure even after drying. This hydrogen-bonded water may also cause decomposition reactions (Kitani et al, 1984 and Lubentsov et al, 1991). We have preferred nonaqueous media because of the above reasons.

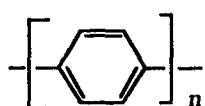
The electro-oxidation behaviour of 2-aminobenzothiazole and 5-aminobenzimidazole on a Pt surface in acetonitrile was investigated using cyclic voltammetry. We have investigated electropolymerization of 2-aminobenzothiazole and 5-aminobenzimidazole in acetonitrile. The effects of 2-aminobenzothiazole and 5-aminobenzimidazole concentration on the formation of polymers and the added anhydrous tetrafluoroboric acid (HBF_4) were elucidated. The polymer films were characterized by their cyclic voltammograms in blank solution and dry conductivities were measured using the four-probe technique.

2. CONDUCTING POLYMERS

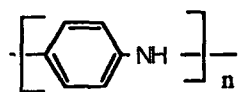
2.1. Conducting Polymers and Synthesis

In principle, the existence of materials now included among conducting polymers has long been known. The first electrochemical synthesis and their characterization as insoluble systems took place well over a century ago. In 1862 Letheby reported the anodic oxidation of aniline in a solution of diluted sulphuric acid, and that the blue-black, shiny powder deposited on a platinum electrode was insoluble in water. The first review on the electrochemistry of polyaniline was published by Goppelsroeder in 1876. He suggested that anodically oxidized aniline had a chain-like, albeit cyclic structure similar to the modern ideas of the structure of this material. In addition, he showed that his system could be electrochemically charged and discharged (Heinze, 1991).

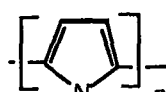
The term “conducting polymers “ was coined after the American scientists Heeger and MacDiarmid discovered in 1977 that doping the “Shirakawa” polyacetylene with iodine endowed the polymer with metallic properties, including an increase in conductivity of 10 orders of. The successful doping of polyacetylene in electrochemical terminology the equivalent of oxidation or reduction-encouraged the same scientists to test polyacetylene as a rechargeable active battery electrode. Their promising results stimulated worldwide efforts to construct a polymer battery (Chiang, C. K. et al, 1977). In the course of these studies conducting polymers with properties similar to polyacetylene were discovered or rediscovered, such as polyparaphenylene, polypyrrole, polythiophene and polyaniline.



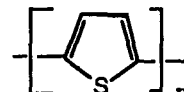
Polyparaphenylene



Polyaniline



Polypyrrole



Polythiophene

However, it soon became apparent that the pathway from inspiration to practical realization can be long and thorny, and that much basic research on a broad, interdisciplinary basis still has to be done. Nevertheless, electrochemistry remains one of the most promising areas in the research of conducting polymers. There are several reasons why electrochemists are interested in this field. The synthesis of polymer by either chemical or electrochemical methods depends upon the intended application of the

polymer. A large variety of electroanalytical methods such as chronoamperometry, chronopotentiometry, cyclic voltammetry are suitable for studying conducting polymers.

A very popular technique is cyclic voltammetry, in which a potential is linearly scanned up to a switching potential and then reversed to its initial value. Many electrochemical studies favour cyclic voltammetry because this method very clearly shows the formation of conducting polymers and also indicates the potential range of its charging and discharging. Multisweep voltammetry in particular provides useful information on the growth rate of conducting polymers.

The method of choice for preparing conducting polymers is the anodic oxidation of suitable monomer species such as pyrrole, thiophene or aniline. Only polyacetylene is synthesized by purely chemical methods. Three aspects of electrosynthesis are of relevance for electrochemists. First, there is the deposition process of the polymers at the electrode surface, which involves nucleation and growth steps. Second, to analyze these phenomena correctly, one has to know the mechanism of electropolymerization. And thirdly, there is the problem of the optimization of the mechanical, electrical and optical material properties produced by the special parameters of electropolymerization.

Electropolymerization of conducting polymers differs markedly from other polymerization reactions. In the usual electrochemically induced polymerization reactions the electrode catalytically triggers chain growth and, consequently, the process requires little electricity. The mechanism of electropolymerization is still not fully understood. The one certainty is that in the very first step the neutral monomer is oxidized to a radical cation. It must have an oxidation potential which is accessible via a suitable solvent-electrolyte system, and should react more quickly with other nucleophiles in the electrolyte solution.

A central point of electrochemical research is the analysis of the doping mechanism. Even in the earliest stage of research it was clear that these processes were not comparable with the classical doping of typical semiconductors. Rather, they correspond to oxidation in the case of p-doping or reduction in the case of n-doping. Thus, in the electrochemical terminology the doping process corresponds to a redox reaction. Especially for applications, it is important to know the phenomenological details of such redox reactions, e.g., in which potential range the charging occurs and what is the maximum level of oxidation before the material starts degrading.

A severe problem in the interpretation on redox states of conducting polymers is the variety of possible shapes and forms of cyclicvoltammetry curves, even when the materials are prepared under more or less similar conditions. Nevertheless, using mild electropolymerization conditions, such as a low formation potential, often produces materials with similar cyclicvoltammetry response. Characteristic features of these systems are, in the case of oxidation, steep anodic waves at the start of charging, followed by a broad flat plateau as potential increases. In the reverse scan a potential shifted cathodic wave typically appears at the negative end of the capacity-like plateau, whose peak-current is normally smaller than that of the anodic peak.



3. CONDUCTING COPOLYMERS

The formation of copolymers is one of the most useful tools in polymer science in that the physical and mechanical properties of a polymer can be controlled and enhanced. In recent years, this tool has been employed for the study of conducting polymers such as polyacetylene and polypyrrole. These polymers not only are important because of the resultant mechanical properties, but also have been of great use in the study of conduction mechanisms.

The preparation of both block and copolymers of polyacetylene has been used to impart mechanical integrity and processability to this polymer. At relatively low polyacetylene compositions the block copolymers can be solubilized allowing their molecular weights to be determined by chromatography. Films of these copolymers containing isolated polyacetylene domains, trapped in insulating matrices, and no significant charge transport is observed. As the composition of polyacetylene is increased, effective processability decreases rapidly with a concurrent improvement in conductivity of the doped film.

One of the most important events that has occurred during the growth of the entire development of research on conducting polymers is the discovery that the polypyrrole when suitably doped is highly conducting ($\sigma \sim 100 \Omega^{-1} \text{ cm}^{-1}$) and is stable against its exposure to air. Unfortunately, polypyrrole too has not yet been developed up to a technologically usable product because of its poor measured mechanical properties. The discovery of polythiophene, polyfuran, polyazulene and also polypyrene do not appear to bridge this gap in the pressing technological need. Thus, search for never conducting polymers with improved mechanical strength is still continuing. Synthesis of new conducting polymeric conductors and the modifications of the known conducting polymers are some of the routes currently being pursued by researchers. It has been experimentally demonstrated that copolymerization is one of the most effective methods to improve upon the mechanical properties of the known brittle polymers. This approach has precisely been followed by different research groups to improve upon the mechanical properties of the conducting polypyrrole. Kumar et al. have electrochemically synthesized a new conducting polymer of polyphenylene oxide-pyrrole, which has better mechanical strength but is slightly less conducting than pure polypyrrole. A copolymer of poly-N-(p-nitrophenylpyrrole)-pyrrole has also been reported. Copolymers of polypyrrole with N-substituted pyrroles such as N-methyl pyrrole has also been reported and Schottky-type

diode of this copolymer with low work function indium has been attempted. To further improve upon the mechanical strength of polypyrrole, its graft copolymerization with styrene has also been recently tried. These investigations show unequivocally that copolymerization affords an additional method for the engineering of conducting polymers and thus permits the controlled growth of films whose growth would otherwise be self-terminating.

The formation of composites of conducting polymers in a nonconducting polymer matrix is also used to prepare modified materials. These composites can show practical advantages over the homogeneous materials. They can demonstrate improved environmental stability, mechanical property, or even good optical transparencies. Often the advantages will far outweigh the small decrease in conductivity. It is surprising that composites formed with low contents of polypyrrole actually demonstrate reasonably high conductivities. This allows to take full advantage of the mechanical integrity of the matrix polymer. An added benefit encountered with these materials is that they can be formed electrochemically and that polymerization conditions such as voltage or current, can be used to control the growth of the conducting polymer.

Composites of polypyrrole with poly(vinyl-chloride) and polyacetylene have also been attempted in an effort to improve upon the processibility of conducting polypyrrole. PVC is one of the most versatile materials produced by the plastic industry and its mechanical properties can be varied simply by blending it with another polymer such as polyvinylalcohol or the addition of a plasticizer. The composite of PVC and polypyrrole (PPY) has been shown to have a conductivity $\alpha \sim 50 \Omega^{-1} \text{ cm}^{-1}$ at room temperature and retains the mechanical strength of PVC. An interesting off-shoot of this investigation is that the appearance of the conductivity on both sides of PVC of this composite of PVC and PPY is critically dependent on the thickness of the electrochemically grown polypyrrole film. Attempts at a synthesis of a composite of polyacetylene-polypyrrole do not appear to have yielded to definite improved mechanical properties of the highly conducting polypyrrole (Bansi et al, 1986).

4. APPLICATION OF CONDUCTING POLYMERS

4.1. Battery Application

One of the major reasons which has prompted the speedy development of conductive polymers is their anticipated use as electrodes in light weight and rechargeable batteries. Compared to lead-acid batteries, polyacetylene $(CH)_x$ battery is not only lighter in weight but also has both higher energy and power densities respectively. However, the major disadvantage still confronting the large-scale commercial exploitation of $(CH)_x/Li$ cell is both the sensitivity of $(CH)_x$ films to air and the inability of fibrillar $(CH)_x$ to accept more than 7-8% of the injected charge. However, with the discovery of polypyrrole and more recently of polythiophene it now appears almost certain that a light-weight, long-lasting and efficient battery will soon become a reality. Polythiophene and polypyrrole have both been found to be insensitive to the exposure of air and can conveniently store 24-30% of the available charge when suitably doped.

A possible improvement over the polythiophene battery would be to use polypyrrole which has a higher conductivity.

Copolymer of polythiophene and polypyrrole which is likely to have a better mechanical strength (consequently better life cycle) and higher conductivity and should easily accept both n- and p-type charge carriers.

4.2. Photo-electrochemical Cell (PEC)

The growth of the industry pertaining to the semi conductor-based photoelectrochemical solar cells had until recently been seriously impeded by the continuous photo degradation of small band gap electrodes.

One of the recent and most promising applications of conducting polymers is their use in the fabrication of an energy storage device using the principles of photo-electro chemistry. A further advantage of polyacetylene (PEC) cell using polythiophene (PT) film in electrolyte of $Pb(ClO_4)_2$ acetonitrile is the resulting photo-induced doping (or charging) of polythiophene (PT) in addition to its photovoltaic effect. However, it will be essential to

carry out extensive investigations to improve upon the conversion efficiency using different conducting polymers.

4.3. Schottky Barriers, Solar Cells and Solid-State Devices

The Schottky barrier-type device is formed by the evaporation of a metal onto a semiconductor such as silicon or gallium arsenide. Technology of today is actively engaged in finding a suitable synthetic material which could replace the widely used semiconductor silicon or metal in the commercially available Schottky devices.

Polyacetylene-(CH)_x shows metallic conductivity when suitably doped either chemically or electrochemically. The solar cells developed using semiconductor polyacetylene and deteriorate with time because of the increasing sensitivity of (CH)_x to air and humidity. Polypyrrole and various polythiophenes synthesized using electrochemical techniques appear to have partially offered adequate resistance to different environmental parameters. A Schottky-type barrier diode consisting of electrochemically prepared copolymer of pyrrole and n-methylpyrrole and low work function indium has been experimentally shown to be viable. Both polythiophene and poly(3-methyl) thiophene films grown electrochemically on indium-tin oxide glasses have been successfully utilized for the fabrication of Al/polymer/Au photovoltaic cells.

4.4. Electro-optic Devices

The optical characteristics of the polymer films undergo changes with the corresponding changes in the conductivity varying from insulator to metallic conductor as a consequence of electrochemical doping.

The as-grown polypyrrole film obtained by electrochemical polymerization is lightly doped with anion and shows dark brown in the transmitted light. As a result of electrochemical undoping in the electrolytic cell, the transmitted color changes from dark brown to yellow green. The absorbance changes in these and a few other conducting polymers such as 3-methylthiophene, 3,4-dimethylthiophene and 2,2'-dithiophene and polyaniline make these materials attractive for electrochromic applications.

4.5. Sensors

Conducting polymers such as polyfuran and polythiophene are expected to have profound uses in humidity sensors and as radiation detectors. A significant change in the conductivity of doped polypyrrole has also been noticed when exposed to toxic gases such as NO, NO₂ and CO. Polyheterocyclics thus have enough scope for being used in humidity sensors, radiation detectors and as gas sensors.

4.6. Medicinal Uses

Polymers such as polystyrene have been used in the past to control the release of various anions such as glutamate (Glu) and ferrocyanide (FeCN). The total amount of anions released from a neurotransmitter fabricated using polypyrrole films is much larger than that reported using other polymers. It has now become possible using repetitive pulses to consecutively release small amounts of anions (Bansi et al, 1986).



5. POLYANILINE

Polyaniline is the oxidative polymeric product of an aniline under acidic conditions and has been known since 1862 as an aniline black. At the beginning of the twentieth century organic chemists began investigating the constitution of aniline black and its intermediate products. Willstatter and co-workers in 1907 and 1909 regarded aniline black as an eight-nuclei chain compound having an indamine structure (Figure 5.1.).

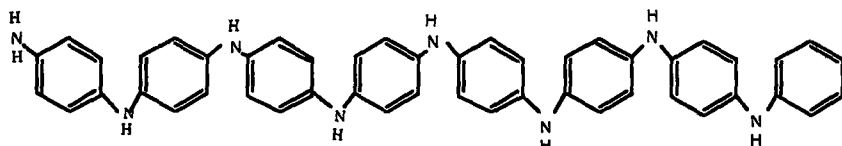


Figure 5.1. Indamine Structure

Polyaniline is a typical phenylene-based polymer having a chemically flexible -NH- group in a polymer chain flanked either side by a phenylene ring. The protonation and deprotonation and various other physico-chemical properties of polyaniline can be said to be due to the presence of the -NH- group.

In 1910 Green and Woodhead were able to report various constitutional aspects of aniline polymerization. These authors carried out oxidative polymerization studies using mineral acids and oxidants such as persulphate, dichromate, and chlorate and determined the oxidation state of each constituent by redox titration using $TiCl_3$.

During that period it did not occur to anyone to investigate its electrical and magnetic properties for the obvious reasons that organic compounds are insulators, though in 1911 Mecoy and Moore suggested electrical conduction in organic solids. Almost 50 years later, Surville et al. in 1968 reported proton exchange and redox properties with the influence of water on the conductivity of polyaniline. Among all conducting polymers polyaniline has a special representation due to its easy synthesis, environmental stability and simple non-redox doping by protonic acids. Non-redox doping by protonic acids is an important aspect where a number of electrons in a polymer chain remain unchanged during the doping process. However, during doping all the hetero atoms in polymer, namely nitrogen became protonated. This protonated form is electronically conducting, and the magnitude of increase in its conductivity is a function of level of protonation as well as functionalities

present in the dopant. The functional group present in the doping acid, its structure and orientation play an important role in solubilizing of a conducting form of polyaniline or for obtaining aqueous dispersion and compatibility with other polymers.

Polyaniline may be synthesized by two principal methods; the direct oxidation of aniline by chemical oxidants and by anodic oxidation on an inert electrode (Handbook, 1995).

Chemical synthesis of polyaniline is a precipitation from an aqueous solution containing typical reagents: ammonium peroxydisulphate (persulphate), acids like hydrochloric, sulphuric, nitric or perchloric, and aniline. This direct route represents the classical approach to polyaniline synthesis in which, aniline, the monomer, is converted directly to a conjugated polymer by a condensation process. One of the disadvantage of this direct approach stems from the experimental observation that an excess of the oxidant and higher ionic strength of the medium lead to materials that are essentially intractable.

Four major parameters affect the course of the reaction, nature of the medium, concentration of the oxidant, duration of the reaction and temperature of the medium

There is at present a two-fold interest in the electrochemical polymerization process. First, electrochemical polymerization reactions provide a new method of polymerization with a fine control of the initiation and termination steps. Second, electrochemical polymerization have technological potential. Besides, one of the important features found in electrochemical polymerization reactions of conducting polymers is that they proceed with electrochemical stoichiometry. This is because electrochemical reactions are often much cleaner, with respect to possible pollutants, than chemical reactions. Moreover, electrons, as a reagent, are inherently pollution-free, at least, at the point of use (Syed et al, 1991).

Electrochemical methods generally employed for electrochemical polymerization of aniline are either galvanostatic (constant current) or potentiostatic (constant potential) or potential scanning/cyclic or sweeping methods.

Electrochemically prepared polyaniline has a structure containing units with repeated benzenoid rings (leucoemeraldine (L)), units with alternating benzenoid and quinoid rings (emeraldine (E)) and units with repeated quinoid rings (pernigraniline (P)). These units may be protonated to varying degrees through nitrogen centers (LH_n , EH_n , PH_n , $n=0-4$) located between the rings and have electron deficiencies in the rings ($LH_n^{+\cdot}$, $EH_n^{+\cdot}$ $n=0-3$) (Figure 5.2.). The positive charges introduced through the protonated nitrogen and/or the radical centers are neutralized by counter-ions in the structure (Pekmez N. et al, 1993).

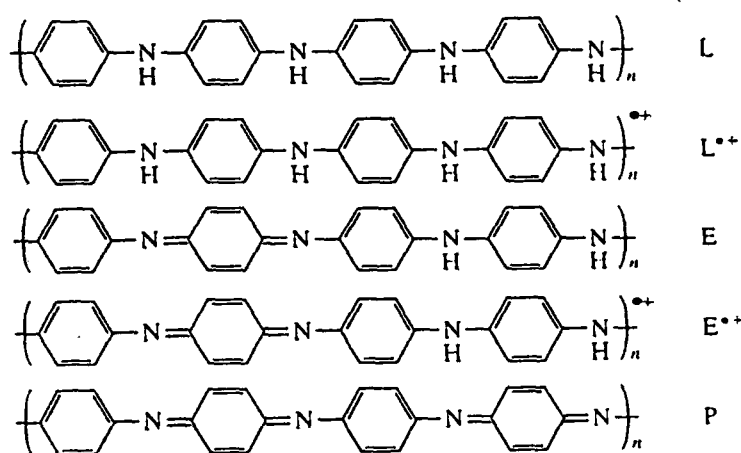


Figure. 5.2. Some of the polyaniline structures

Mohilner et al., Breitenbach and Heckner, Hand and Nelson, and Genies and co-workers have proposed mechanisms for electropolymerization of aniline. The point of agreement in the proposed mechanisms is the first step of oxidation of aniline, i.e., formation of the radical cation. This radical cation gives three different resonance forms as shown in Figure 5.3.

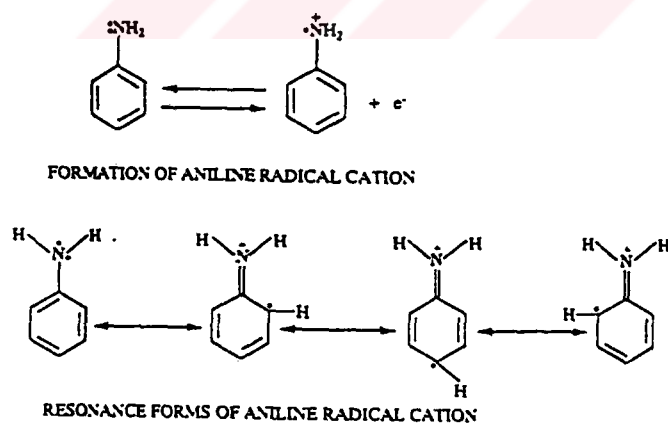


Figure 5.3. Formation of aniline radical cation and its resonance forms.

Electrochemical polymerization of aniline is a radical combination reaction and is diffusion controlled. The radicals generated thus diffuse together and react faster than they can diffuse away from the electrode vicinity. Hence at lower potentials the generation of radicals can be controlled in such way that diffusion away from the electrode surface is minimized to avoid a disproportionate reaction of these free radicals. The mechanism is displayed in Figure 5.4.

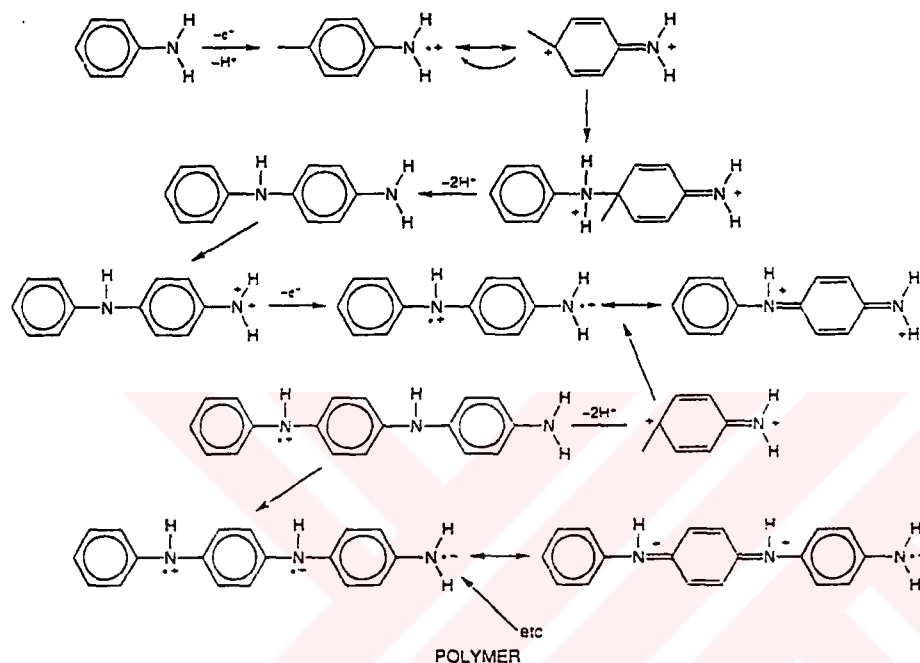


Figure 5.4. Electrochemical polymerization of aniline

Two mechanisms for the anodic oxidation of aniline in acidic and alkaline media have been reported. The products of anodic oxidation of aniline are shown in Figure 5.5. (Pekmez N., 1992)

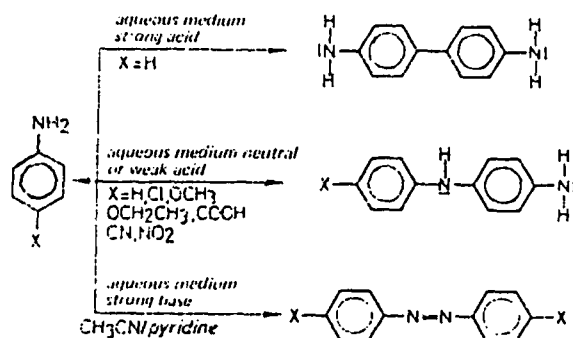


Figure 5.5. Possible aromatic coupling mechanism for the oxidation of aniline

Electropolymerization of aniline is usually carried out in aqueous acid solutions. The major disadvantage of these media is the decomposition of polyaniline to form quinone and hydroquinone type products. The formation of a large quantity of quinone indicates homolytic cleavage of the NH group from the phenyl rings to yield degradation products such as quinone and other oligomers. The degradation mechanism as proposed by Kobayashi et al. (1984) is given in Figure 5.6.

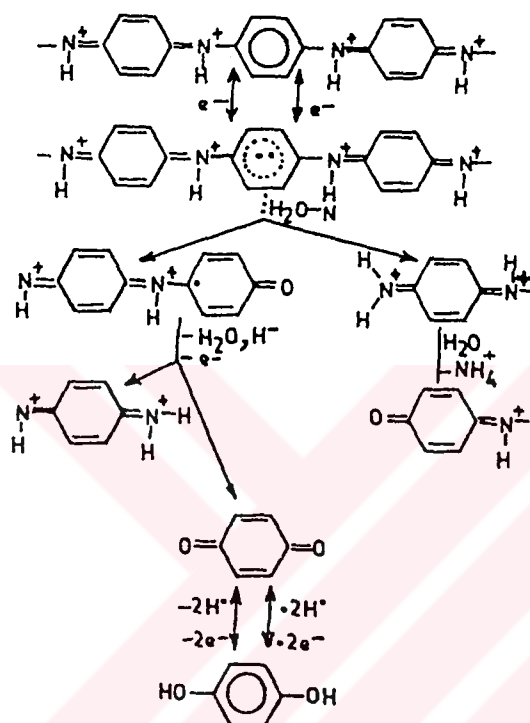


Figure 5.6. The electrochemical degradation of polyaniline to benzoquinone

6. ELECTROCHEMICAL TECHNIQUES

6.1. Cyclic Voltammetry

In cyclic voltammetry, the sweep traces a triangular form; that is, the potential is first increased linearly to a peak and then decreased to its starting point at the same rate. Generally, the cycle is completed in a fraction of a second to a few seconds (Skoog, 1985).

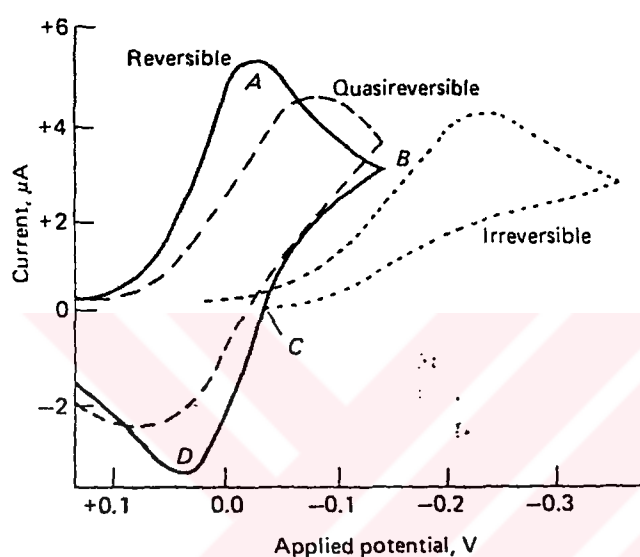


Figure 6.1. Cyclic voltammograms

Figure 6.1. shows cyclic voltammetric curves for three reducible analytes. The solid curve is for a reversible reaction. When the potential is first reversed (point B), the current remains positive and is largely due to the diffusion-controlled reduction of the analyte. Ultimately, however, potential C is reached at which the analyte is no longer reduced; the current here is zero with further positive changes in the potential, oxidation of the previously reduced species begins and proceeds until its concentration reaches zero. The anodic peak D results.

The curve labeled quasireversible is the voltammogram for a system in which the electron transfer process is not instantaneous. Here, the difference in potential between the cathodic

and anodic peaks provides a measure of the relative rates of the reduction and oxidation reactions.

The third curve in Figure 6.1. is a voltammogram for an irreversible electrode process. Here, only a cathodic peak is observed because the product formed in the initial reduction is not reoxidized at a significant rate.

Cyclic voltammetry, while not used for routine quantitative analyses, has become an important tool for the study of mechanisms and rates of oxidation-reduction processes, particularly in organic and metal-organic systems. Often cyclic voltammograms will reveal the presence of intermediates in oxidation-reduction reactions. Usually platinum is used for fabrication of microelectrodes used with this technique.

6.2. Potentiostatic Coulometry

The potentiostatic coulometry involves maintaining the potential of the working electrode (the electrode at which the analytical reaction occurs) at a constant level such that quantitative oxidation or reduction of the analyte occurs without involvement of less reactive species in the sample or solvent. Here, the current is initially high but decreases rapidly and approaches zero as the analyte is removed from the solution Figure 6.2.

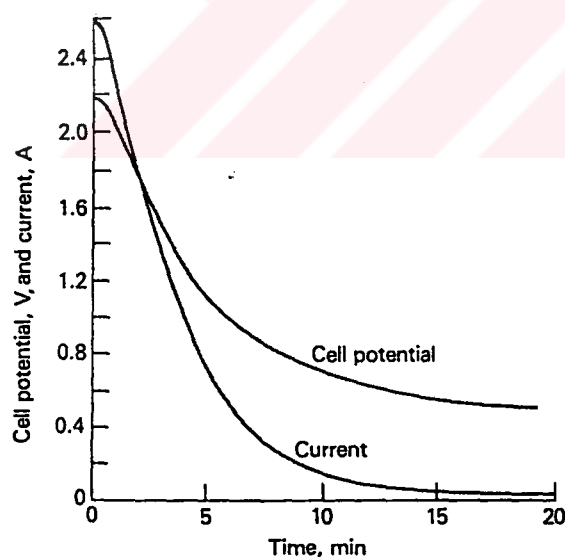


Figure 6.2. Changes in applied potential and current during a controlled cathode potential electrolysis (Skoog, 1985).

The quantity of electricity required is most commonly measured with an electronic integrator. The quantity of electricity or charge is measured in units of the coulomb (C) and the faraday (F). The coulomb is the quantity of charge that is transported in one second by a constant current of one ampere.

Thus for a constant current of I amperes operating for t seconds, the number of coulombs Q is given by the expression.

$$Q = I.t$$

For a variable current, the number of coulombs is given by the integral

$$Q = \int_0^t I.dt$$

The faraday is the quantity of electricity that will produce one equivalent of chemical change at an electrode. Since the equivalent is an oxidation-reduction reaction corresponds to the change brought about by one mole of electrons, the faraday is equal to 6.02×10^{23} electrons. One faraday is also equal to 96,487 C.

6.3. Four Probe Technique

The electrical conductivity (σ) of a polymer may be defined as the ratio of net charge motion, J (or current density), brought about by an electric field, E.

$$\sigma = J / E$$

Both DC and AC conductivity experiments are reported in the literature. In DC conductivity studies, only the net charge which traverses the entire polymer is measured. In contrast, for AC conductivity experiments, the electrical conductivity is measured as a function of the frequency of an alternating electric field.

A film or thin 13 mm diameter pellet previously compressed was placed on four gold conductors and its conductivity was measured. Here, four points of contact, almost equally spaced on the periphery of the sample, can be made with a conductive paste.

Alternatively, four wires can be embedded into the periphery of the sample. Current (I) is passed through two adjacent contacts while the voltage drop (V) is measured across the other two conductors. The technique takes into account the sample thickness (d) and thus it must be measured along with the current-voltage characteristics of the sample. The formula employed for the measurement of conductivity (Syed et al, 1991),

σ , is ;

$$\sigma = \frac{\ln 2}{\pi} \cdot \frac{I}{V.d} = 0.22 \cdot \frac{I}{V.d}$$

(Pekmez, N., 1992)



7. EXPERIMENTAL

7.1. Apparatus

7.1.1. Electronic Equipment

The electrochemical instrumentation consisted of a PAR model 173 potentiostat-galvanostat coupled to a PAR model 175 universal programmer and a PAR model 179 digital coulometer. The current-voltage curves were recorded using a BBC Metrawatt Goertz X-Y recorder.

7.1.2. Electrochemical Cell and Electrodes

The electrochemical cell used was of the three-electrode type with separate compartments for the reference electrode (Ag/AgCl (sat.)) and the counter-electrode (Pt spiral). The acetonitrile +0.1 M TBAFB (tetra-n-butylammonium tetrafluoroborat) solution in the reference electrode compartment was saturated with AgCl. The working electrode for the cyclic voltammetric studies was a Pt disk (area 0.0132 cm²). The macrosamples of polymer films were prepared on a Pt macro-electrode (area, 1.0 cm²). The working micro-electrode was cleaned by polishing with Cr₂O₃ slurry. The macro-electrode was cleaned by holding it in a flame for a few minutes. The electrodes were rinsed with acetonitrile and dried before use.

7.1.3. Preparation of Electrochemical Cell

In nonaqueous electrochemical studies, it is very important to remove O₂ and water from working cell in order to investigate electrochemical behaviour of any substance correctly. For that reason all electrochemical experiments carried out under very pure nitrogen atmosphere (BOS, 99.99%).

A special electrochemical cell was used in all experiments which is shown in Figure 7.1. It has five necks. Three of them belong to the electrodes which are used as working,

reference and counter electrode. The others are used to nitrogen inlet and outlet (Özyörük, 1979).

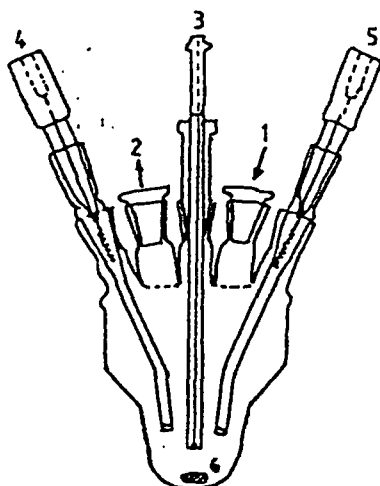


Figure 7.1. 1: Nitrogen entrance 2: Nitrogen exit 3: Working electrode 4: Reference electrode 5: Counter electrode 6: Magnet.

Before electrochemical experiments, the cell was washed with basic KMnO_4 , concentrated HCl , acidic $\text{K}_2\text{Cr}_2\text{O}_7$, distilled water and alcohol. Then it was dried at $100\text{ }^\circ\text{C}$. After these washing and drying procedure that it is ready to use the cell for electrochemical experiments. Enough electrolyte (0.1M) was transferred to the cell and dried at $120\text{ }^\circ\text{C}$ under vacuum at 3-4 hours. Then vacuum was cut off and nitrogen was passed through and nonaqueous acetonitrile was added to the cell under nitrogen atmosphere. Finally analyte, can be solid or liquid or gaseous phase, was added to the solution and the electrodes were put into the cell and connected with cables to potentiostat/galvanostat. Now it is ready to make an electrochemical experiment.

7.1.4. Solvent and Substances

Acetonitrile is very common solvent in nonaqueous electrochemical studies which has a resistance opposite to oxidation and reduction processes. Also dielectric constant of acetonitrile is 37.5 at $20\text{ }^\circ\text{C}$. Acetonitrile was purified with 5 steps of fraction distillation.

Aniline (BDH) was vacuum distilled ($67\text{ }^\circ\text{C}$). Both acetonitrile and aniline were kept under a nitrogen atmosphere.

2-Aminobenzothiazole (Fluka, 98%) was used directly without any purification.

2-aminobenzimidazole (Aldrich, 97%) was used directly without any purification.

5-aminobenzimidazole was synthesized from 5-nitrobenzimidazole by chemical reduction process which is explained below;

5.0 g (30.6 mmol) of 5-nitrobenzimidazole was dissolved in 15 ml of concentrated HCl and 55 ml of water. After that the solution was heated and stirred to solve all 5-nitrobenzimidazole. When the temperature of the solution was reached to the boiling point than 7.26 g (61.2 mmol) of Sn was added slowly. 5 ml of concentrated HCl was again added to solve Sn completely and it was diluted to 120 ml with water. 10 ml of NH_3 was added drop by drop to adjust acidity of the solution (pH= 2). After reduction H_2S was passed through the solution in order to remove Sn from the solution as SnS. SnS was filtered until clear was obtained. Then solvent was evaporated until the volume of 25 ml. Concentrated NH_3 was added in order to adjust pH 8-9.5 under nitrogen atmosphere. At the end of the reaction the colour of the solution changes from yellow to reddish-brown. This solution was held at 25 °C (room temperature) to ensure that the substance was completely precipitated. After that it was filtered and recrystallized from the minimum volume of hot water and dried in a vacuum oven. The cyclic voltammogram of the synthesized substance showed that it was not pure . It has a salt form of hydrochloride. Then the salt was dissolved in nonaqueous acetonitrile and gaseous NH_3 was passed through this solution in order to remove Cl^- as a precipitate of NH_4Cl . Finally, it was filtered and dried under nitrogen atmosphere. Melting point of the red product is 104-105°C.

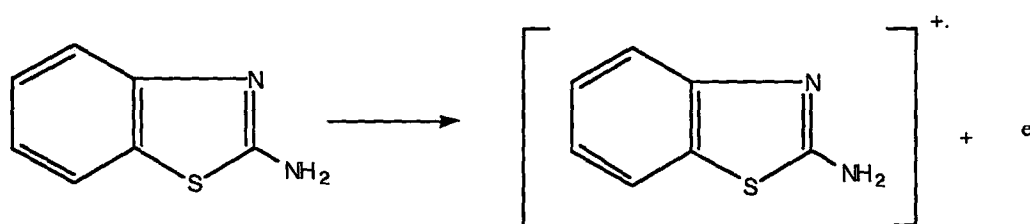
Nonaqueous HClO_4 was produced by coulometric method. For this method tetrabutylammonium perchlorate (TBAP) and H_2 were used. Firstly TBAP was dissolved in nonaqueous acetonitrile and H_2 was passed through this solution. H_2 oxidized to H^+ with platinum working electrode. Then perchlorate anion was reacted with H^+ to give nonaqueous HClO_4 (Pekmez K., 1991). Tetra-n-butylammonium fluoroborat (TBABF_4) was used as a supporting electrolyte. TBABF_4 was prepared by reacting tetrafluoroboric acid (Aldrich) with a 40% aqueous solution of tetrabutylammonium hydroxide (TBAOH) (Aldrich). It was recrystallized from 70% ethanol several times and kept a nitrogen atmosphere after vacuum drying for 24 hours at 120 °C.

8. RESULTS AND DISCUSSION

8.1. The Electrochemical Behavior of 2-aminobenzothiazole, 2-aminobenzimidazole, 5-aminobenzimidazole in acetonitrile

8.1.1. The Electrochemical Behavior of 2-aminobenzothiazole (2-abt)

The electrooxidation of 2-aminobenzothiazole (2-abt) occurs at +1.20 V (vs. Ag/AgCl (sat.)) in acetonitrile +0.1 M TBABF₄ medium as seen in cyclic voltammogram (Figure 8.1.a). There is no reverse cathodic peak.



Upon the addition of increasing amounts of anhydrous HBF₄ to 5 mM 2-abt solution oxidation peak current first decreases and then disappears when an equivalent amount of anhydrous HBF₄ acid is added. (Figure 8.1.b, c, d, e). This means that protonation of 2-abt occurs.

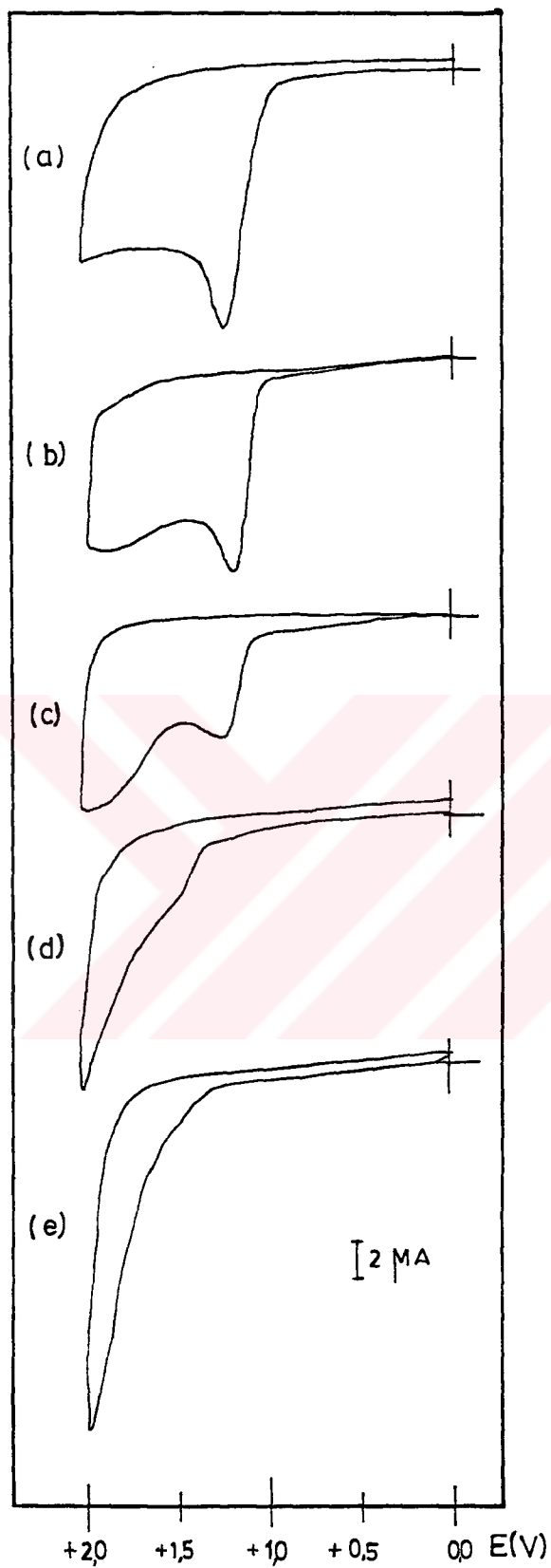


Figure 8.1. The first anodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 2-abt b) 5 mM 2-abt + 2 mM HBF₄ c) 5 mM 2-abt + 5 mM HBF₄ d) 5 mM 2-abt + 8 mM HBF₄ e) 5 mM 2-abt + 10 mM HBF₄. Scan rate: 100 mV/sec.

There is no reduction peak of 2-abt between 0.0 and -2.0 V in this medium (Figure 8.2.a). When increasing amounts of anhydrous HBF_4 was added to 5 mM 2-abt solution, two-step electroreduction of 2-abt was observed as seen in cyclic voltammogram (Figure 8.2.b, c, d, e). The recorded peak potentials of these reductions are -0.65 V and -0.90 V (the reduction of protonated aniline and its derivatives occurs at about -1.0 V). This shows that 2-abt can be protonated at two centers of the molecule and these two protonated structures are in equilibrium with each other, as shown below.



Since the peak at -0.65 V appears at lower acid concentrations and the peak current at -0.65 V is higher than that at -0.90 V, the equilibrium between the two protonated species lies to the right.

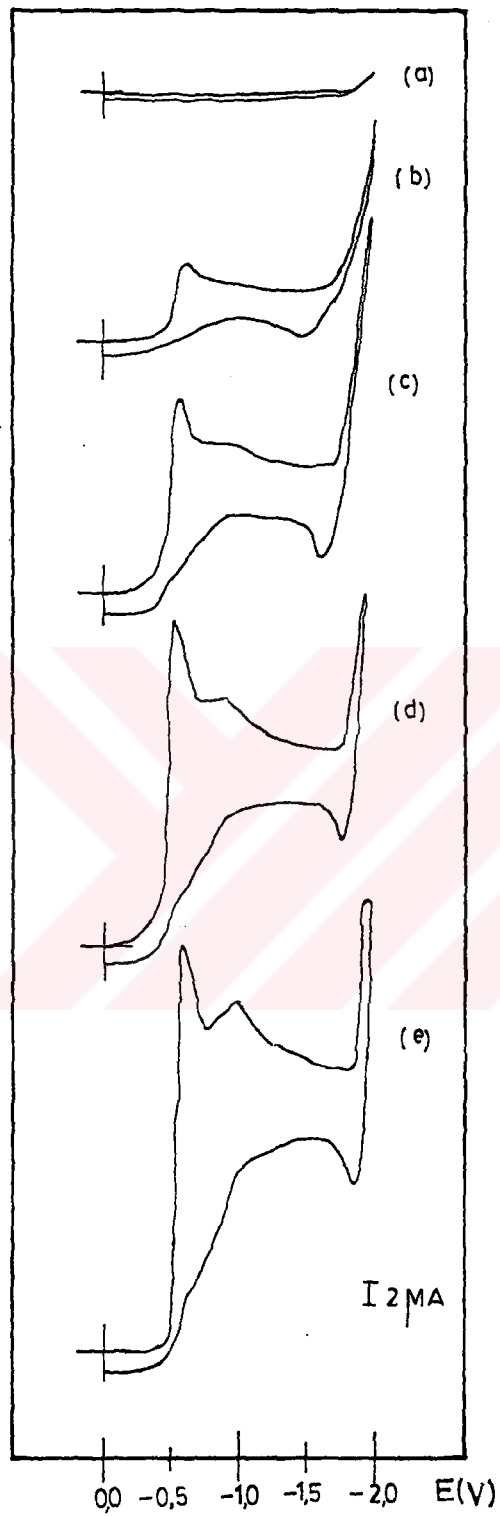
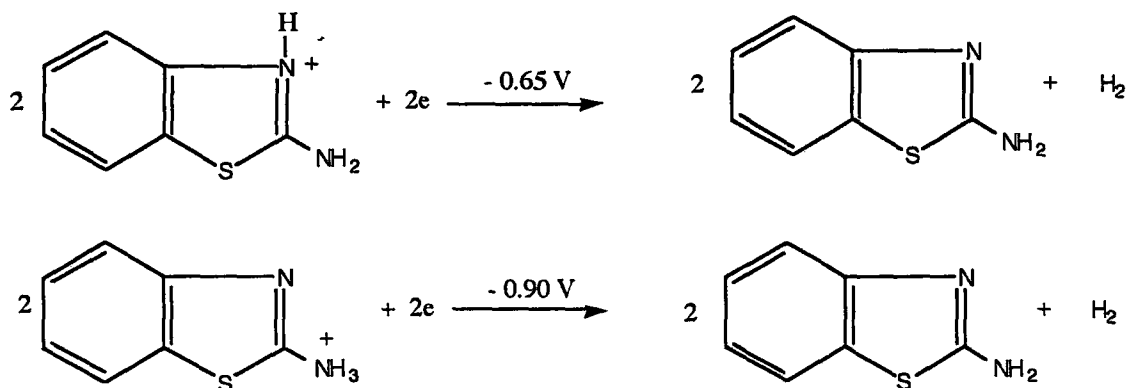


Figure 8.2. The first cathodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 2-abt b) 5 mM 2-abt + 2 mM HBF₄ c) 5 mM 2-abt + 5 mM HBF₄ d) 5 mM 2-abt + 8 mM HBF₄ e) 5 mM 2-abt + 10 mM HBF₄. Scan rate: 100 mV/sec.

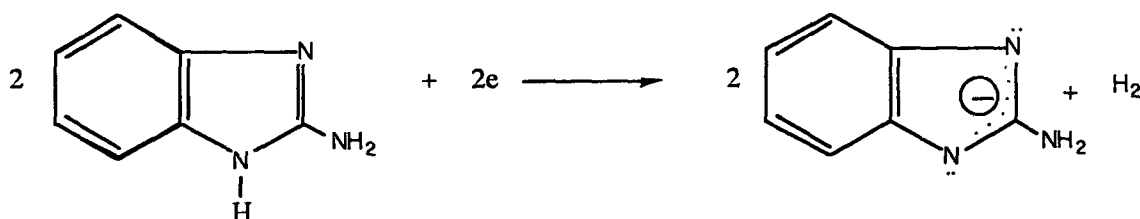
The electroreduction of protonated 2-abt molecules proceeds as follows:



As is seen from Figure 8.1., the oxidation peak current is reduced to about the half of the initial intensity when an equivalent amount of acid is added. It vanishes almost completely when twice as much acid is added. These results indicate also that there are two successive protonation processes occurring at two different centers of this molecule as was pointed out above when the electroreduction behavior of this molecule was discussed.

8.1.2. The Electrochemical Behavior of 2-aminobenzimidazole (2-abi)

The electro-reduction of 2-aminobenzimidazole (2-abi) is recorded at peak potential of -1.90 V (vs. Ag/AgCl (sat.)) in acetonitrile +0.1 M TBABF₄ as seen in the cyclic voltammogram (Figure 8.3.a). There is no the reverse peak. The reduction of hydrogen bonded clusters of imidazoles were observed at between -1.0 V and -2.0 V . (Pekmez K., 1996)



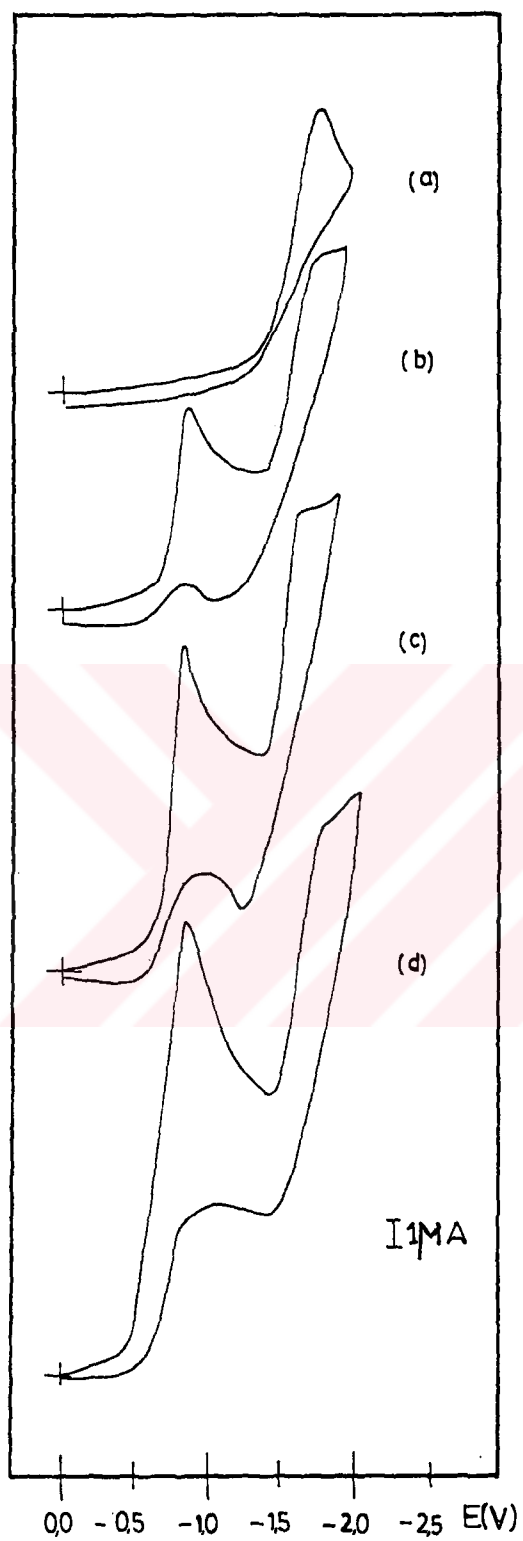
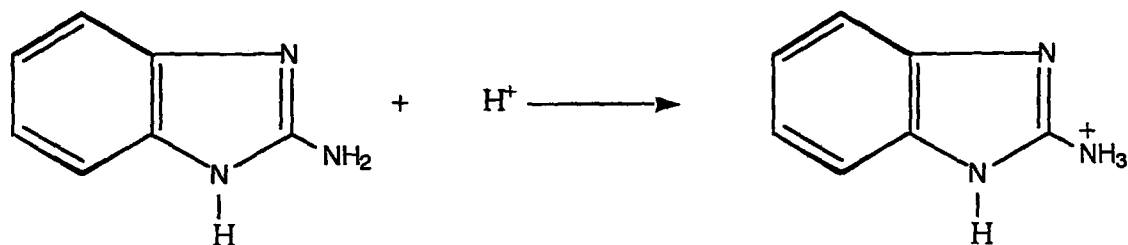
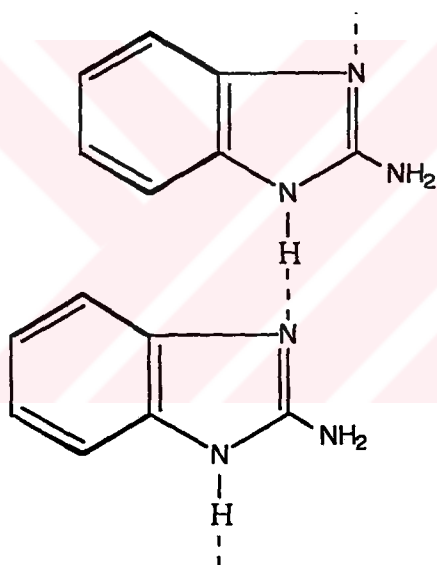


Figure 8.3. The first cathodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 2-abi b) 5 mM 2-abi + 3 mM HBF₄ c) 5 mM 2-abi + 5 mM HBF₄ d) 5 mM 2-abi + 10 mM HBF₄. Scan rate: 100 mV/sec.

When increasing amounts of anhydrous HBF_4 were added to 5 mM 2-abi (Figure 8.3. b, c, d) a second reduction peak was observed at -1.0 V. The observation of only one reduction peak means that the protonation occurs at only one center of the molecule.

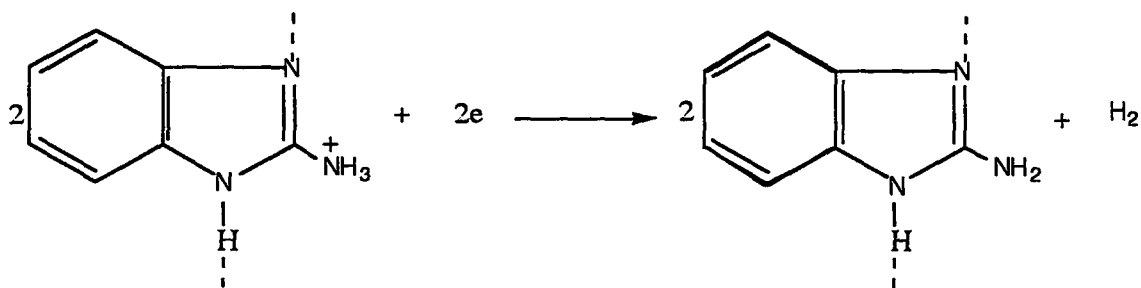


The following, intermolecular hydrogen bonding may be the reason for the absence of the two reduction peaks which belong to two different types of protonated species as was the case for 2-abt.

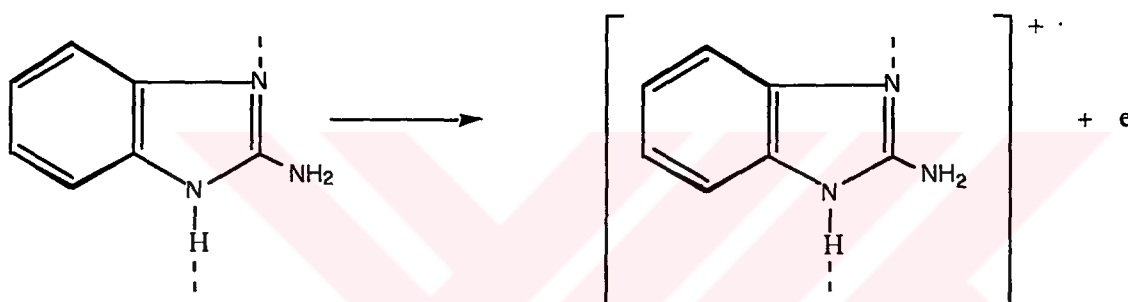


The high melting point of 2-abi (225 °C) supports the formation of the intermolecular hydrogen bonding. The melting point of 2-abt is between 126-129 °C. Where no intermolecular hydrogen bonding occurs.

The reduction of 2-abi at -1.0 V occurs as follows:



The oxidation peak of 2-abi was observed at +0.8 V in this medium as seen in the cyclic voltammogram (Figure 8.4.a).



When increasing amounts of anhydrous HBF_4 were added to 5 mM 2-abi solution, the oxidation peak current decreases and then almost disappears in 2-abi solution containing an equivalent amount of anhydrous HBF_4 acid because of the formation of the protonated 2-abi (Figure 8.4.b,c,d). The fact that there is only one protonation center was evidenced from the following finding. When an equivalent amount of acid is added the oxidation peak current vanishes almost completely (Fig.8.4.c).

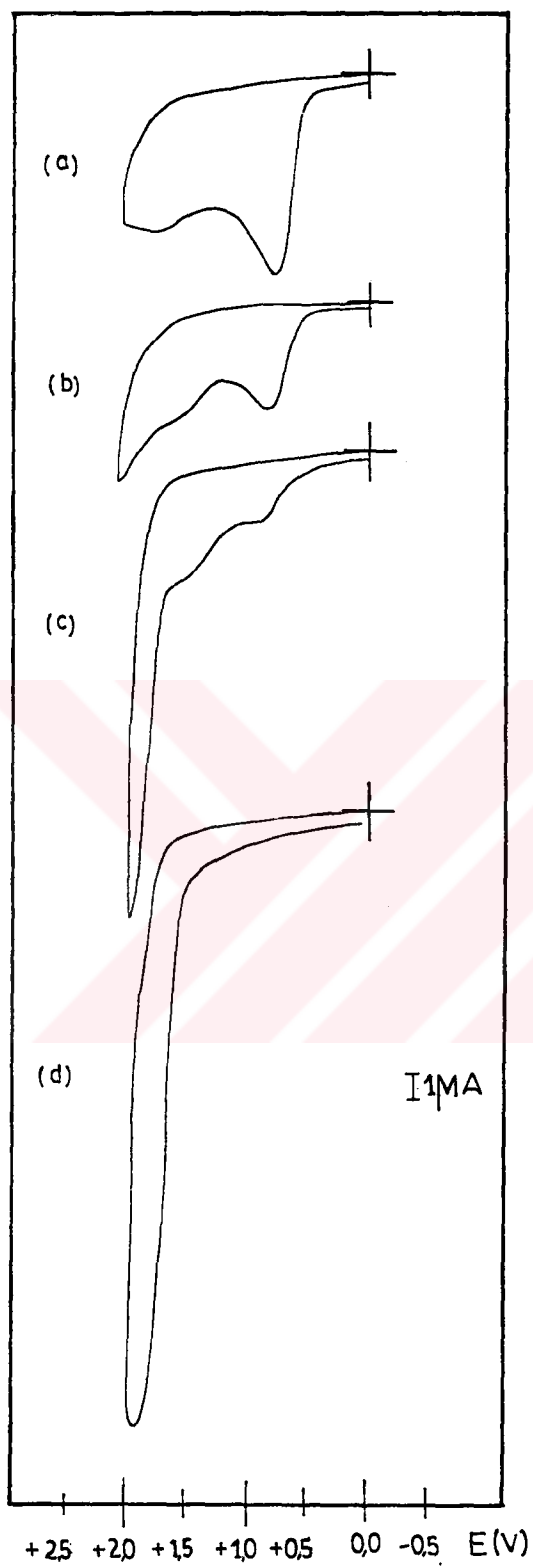
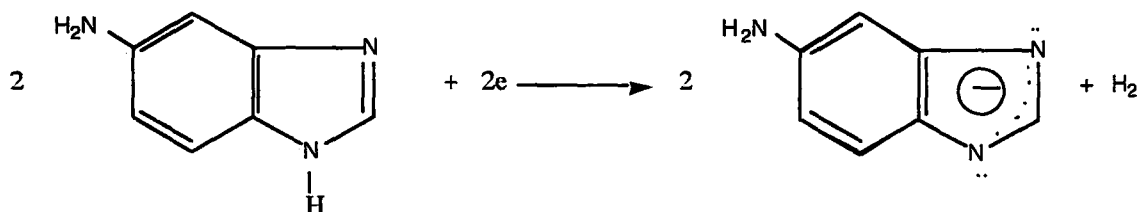


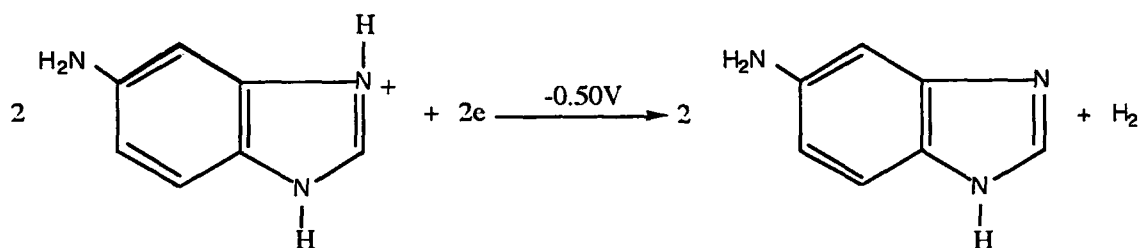
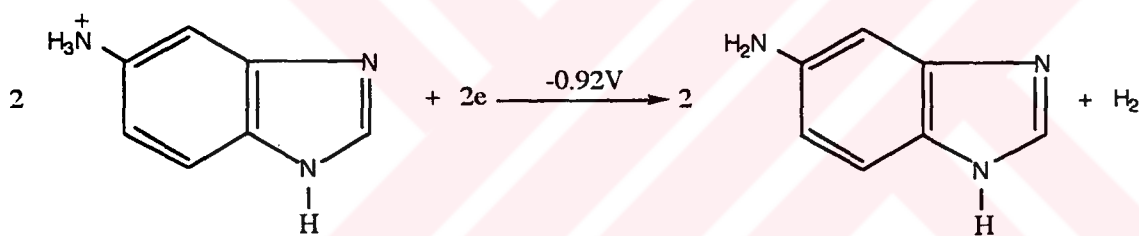
Figure 8.4. The first anodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 2-abi b) 5 mM 2-abi + 3 mM HBF₄ c) 5 mM 2-abi + 5 mM HBF₄ d) 5 mM 2-abi + 10 mM HBF₄. Scan rate: 100 mV/sec.

8.1.3. The Electrochemical Behavior of 5-aminobenzimidazole (5-abi)

The electro-reduction of 5-aminobenzimidazole (5-abi) is recorded at peak potential of -1.90 V (vs. Ag/AgCl (sat.)) in acetonitrile + 0.1 M TBABF₄ as seen in the cyclic voltammogram (Figure 8.5.a). There is no the reverse peak.



When increasing amounts of anhydrous HBF₄ were added to 5mM 5-abi solution (Figure 8.5.b,c,d,e), up to 2 mM HBF₄ addition, the second reduction peak was observed at -0.92 V and above this concentration of the acid, a third peak at -0.50 V. was recorded due to the following reactions,



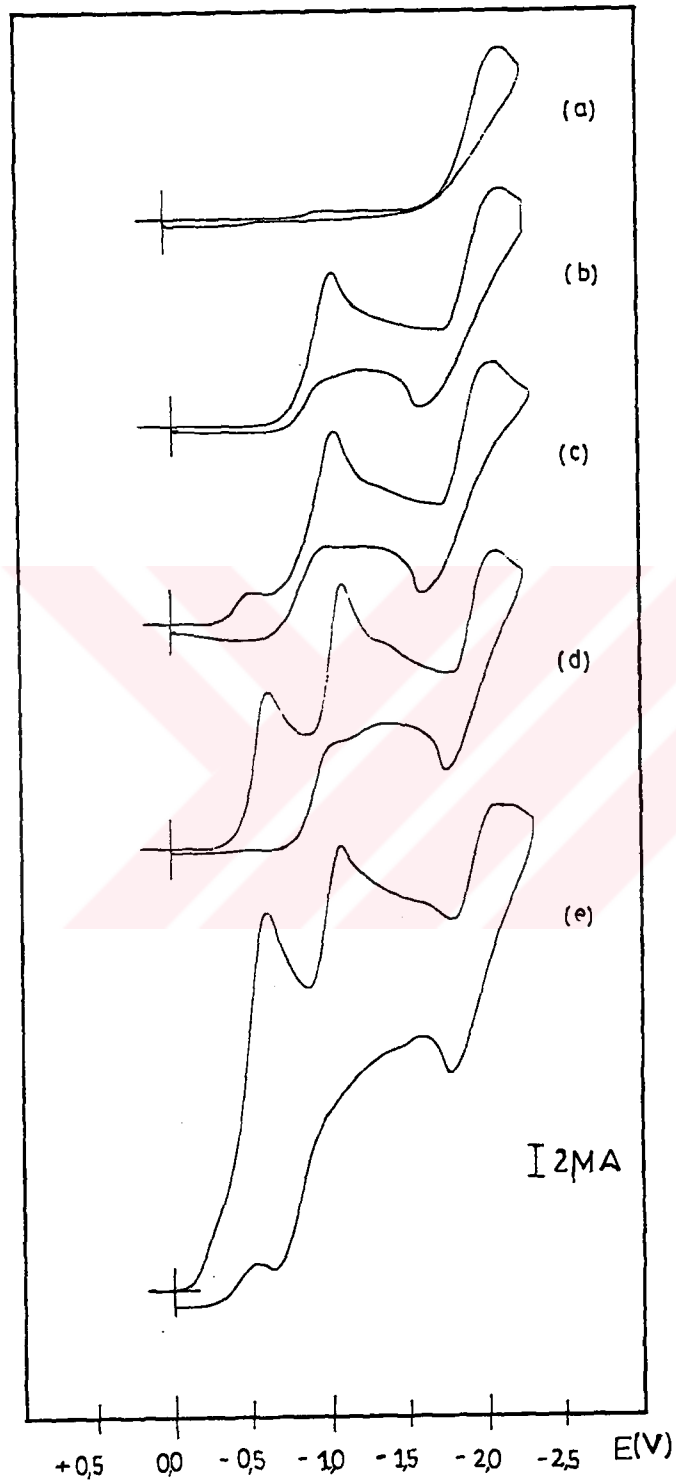
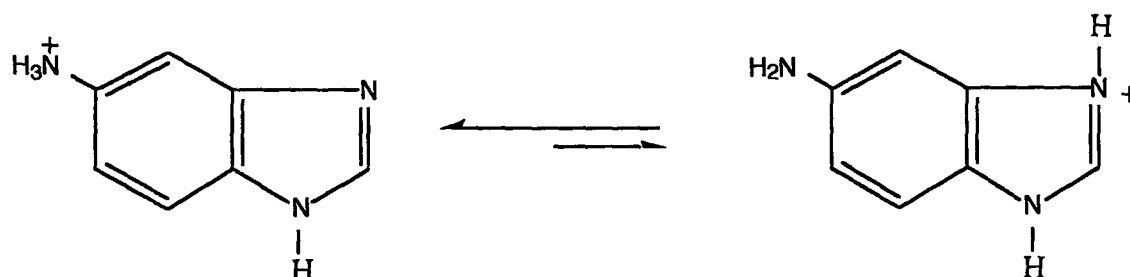
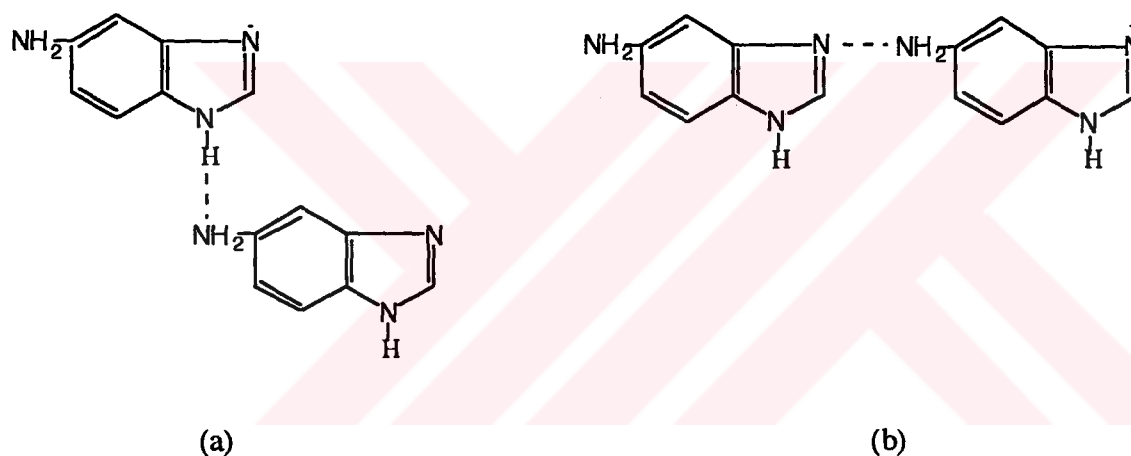


Figure 8.5. The first cathodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 5-abi b) 5 mM 5-abi + 2 mM HBF₄ c) 5 mM 5-abi + 3 mM HBF₄ d) 5 mM 5-abi + 5 mM HBF₄ e) 5 mM 2-abt + 10 mM HBF₄. Scan rate: 100 mV/sec.

5-abi can be also protonated at two centers of the molecule and these two protonated structures are in an equilibrium with each other. Since the reduction peak at -0.92 V is observed first, the equilibrium between the two protonated species lies to the left in this case, in contrast to the 2-abt.

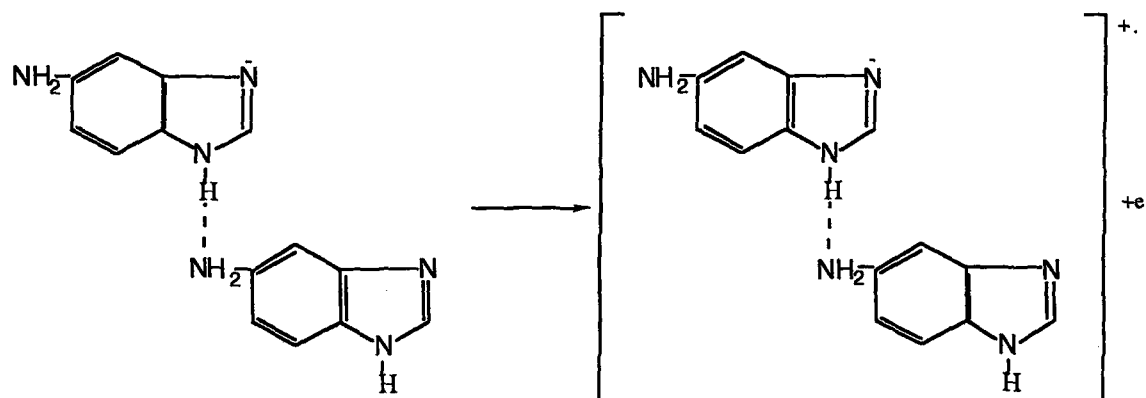


Intermolecular hydrogen bonding in this molecule can occur in two ways.

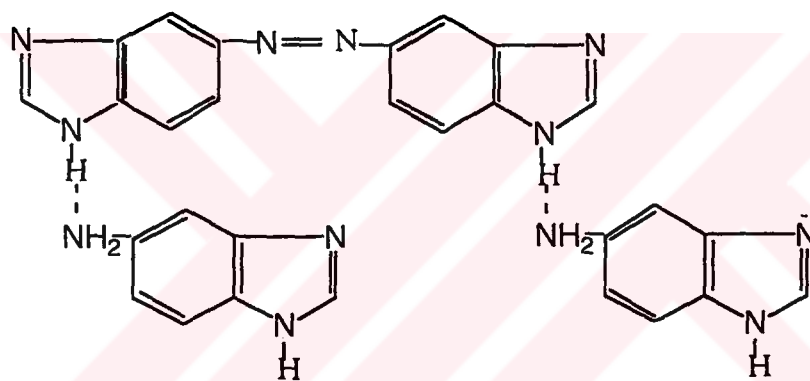


Due to the appearance of the reduction peak at -0.90 V first, the nitrogen center of the $-\text{NH}_2$ group is more basic than the nitrogen center in the imidazole ring. This also means that structure (a) is favored over structure (b) in hydrogen bond formation.

The oxidation of 5-abi occurs in two steps in this medium (Figure 8.6.a). The first oxidation peak is recorded at a potential of $+0.45$ V and the second sharp oxidation peak potential is found at $+1.30$ V. There are no corresponding reverse peaks. Because of formation of the hydrogen bonded units (dimers, trimers,.....) the oxidation of terminal $-\text{NH}_2$ group is shifted from about $+0.90$ V to $+0.45$ V.



The second sharp oxidation peak at +1.30V may belong to the oxidation of the following azobenzene type product formed after the first oxidation of the parent compound (Lund and Baizer, 1991), (Genies et al., 1990).



It is known that azobenzene is easily formed by the oxidation of aniline in alkaline solutions (Lund and Baizer, 1991), (Genies et al., 1990). When increasing amounts of anhydrous HBF_4 were added to 5mM 5-abi (Figure 8.6 b, c, d, e) the first oxidation peak at +0.45 V shifts to more anodic potentials and the second oxidation peak disappears. The hydrogen bonds are broken upon acid addition forming $-\text{NH}_3^+$ and oxidation of $-\text{NH}_2$ group shifts to its normal potentials of +0.90V. The second oxidation peak disappears upon the addition of acid to the medium. This provides a further evidence for the formation of azobenzene type products in alkaline medium.

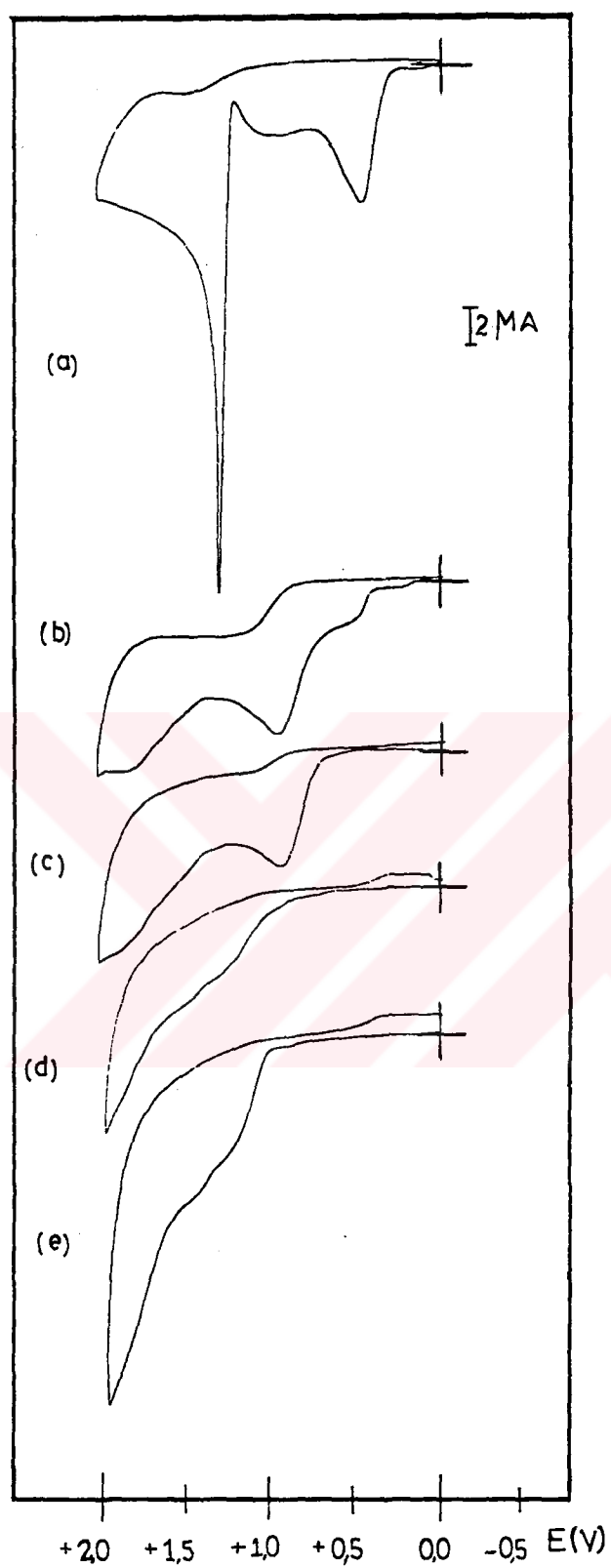


Figure 8.6. The first anodic cyclic voltammograms of acetonitrile/0.1 M TBABF₄ solution containing a) 5 mM 5-abi b) 5 mM 5-abi + 2 mM HBF₄ c) 5 mM 5-abi + 3 mM HBF₄ d) 5 mM 5-abi + 5 mM HBF₄ e) 5 mM 2-abt + 10 mM HBF₄. Scan rate: 100 mV/sec.

Normally the imidazole ring is not reducible unless hydrogen-bonded clusters are formed at the electrode surface (Pekmez, K., 1996). In the case of 5-abi and 2-abi broad reduction peaks were easily observable at around -1.90V in the absence of added acid, indicating the formation of hydrogen bonded clusters. In the case of 2-abt no such reduction peak is observed due to the absence of the hydrogen-bonded clusters in this molecule.

When anhydrous acid is added, the hydrogen bonds between -NH_2 centers and N centers in the imidazole rings are broken in 5-abi because of the protonation of -NH_2 groups. A new hydrogen bonded clusters are now formed between N centers and NH centers of the imidazole rings as in the case 2-abi. This is apparent from the Figure 8.5 which shows a broad reduction peak of hydrogen bonded imidazole clusters beyond -1.9 V.

The oxidation peak of aniline disappears when 5-abi coexist with aniline in solution (Figure 8.7.b). As one adds acid to this solution the oxidation peak of aniline starts to appear gradually. This oxidation peak first appears at more positive potentials than the potentials of aniline oxidation (Figure 8.7.c) and then returns to its normal potential as more acid is added (Figure 8.7.d). The above results show that 5-abi bonds to aniline monomer with hydrogen bonding, forming hydrogen-bonded oligomers and thus making the oxidation of aniline more difficult. As the hydrogen bonds are broken upon the addition of acid the normal oxidation behavior of aniline is reexhibited. No such behavior of aniline oxidation is observed with solutions containing aniline and 2-abt, indicating that 2-abt does not form hydrogen bonded oligomers with aniline. It is note worthy that neither benzimidazole and nor imidazole cause any such shifts in the oxidation peak of aniline when these two compounds coexists with aniline in solution. This means that hydrogen bond formation of imidazole derivatives with aniline can only be possible if these derivatives have an amino group substituted at 5-position. Since 2-abi is not soluble in acetonitrile in high concentrations, no such comparison was possible related to this compound.

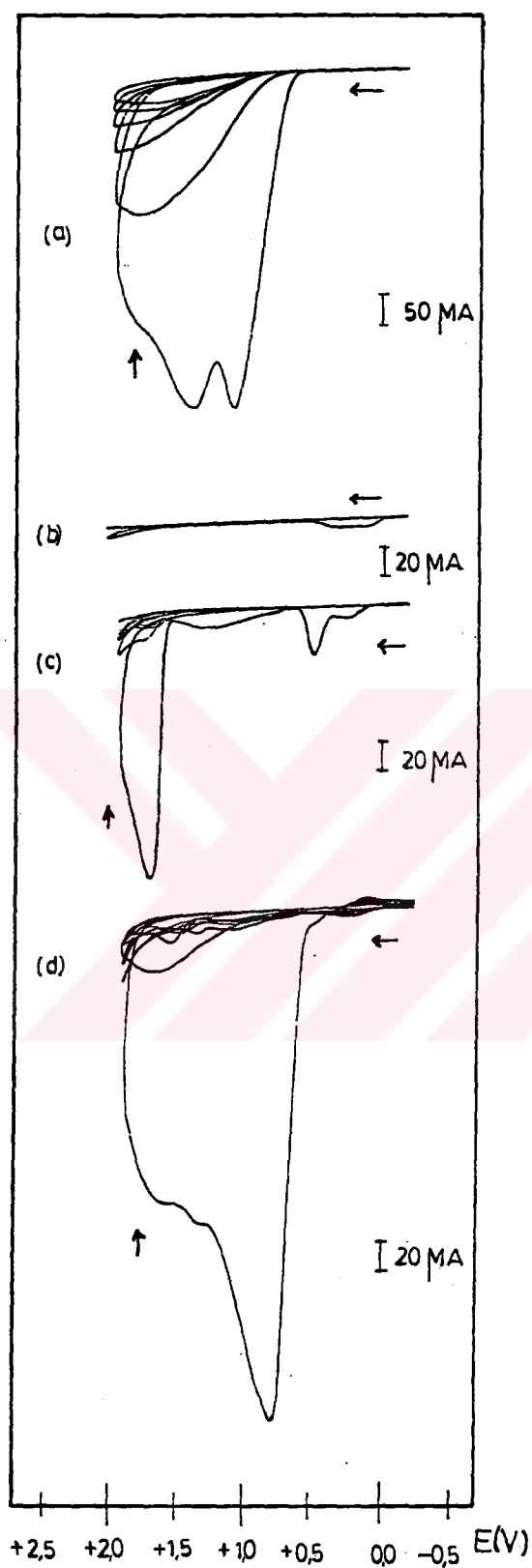


Figure 8.7. The first six cyclic voltammograms of the acetonitrile/0.1 M TBABF₄ solution containing a) 150 mM aniline b) 150 mM aniline+100 mM 5-abi c) 150 mM aniline+100 mM 5-abi+25 mM HBF₄ d) 150 mM aniline+100 mM 5-abi+50 mM HBF₄. Scan rate: 100 mV/sec.

8.2. The Effect of 5-aminobenzimidazole and 2-aminobenzothiazole on Polyaniline Films

Figure 8.8.a shows the first six cyclic voltammetric sweeps taken during the oxidation of aniline in acetonitrile +0.1 M TBABF₄ solution between -0.20 V and +1.90V. Figure 8.8.b shows subsequent sweeps obtained in the same solution. The formation and growth of the polyaniline film can be easily seen in this Figure. The peak due to the oxidation of aniline shifts to the higher potentials and gradually disappears (Figure 8.8.a), and the peaks due to the oxidation and reduction of the film increase in intensity (Figure 8.8.b) as the film grows. Figure 8.8.c shows the cyclic voltammetric behaviour of this film in acetonitrile +0.1 M TBABF₄ (blank solution). The film exhibits two broad oxidation peaks and two reduction peaks.

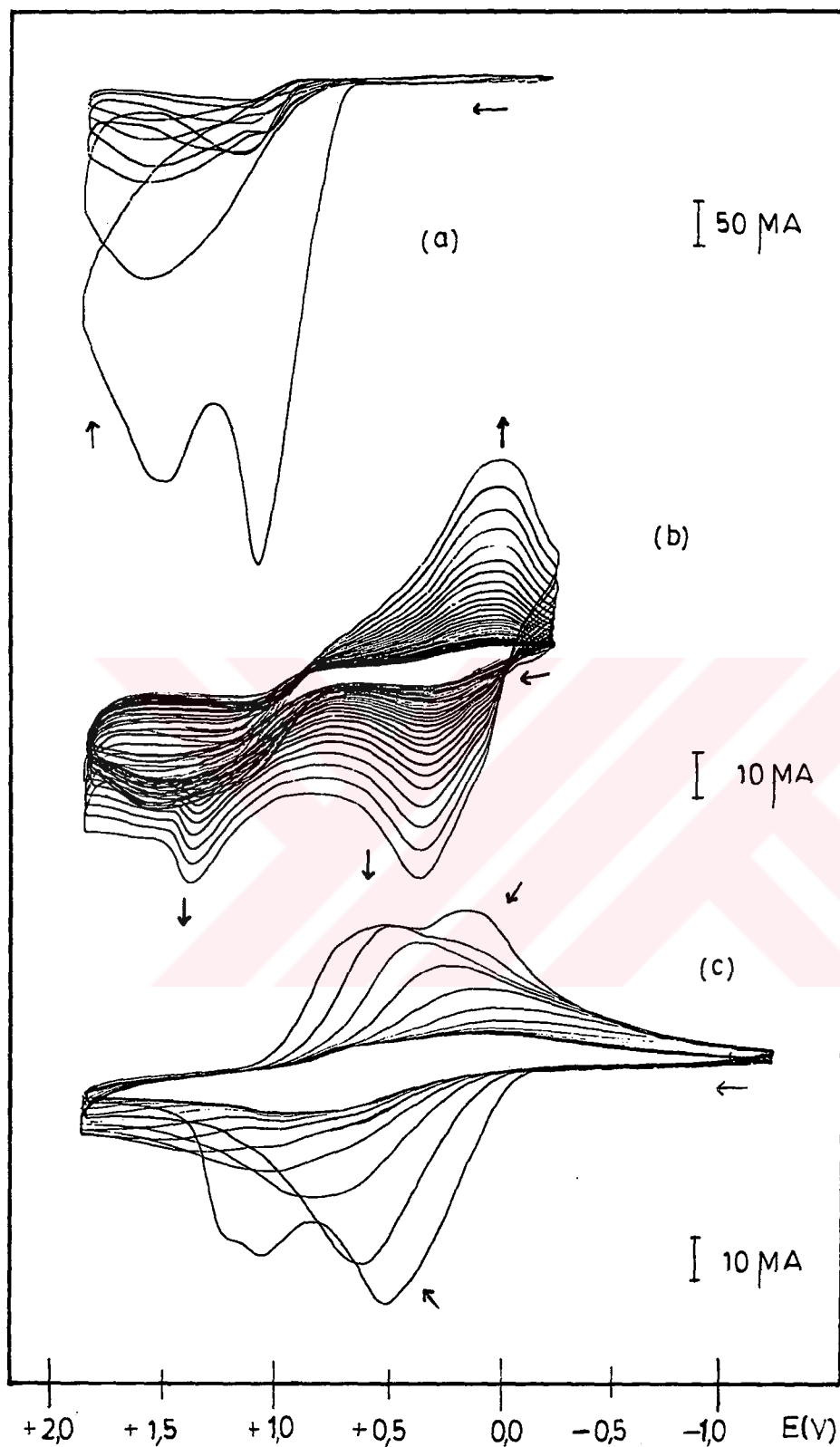
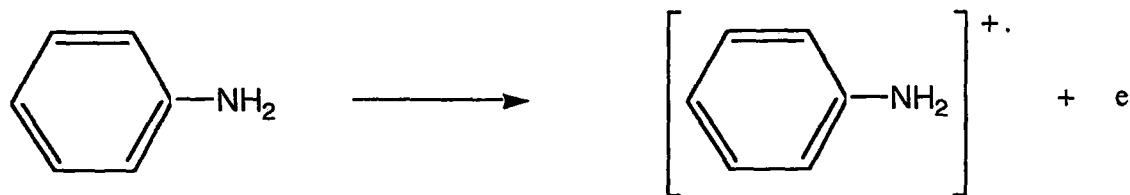


Figure 8.8: Cyclic voltammograms of the acetonitrile solution containing 150 mM aniline/0.1 M TBABF₄. a) Initial b) Multisweep cyclic voltammograms c) Behavior of the polyaniline film in blank solution. Scan rate: 100mV/sec.

In accordance with the cyclic voltammogram the electro-oxidation mechanism of aniline can be summarized as follows. Aniline is oxidized at +0.1 V in this medium forming the anilinium cation radical:



Dimerization of this cation radical forms p-aminodiphenylamine which can also be oxidized at these potentials. Continuation of reactions of the same type results in formation of the oligomers and eventually the polymer.

Figure 8.9 shows the multisweep cyclic voltammograms of 5-abi and 2-abt in acetonitrile +0.1 M TBABF₄ solution. Electro-oxidation peaks of 5-abi and 2-abt were observed at +1.80 V (Figure 8.9.a) and +1.20 V (Figure 8.9.b), respectively. There are no reduction peaks on reverse potential scans. After multisweep cyclic scans between -0.20 V and +1.90 V (vs. Ag/AgCl (sat.)) a dark brown film from 5-abi and yellow film from 2-abt were deposited on Pt surface is not a conducting film.

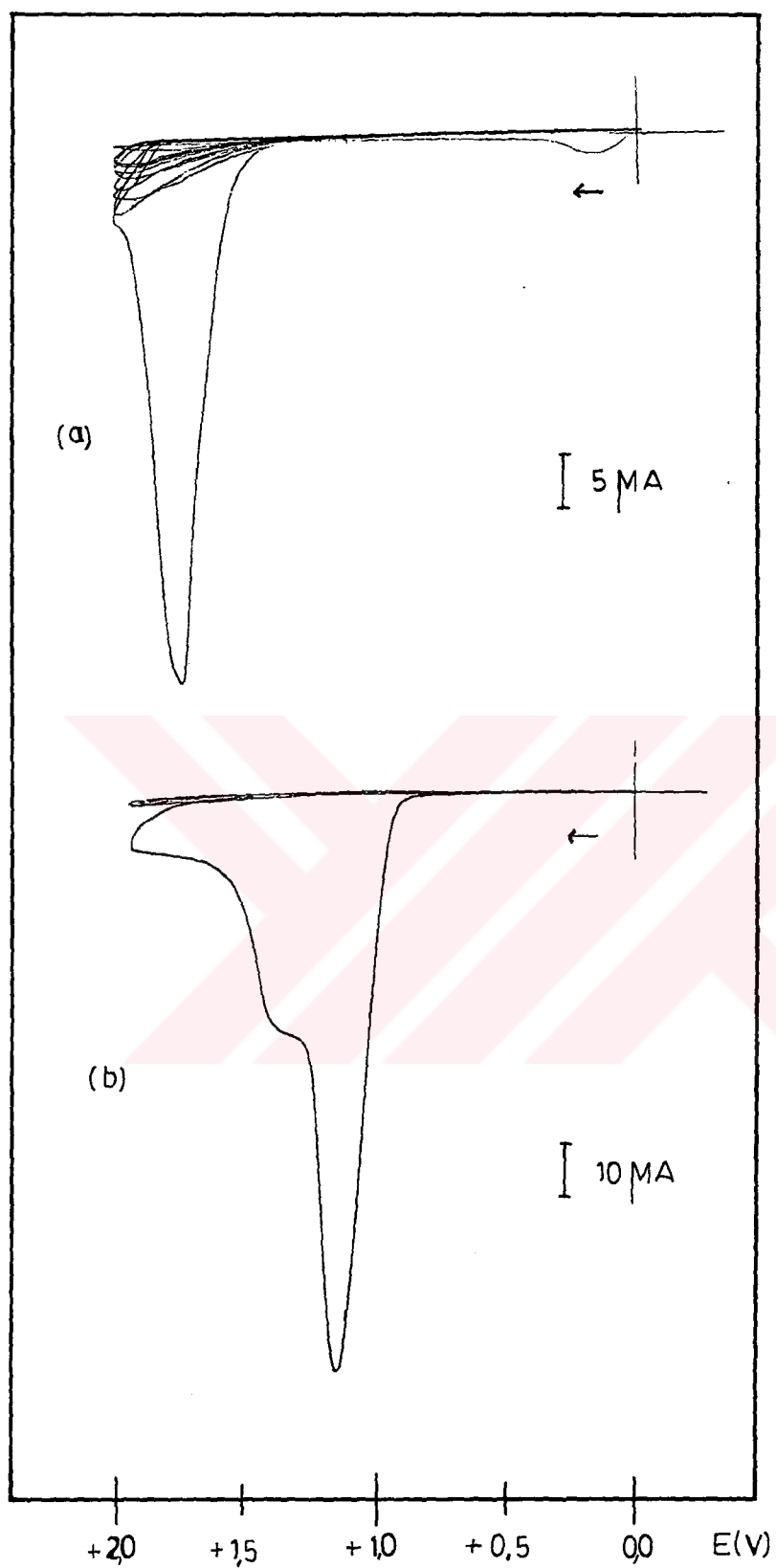
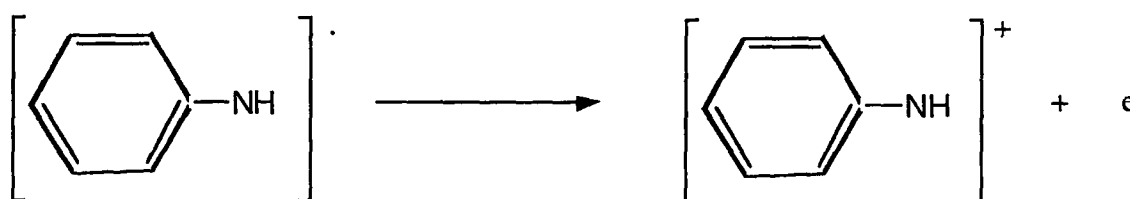


Figure 8.9. Multisweep cyclic voltammograms of a) 100 mM 5-abi b) 100 mM 2-abt in acetonitrile/ 0.1 MTBABF₄. Scan rate: 100 mV/sec.

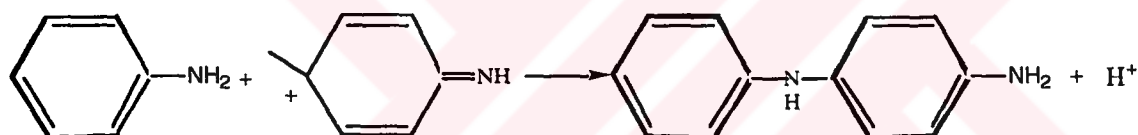
The charge passed during the electro-oxidation of polyaniline in blank solution is a measure of the amount of the deposited film. As long as there is no loss of electroactivity during the cyclic voltammetric run, the amount of film deposited can be assumed to be proportional to the charge passed during the oxidative cycle of the cyclic voltammogram.

This result shows the anilinium cation radical can lose its proton, forming neutral anilino radical, particularly if there is a sufficient amount excess unreacted aniline in the medium.

The neutral anilino radical is also easily oxidizable to the nitrenium cation at the potentials of aniline oxidation:



The nitrenium cation can undergo the following reaction with aniline, forming p-aminodiphenylamine:



Some of the p-aminodiphenylamine escapes electro-oxidation and is lost to the solution. This means that there is some loss in the polymer formation, In other words, conditions favoring the formation of nitrenium type cations will results in a certain decrease in the amount of polyaniline film that is deposited on the electrode.

In order to determine the effect of 5-abi and 2-abt on the growth of the polyaniline film from aniline solutions, the films were grown in solutions of varying 5-abi and 2-abt concentrations in the range 0-100 mM by cycling the potential between -0.20V and +1.90V for the same period of time (30 min.).

Figure 8.10.a and b show that the added 5-abi and 2-abt are more basic and thus more effective than the unreacted aniline in forming the neutral anilino radical which is the cause of the decrease in film formation.

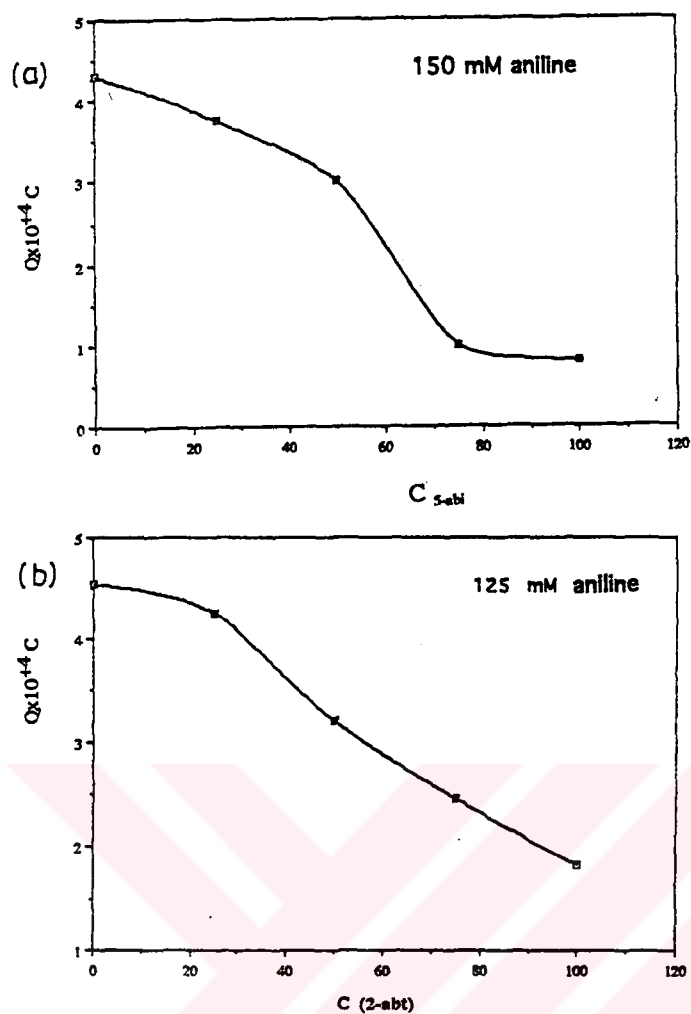


Figure 8.10 Plot of the charge passed during the electro-oxidation of polyaniline films in acetonitrile +0.1M TBABF₄ solution vs. The concentration of the added a) 5-abi: aniline concentration, 150 mM b) 2-abt: aniline concentration 125 mM.

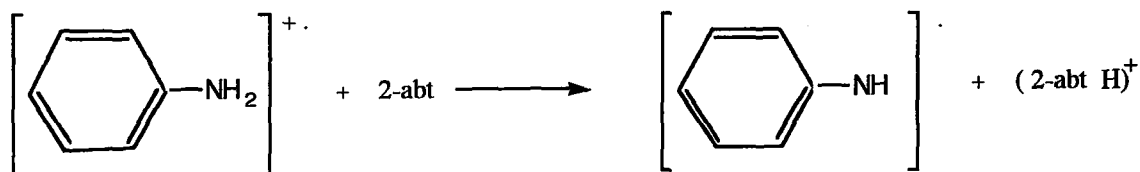
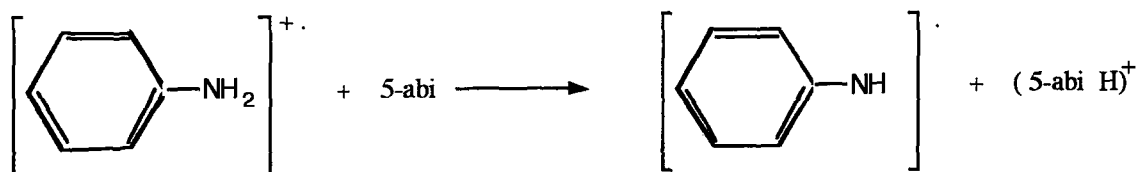


Figure 8.11.a and b show the effect of the addition of acid on the amount of film formed. In the presence of the 5-abi and 2-abt in solutions of aniline, the amount of the polyaniline film increases with the added acid. After a certain concentration of the added acid, the unprotonated 5-abi (Figure 8.11.a) or 2-abt (Figure 8.11.b) decreases and thus limits the amount of the polymer formed. The optimum amounts of acid are seen in Figure 8.11.a and b.

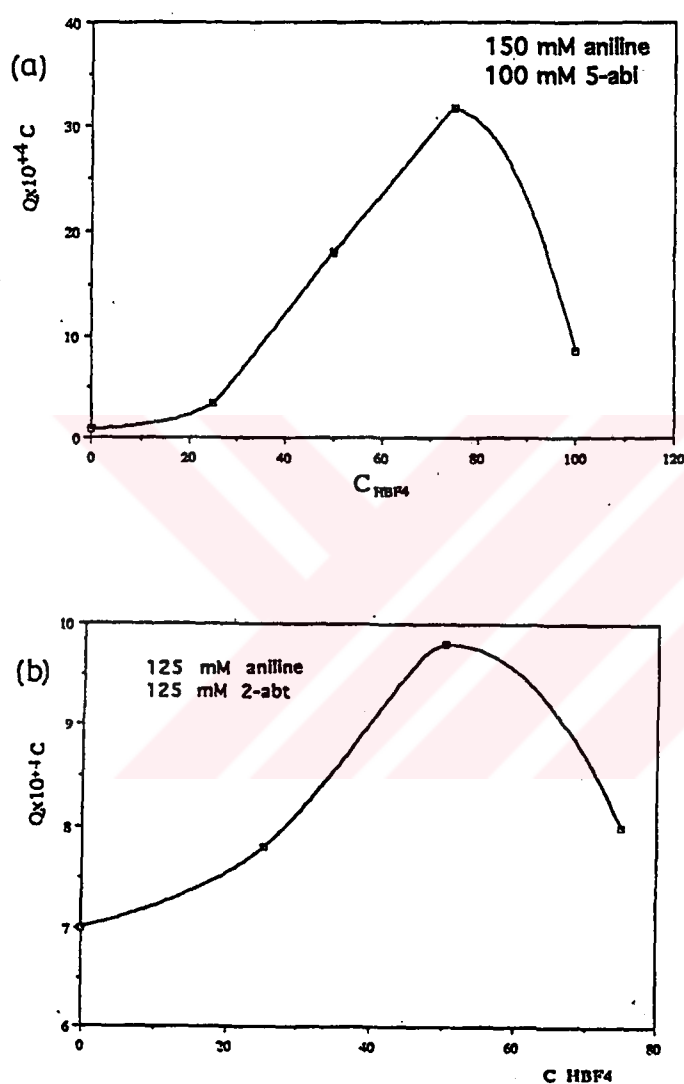


Figure 8.11 Plot of the charge passed during the electro-oxidation of polyaniline films in acetonitrile +0.1M TBABF₄ solution vs. The concentration of the added anhydrous acid a) in the presence of 150 mM aniline+100 mM 5-abi b) in the presence of 125 mM aniline+125 mM 2-abt. Scan rate: 100 mV/sec.

Figure 8.12.a shows the cyclic voltammograms during the growth of polyaniline film from a solution containing optimum amounts of aniline and 5-abi. Figure 8.12.b shows the multisweep cyclic voltammograms of this film in a blank solution.

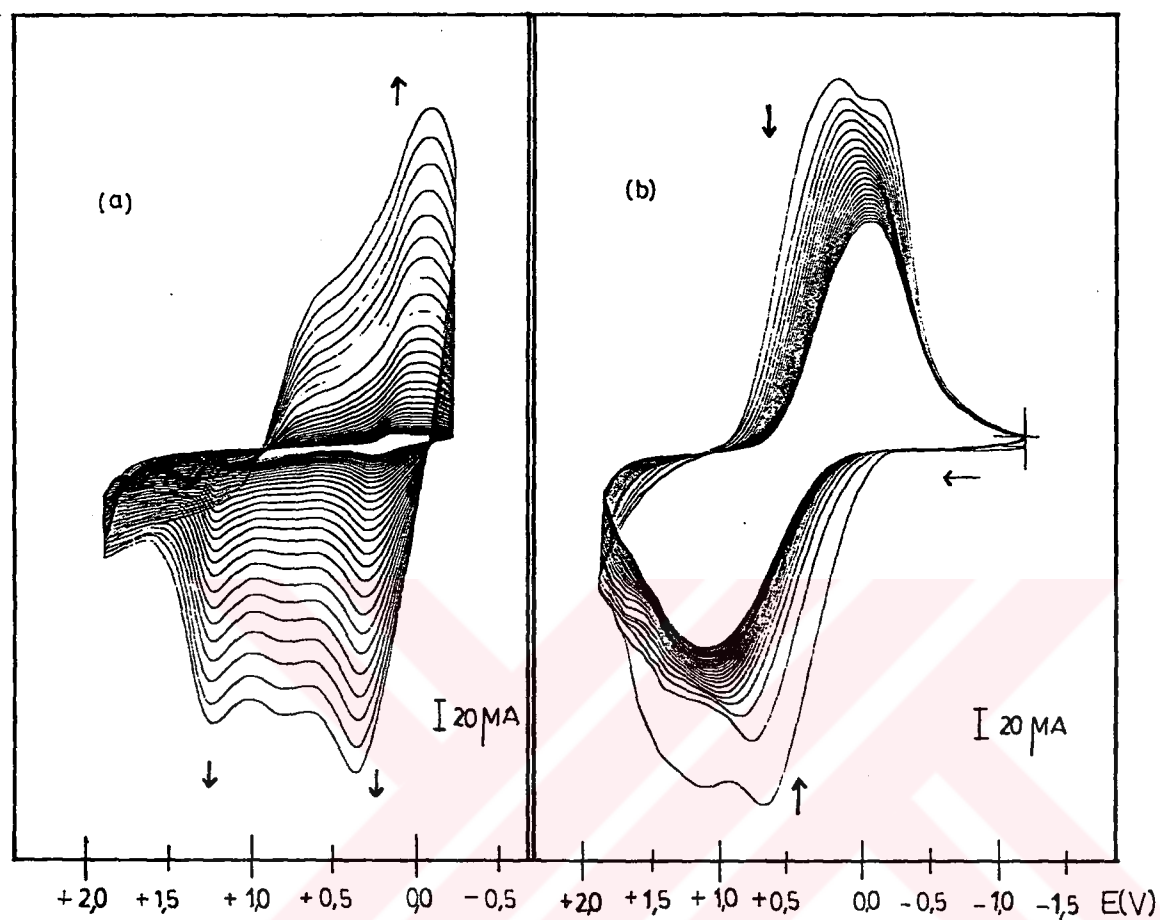


Figure 8.12. a) Multisweep cyclic voltammograms taken during the growth of polyaniline film in acetonitrile solution containing 150 mM aniline+100 mM 5-abi+75 mM HBF_4 b) Cyclic voltammogram of polyaniline film in acetonitrile/0.1 M TBABF_4 (blank solution). Scan rate: 100 mV/sec.

Figure 8.13.a shows the cyclic voltammograms during the growth of polyaniline film from a solution containing optimum amounts of aniline and 2-abt Figure 8.13.b shows the multisweep cyclic voltammograms of this film in a blank solution.

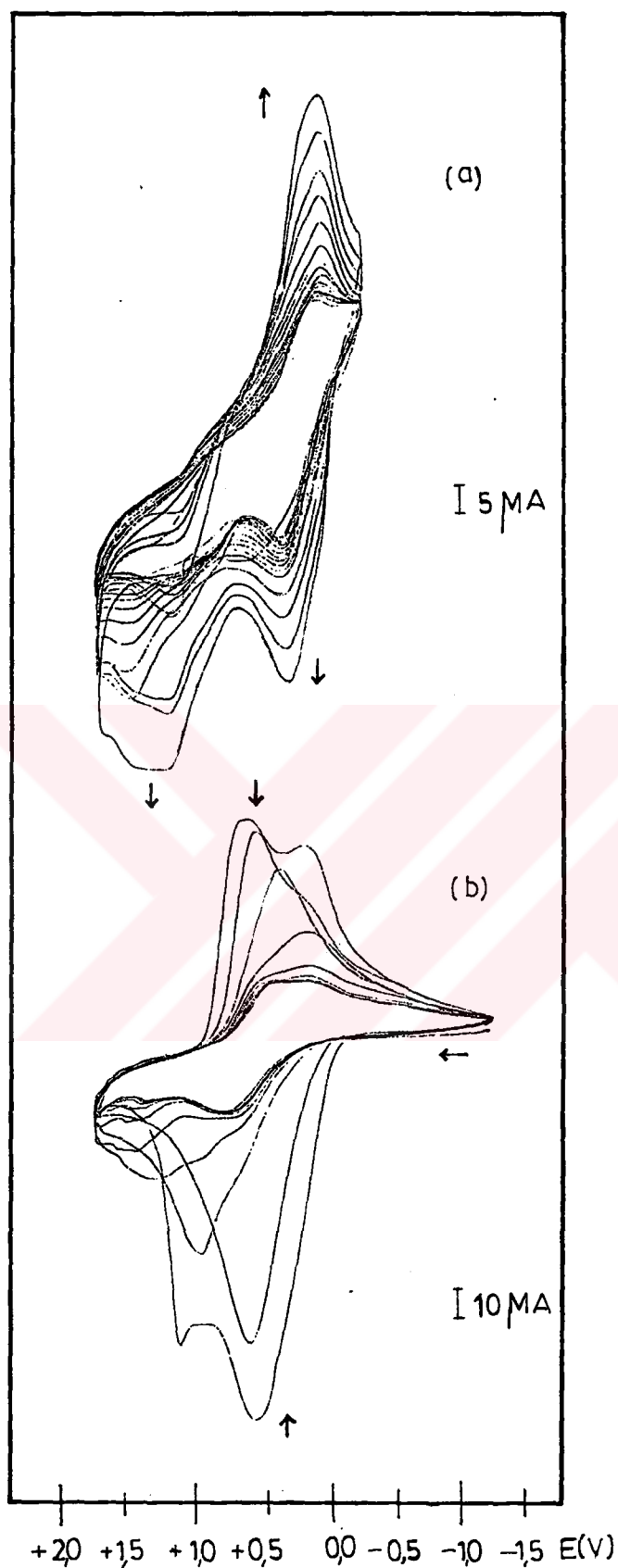


Figure 8.13. a) Multisweep cyclic voltammograms taken during the growth of polyaniline film in acetonitrile solution containing 125 mM aniline+125 mM 2-abt+50 mM HBF_4 b) Cyclic voltammogram of polyaniline film in acetonitrile/0.1 M $TBABF_4$ (blank solution). Scan rate: 100 mV/sec.

As was discussed above, the electroactivity of the polyaniline film gradually decreases and eventually disappears upon cycling the potential applied to the film in a blank solution (Figure 8.8.c). When polyaniline film is produced from solutions containing aniline and 5-abi (or 2-abt) the electroactivity loss of the film is much less in blank solutions (Figure 8.14.a and 8.14.b). This might be due to the formation of hydrogen bonds between these compounds and the polyaniline film during the cycling. The protonated forms of 5-abi and 2-abt are formed during the oxidation of polyaniline with a subsequent release of protons. These protonated forms of 5-abi or 2-abt are not lost into the solution as a result of the formation of hydrogen bonds between these protonated species and the polymer matrix. When the polymer is rereduced during the reductive scan the protons are resupplied by these protonated species to the polymer.



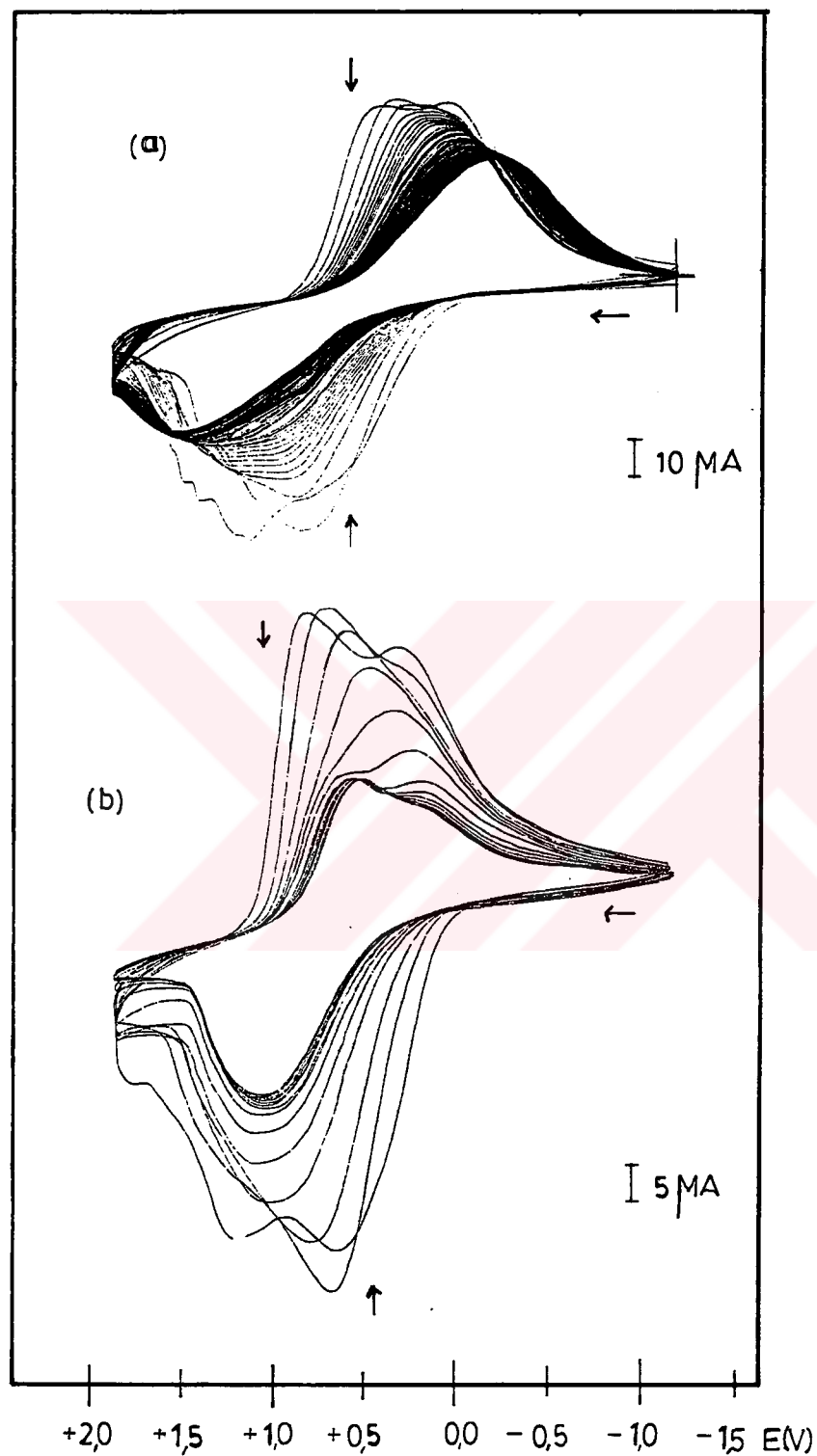


Figure 8.14. Cyclic voltammogram of polyaniline film obtained in a) 200 mM aniline+200 mM 2-abt+150 mM HBF_4 solution b) 150 mM aniline+100 mM 5-abi+25 mM HBF_4 in acetonitrile/0.1 M TBABF_4 (blank solution). Scan rate: 100 mV/sec.

The conductivities of polyaniline also is improved when such hydrogen bonded units coexist in the polymeric matrix during its growth. Table 8.1. indicates that there is at least an order of magnitude difference in dry conductivity values.

Table 8.1. The charge and dry conductivity values of the polymer which was obtained in different solutions.

| Solutions | Charge (Coulomb) | Conductivity (S/cm) |
|---|----------------------|----------------------|
| 150 mM Aniline | 5.4×10^{-4} | 1.6×10^{-5} |
| 200 mM Aniline 100 mM 5-abi 75 mM HBF ₄ | 3.8×10^{-3} | 9.4×10^{-5} |
| 200 mM Aniline 200 mM 2-abt 150 mM HBF ₄ | 1.1×10^{-3} | 0.076 |

9. CONCLUSION

1- The electroreduction and electrooxidation behavior of 2-aminobenzothiazole (2-abt), 5-aminobenzimidazole (5-abi) and 2-aminobenzimidazole (2-abi) in acetonitrile/TBABF₄ in the presence and absence of anhydrous acid revealed that 2-abi forms intermolecular hydrogen bonded clusters as was the case for imidazole and benzimidazole. Hydrogen bond is formed between the NH center and the N center in imidazole rings. Whereas 2-abt does not form such clusters. 5-abi on the other hand, forms intermolecular hydrogen bonds between the -NH₂ group on the benzene ring and the -NH center on the imidazole ring.

2- Aniline oxidation peak is shifted to more positive potentials in the presence of 5-abi so that it is not observable before the electrolyte breakdown. Addition of increasing amounts of anhydrous acid, HBF₄, to the medium brings the oxidation to the less positive potentials so that it is observable. Eventually the aniline oxidation is recorded at its normal potentials. This behavior is interpreted as the result of the formation of a strong hydrogen bonding between 5-abi and aniline which are broken if anhydrous acid is added. Such behavior was not observed for 2-abt, imidazole and benzimidazole, indicating that no hydrogen bonding is formed between aniline and these molecules.

3- The polyaniline formation from aniline is also effected by the presence of 5-abi, 2-abt. The amount of the polymer film decreases when these imidazole derivatives coexist in solutions of aniline. If the protonated forms of these imidazole derivatives are used the amount of the film electrodeposited and the dry conductivity values increase and the electroactivity loss of the film decreases.

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