Electrochemical Behavior of Poly 8-(3-Acetylimino-6-methyl 2,4-dioxopyran)-1-aminonaphthaline in Aqueous and Non Aqueous Media

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The electrooxidation of 8-(3-acetylimino-6-methyl 2,4-dioxopyran)-1-aminonaphthaline (AMDAN) in aqueous and non aqueous media led to the formation of polymeric films, poly (AMDAN). The monomer, undergo anodic oxidation through the formation of a monocation radical irrespective of the nature of the medium. In aqueous medium, the monocation radical undergoes, through its resonance structures, dimerisation involving tail-to-tail, head-to-tail and even head-to-head coupling. The products formed, being more easily oxidisable than the parent substance, undergo further oxidation at the same potential so that the overall oxidation involves a one-step (*i.e.*, a single wave), two-electron process. In non-aqueous medium, the monocation radical does not undergo dimerisation through coupling reactions. Retaining its identity, monomer oxidise in two steps involving one electron in each step. The fact that the cathodic peaks corresponding to these anodic peaks are rarely observed indicates fast consumption of the electrogenerated monocation radicals and dications by follow-up chemical reactions to produce polymeric products (poly AMDAN). The electrochemical behavior of the formed polymer films was investigated in both non aqueous and aqueous media. The films prepared in non aqueous medium were found to be more electroactive than that the films prepared in aqueous medium. This is confirmed with the results in litreature which illustrate that the film prepared in aqueous solution hold water in its structure via hydrogen bonding, which causes decomposition reactions.

Key Words : Electrooxidation polymerization, Cyclic voltammetry, Modified electrode, Aqueous medium, Non aqueous medium

Introduction

Conducting polymers have been extensively investigated in the last two decades due to their potential application as active electrode material in energy conversion systems and more particularly in electrochemical suppercapacitors.[1-5] Moreover, conducting polymers offer both advantages of high change capacity and low-production cost which are necessary conditions for an industrial development.[6]

The electropolymerization of aromatic compounds is a useful method for obtaining various types of conducting polymers in the film state.[5] In this method the film formation and the electrical properties of the resulting films are affected strongly by the preparation condition.[7] In the case of electropolymerization, an acidic aqueous solution (pH < 4) is generally used as the electrolyte solution. In an acidic aqueous solution, however, the degradation of polyaniline takes place in the potential region more positive than 0.8 V (in case of polyaniline).[8] Electropolymerization in a non aqueous solution is one method used to avoid the degradation of the polymer during polymerization the use of aprotic media for the electrooxidation process appear to be a good alternative. The nature of aprotic solvent must be recognized, for example. acetonitrile has been the most commonly used solvent, due to its protophobic nature, however, dimetlyl formamide and propylene carbonate
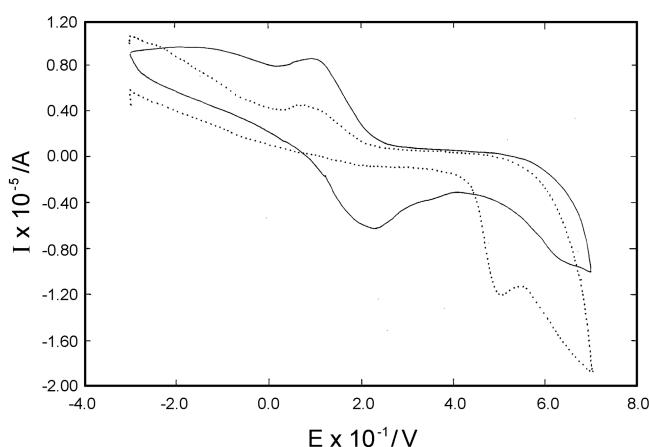
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which have a protophilic nature do not permit the film formation unless the solvent is buffered by addition of a protic acid.[9] The electrooxidative polymerization of 1-naphthylamine, 1,8-diaminanaphthaline (1,8 DAN) and 1,5-diaminonaphthaline (1,5 DAN) has attracted the attention of some group.[10,11] In general, the behavior of the polynuclear amines was found to follow the general rules of mononuclear amines[11] the over all electrode process follows an ECE type of mechanism.[9,11]

Previously, our group have reported the electrooxidation of AMDAN as a derivatives of 1,8-DAN in non-aqueous medium[12] and in aqueous medium,[13] because synthetic conditions are affected strongly on electrical properties of the resulting polymer film.[7] For this reason, the aim of this study is to compare the electrooxidative properties of AMDAN in aqueous and non-aqueous media.

Experimental Section

Lithium perchlorate, 1,8-diaminonaphthalene, dehydroacetic acid, acetonitrile and sulfuric acid were analytical grade chemicals (Aldrich) and used without further purification. Aqueous solutions were prepared from bidistilled water. Electrochemical measurements were performed using the EG & G PAR computer measuring system model (250) and a Hewlett-Packard X-Y recorder model (7440). A three-electrode electrolytic cell (Bioanalytical system, model C-1A) with a platinium disc electrode (Pt) (3.0 mm diam), was

Figure 1. Cyclic voltammograms for oxidative polymerization of 2×10^{-3} M AMDAN on Pt electrode in 0.1 M HClO$_4$ in pot. Range between -0.3 and 0.7 V at scan rate 0.1 Vs^{-1} (----) 1st cycle, (—) 30th cycle.

used as working electrode, a platinium wire as counter electrode and Ag/AgCl as refrence electrode. AMDAN Schiff base was previously prepared and characterized.[12,13]

Results and Discussion

The anodic oxidation of AMDAN on Pt electrode was carried out in 0.1 M HClO$_4$ aqueous solution and in non aqueous solution using continuous scan cyclic voltammetry (CV).

In acidic aqueous solutions, the degradation of the deposited film takes place, in the potential region more positive than 0.8 V.[8] Therefore, the electrooxidation process was carried out in potential range between -0.3 and +0.7 V, to avoide the oxidative degreadation of the film. Typical cyclic voltammograms of 2×10^{-3} M AMDAN in 0.1 M HClO$_4$ solution with Pt electrode are shown in Figure 1. The electrode potential was sweept continuously at scan rate of 0.1 Vs^{-1} between -0.3 and +0.7 V. The monomer was electrooxidized irreversibly in one anodic peak at *ca.* 0.5 V. This anodic peak was shifted to more positive potentials and a gradual decrease in current was recorded, in the following scans. The formation of a single peak during the first forward (oxidation) scan can be easily explained on the basis of an ECE mechanism.[9,11] According to this mechanism, amine during oxidation losses one electron to produce a cation radical which through resonance structures undergoes head-to-tail and tail to tail coupling (Scheme 1), both of which being more readily oxidisable than the parent substance, undergo further oxidation at the same potential. This accounts for the formation of a single oxidation peak during the first forward scan.[9-14] During the first cycle, the cathodic wave recorded at 0.1 V can be attributed to the reduction of the oxidized forms of dimeric product. In the second forward scan, a new anodic peak was recorded at ca +0.2 V, which corresponds to the cathodic peak at 0.1 V. By continuous cycling, it was observed that the peak current of the system 0.2/0.1 V increases, showing also the characteristic
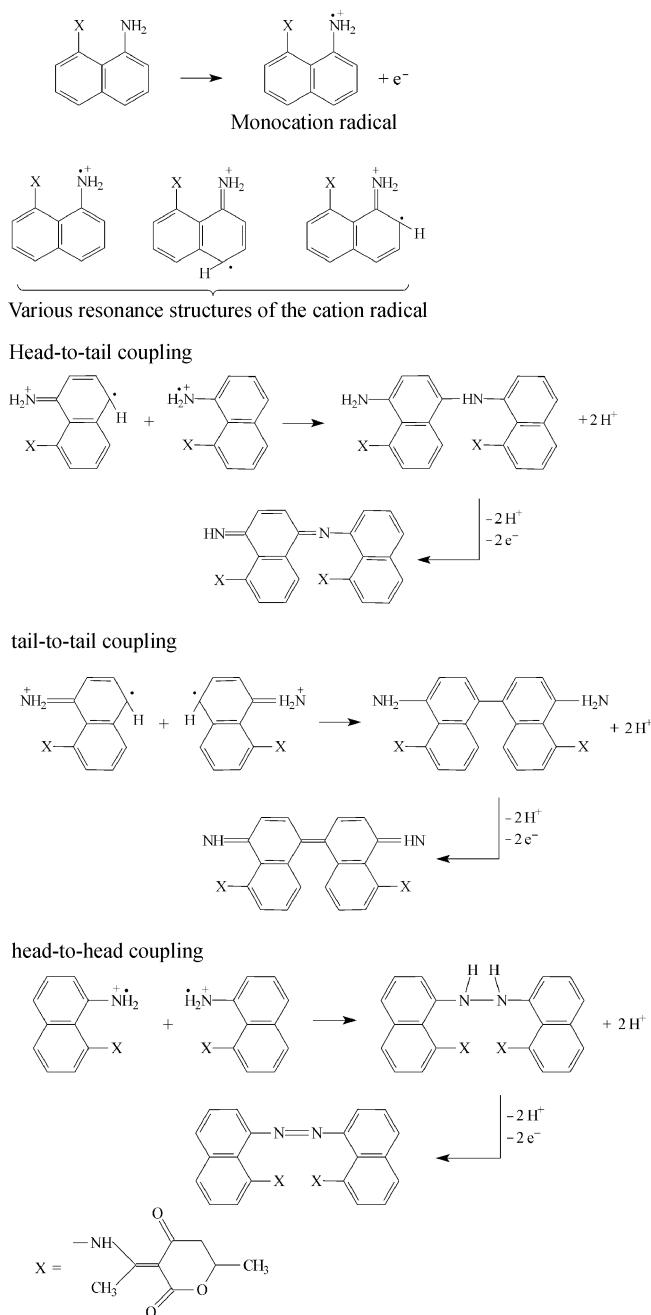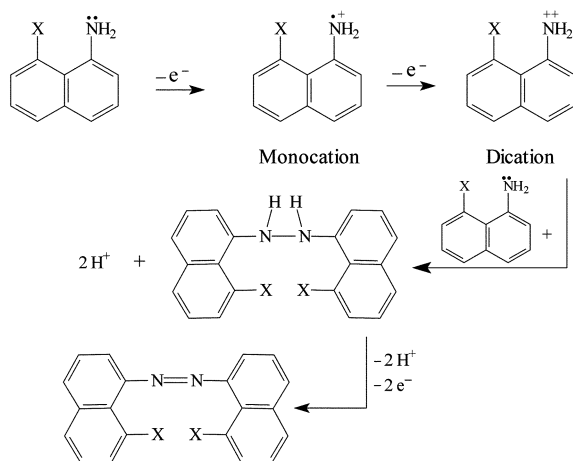

Scheme 1

behavior of a deposited electroactive substance.[15,16]

On the other hand the anodic polymerization of 2×10^{-3} M AMDAN in CH$_3$CN solution containing 10^{-1} M LiClO$_4$ with Pt electrode are shown in Figure 2, the electrode potential was sweept continuously at scan rate 0.1 Vs^{-1} between -0.4 and 1.4 V. As can be seen, two oxidation peaks at 0.6 V (peak A) and 1.27 V (peak B) are obtained in the first forward scan. This observation is strikingly different from the one reported in aqueous solutions in which only one oxidation peak is obtained in the first oxidation. During oxidation process the amine group loses one electron to give as usual, the monocation radical (Scheme 1). This accounts for the formation of the first oxidation peak. Unlike its
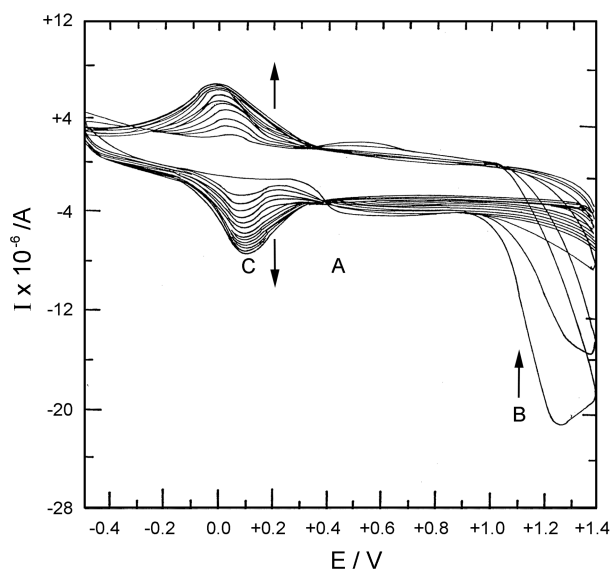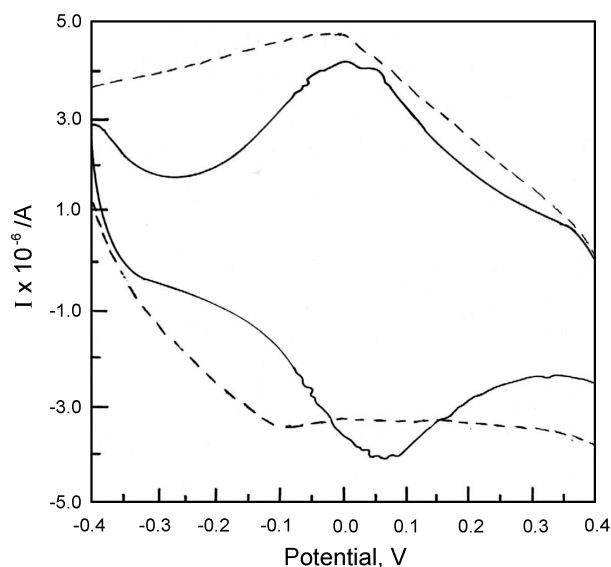
Figure 2. Cyclic voltammograms for the oxidative polymerization of 2×10^{-3} M AMDAN on Pt electrode in CH_3CN/0.1 M $LiClO_4$ in pot. range between -0.4 and 1.4 V at scan rate 0.1 Vs^{-1}.

Scheme 2

Figure 3. The electrochemical response of the modified electrode in CH_3CN/0.1 M $LiClO_4$ solution, (----) Film prepared in aqueous 0.1 M $HClO_4$ containing 2×10^{-3} M AMDAN in pot. range between -0.3 and 0.7 at scan rate 0.1 Vs^{-1} for 30 scans. (—) Film prepared in non aqueous CH_3CN/0.1 M $LiClO_4$ solution containing 2×10^{-3} M AMDAN on Pt electrode in pot. range between -0.4 and 1.4 V at scan rate 0.1 Vs^{-1} for 30 scans.

Cyclic voltammograms of electropolymerized poly AMDAN on Pt electrode, dipped in CH_3CN solution containing 0.1 M $LiClO_4$ in potential range -0.4 and +0.4 V are shown in Figure 3. The voltammograms show that the film prepared in non aqueous medium gave a pair of a well defined redox system at 0.05 V. with a relative large anodic peak current
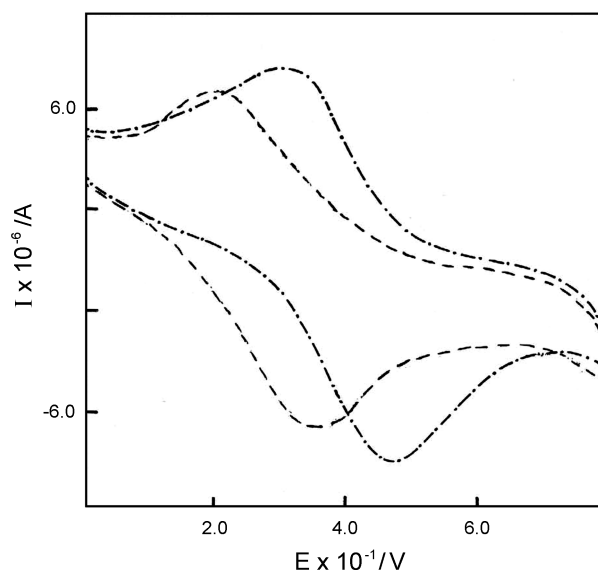
behavior in aqueous medium, the cation radical does not undergo any type of coupling reactions in non aqueous medium which does not appear to be conductive to such reactions. Therefore, retaining its identity, the catoin radical undergoes another one electron oxidation at a higher potential to form a dication (Scheme 2). This accounts for the formation of the second oxidation peak,[17-19] the dication radical with two positive charges on the same N-atom is not stable and hence it undergoes head-to-head coupling with a neutral monlecule of monomer with stimulaneous removal of two protons (Scheme 2). During the first cycle, the cathodic wave recorded at 0.0 V can be attributed to the reduction of the oxidized forms. On scan repetition a new anodic peak was recorded at 0.1 V which correspond to the cathodic peak at 0.0 V. By continuous cycling, it was observed that the peak current system 0.1 V/0.0 V increase and grow, indicating the characteristic behavior of a deposited electroactive substance.[15,16]

Figure 4. The electrochemical response of the modified electrode in 0.1 M H_2SO_4. (----) Film prepared in aqueous 0.1 M $HClO_4$ containing 2×10^{-3} M AMDAN in pot. range between -0.3 and 0.7 at scan rate 0.1 Vs^{-1} for 30 scans. (-·-·-) Film prepared in non aqueous CH_3CN/0.1 M $LiClO_4$ solution containing 2×10^{-3} M AMDAN on Pt electrode in pot. range between -0.4 and 1.4 V at scan rate 0.1 Vs^{-1} for 30 scans.

while the film prepared in aqueous solution gave a pair of abroad peak at -0.1 V/-0.05 V. with relative low anodic peak current.

Figure 4 shows the cyclic voltammograms of the electro-polymerized poly AMDAN on Pt electrode dipped in 0.1 M H_2SO_4 in potential range 0.0 V and 0.8 V. We can see that poly AMDAN films are also electroactive in aqueous medium and also the anodic peak current in case of film prepared in non-aqueous solution is higher than that in case of film prepared in aqueous solution.

From the above obtained results it was observed that the films obtained from non aqueous medium, showed better electrochemical response. This is in accordance with the previously reported results, which illustrate that the electro-polymerization of monomer from aqueous media leads to a partial oxidative degradation of the deposited film.[8] More-over, in acidic aqueous solutions Kitani *et al.* found that the deposited film can hold water in its structure *via-* hydrogen bonding.[20] In addition it is known that polyaniline for example, may hold up to 40% water in its structure, via hydrogen bonding.[20,21] This hydrogen bonded water may provide a reservoir for the degradative side reactions and is responsible for the decrease in conductivity and the loss of stability of polymer. For these reasons, there have been some attempts to prepare polymer in a non aqueous medium.[22-25] Further more, using non aqueous media, during electro-oxidation, it can provide access to higher cell voltage due to an increased window of stability of the solvent. It is well known that CH_3CN is a protophobic solvent.[22,23] Therefore, the protons released during monomer oxidation can be retained in the reaction layer in CH_3CN. These protons could protonate the polymer matrix, increasing its conductivity and allowing the film growth.[24]

Conclusion

The electropolymerization of AMDAN in aqueous and non aqueous solution led to formation of conducting polymer films on platinum electrode with good electro-chemical response. The poly AMDAN films were found to be active in both aqueous and non aqueous solutions. The results has been shown that the polymer prepared in a non aqueous solutions was more electroactive than that prepared in aqueous solutions. So the electropolymerization in non aqueous solution is one of the methods to avoid the degradation of polymer during its formation as in litreature. This is due to the fact that in aqueous solutions the film suffers degradation, also the deposited film can hold water molecules in its structure via-hydrogen bond, which causes decomposition reactions.

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