Studies of the Electrochemical Behavior of Poly 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene Films Doped with an Anionic Surfactant

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Poly 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene (PAMDAN) electrode films were synthesized from aqueous solutions of 0.2 M H₂SO₄ in absence and presence of dodecylbenzene sulphonate (DBS). The electrochemical behavior of both electrodes was investigated using cyclic voltammetry technique. The film formed in presence of DBS (PAMDAN/DBS) showed higher stability as well as cyclability than the film obtained in absence of the surfactant (PAMDAN). The electroactivity of PAMDAN/DBS electrodes was found to increase with the increase of initial concentration of DBS till reaching a maximum at critical micelle concentration (cmc) after which the activity declines. At cmc, the film electroactivity were greatly decreased and was attributed to the formation of DBS micelles. The micellar aggregates may hinder the charge transfer through the film. The improved properties in PAMDAN/DBS electrodes allow them possible to be used in rechargeable lithium batteries.

Keywords: Electropolymerization; Conducting polymers; Surfactants; Cyclic voltammetry; Modified electrodes

1. INTRODUCTION

In a previous work, we described the formation of poly 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene (PAMDAN) films in presence of inorganic counter ions from aqueous and nonaqueous media. Unfortunately, the obtained modified electrode suffered from low stability [1,2] On the other hand, several authors reported the synthesis of conducting polymeric films in the presence of surfactants [3-6] The polymer electrodes synthesized in presence of surfactants are reported to have improved mechanical and electrochemical properties [7]. Surfactants are characterized by their amphiphilic nature where the same molecule possesses both hydrophilic (polar part) and
hydrophobic (nonpolar part) characters. The hydrophobic part is responsible for the phenomena of surface activity and micellization \[8-10\].

The present manuscript reports on electrosynthesis of poly-AMDan electrode films deposited from 0.2 \(M\) \(H_2SO_4\) containing different concentrations of dodecylbenzene sulphonate anion (DBS) in order to investigate, the effect of the presence of surfactant in different concentrations on the electroactivity, the stability and electroreversibility of PAMDAN modified electrodes.

![Chemical structure of AMDAN and DBS](image)

**Figure 1.** Chemical structure of, (a) 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene (AMDan); (b) sodium dodecylbenzene sulphonate (DBS).

### 2. EXPERIMENTAL PART

Sodium dodecylbenzene sulphonate (DBS) was obtained from Sigma, dehydroacetic acid, \(H_2SO_4\) and 1,8-diaminonaphthalene were of analytical grade and were used as received. Bidistilled \(H_2O\) was used to prepare the aqueous solutions. Electrochemical measurements were performed using the EG & G PAR computer measuring system (model 250) and a Hewlett-Pachard X-Y recorder (model 7440). A three electrode electrolytic cell (Bioanalytical system, model C-1A) with a platinum disk electrode (3.0 mm diam) was used as working electrode, a platinum sheet (area 2 cm\(^2\)) as counter electrode and \(SCE\) reference electrode. All experiments were done at room temperature. AMDAN
Schiff-base was previously prepared and characterized [1] The chemical structures of AMDAN and DBS are shown in Fig.1 The PAMDAN films were electrochemically grown onto platinum electrodes by cyclic voltammetry ($v = 50 \text{ mV/s}$) between -0.2 and 0.8 $V$ (versus SCE) for 20 cycles in aqueous solution of $2 \times 10^{-3} \text{ M AMDAN}$ and 0.2 M H$_2$SO$_4$ at zero concentration of DBS (PAMDAN), then in presence of DBS at different concentration in the range of $1 \times 10^{-6}$ to $1 \times 10^{-2} \text{ M (PAMDAN/DBS)}$. After the film deposition onto Pt electrode, it was rinsed with purified water and then placed in electrochemical cell containing monomer free aqueous electrolytic solutions to measure the electrochemical response of the formed films. Surface tension studies were carried out using TENSIOMETRE DOGNON ABRIBAT, PROLABO-France. The surface tension measurements at the liquid-air interface were determined by the use of the platinum plate method [11] The platinum plate was carefully cleaned by flaming. It is essential that the plate should be flat and the liquid must wet the plate. The measurements were done for solutions of DBS, DBS/H$_2$SO$_4$ and DBS/H$_2$SO$_4$/AMDAN.

3. RESULTS AND DISCUSSION

The cyclic voltammogram of polymer growth of $2 \times 10^{-3} \text{ M AMDAN}$ monomer solution in 0.2 M H$_2$SO$_4$ was recorded as shown in Fig 2. In the first cycle, AMDAN electrooxidized mainly in an irreversible peak at $0.44V$ followed by another one at $0.7 V$ together with a reduction peak at $-0.66V$ On scan repetition (20 cycles), the first peak diminishes with the appearance of a new redox system at 0.02$V$ The limiting currents of this new system increase by continuous cycling which indicates an accumulation of electroactive polymer film on the electrode surface.

**Figure 2.** Typical cyclic voltammograms obtained during the growth of the film in $2\times10^{-3} \text{ M AMDAN}$; In 0.2 M in H$_2$SO$_4$ electrolytic solution (PAMDAN),a) (- - -) 1$^{st}$ cycle,b) (-----) 20$^{th}$ cycle; The film was prepared at $v = 50 \text{ m Vs}^{-1}$ between -0.2 and 0.8 $V$ (vs SCE) for 20 cycles at Pt electrode
Figure 3. Typical cyclic voltammograms obtained during the growth of the film in $2 \times 10^{-3} \text{M} \text{AMDan}$; in $0.2 \text{M} \text{H}_2\text{SO}_4$ and $5 \times 10^{-6} \text{M DBS (PAMDan/DBS)}$, (- - -) 1st cycle, (---) 20th cycle. The film was prepared at $\nu = 50 \text{ mVs}^{-1}$ between -0.2 and 0.8 V (vs SCE) for 20 cycles at Pt electrode.

Figure 4. Voltammograms of PAMDan (- - -) and PAMDan/DBS (---) film electrodes in 0.2 M H$_2$SO$_4$ electrolyte solution. Scan rate: 50 mVs$^{-1}$. The film formed as in Fig.2 and Fig 3 respectively.

The above experiment was repeated in the presence of $5 \times 10^{-6} \text{M DBS}$. During the first positive potential scan, only one anodic peak was observed at $0.43\text{V}$ On the negative sweep, a reduction peak at $0.05\text{V}$ appeared. After 20 cycles, the first oxidation peak was disappeared and a new redox system at
0.1V and 0.05V was obtained (Fig. 3). After being synthesized and washed, the electrode films were carefully dried and the electrochemical behavior was investigated. Fig 4 illustrates the voltammograms of NPAMDA and PAMDAN/DBS film electrodes in 0.2 M H₂SO₄ electrolyte solution. The comparison between the behaviors of the two electrodes shows higher currents (Ipa and Ipc) and low peak separation (ΔE) for PAMDAN/DBS compared with PAMDAN. This indicates that PAMDAN/DBS films are characterized by faster and more reversible electrochemical redox processes. The shape of PAMDAN/DBS voltammogram change from that of PAMDAN indicating that the presence of DBS plays an important role in the electrochemical response of the PAMDAN/DBS films. The currents response (Ipa) of PAMDAN/DBS films increase gradually as the number of cycles increases during film formation from 5 to 20 cycles (Fig. 5). Afterwards, Ipa starts to decrease by increasing the number of cycles which was examined up to 30 cycles. Therefore, we can conclude that the ions do not diffuse only in the bulk of the liquid electrolyte but also through the polymer formed on the electrode surface. This could explain the decrease of Ipa as the number of cycles increases (more than 20 cycles) and the polymer was accumulated on the electrode surface. So, we can assume slow ions diffusion through the polymer film than that in the liquid electrolyte.

![Graph showing dependence of current response on number of cycles](image)

**Figure 5.** Dependence of the current response of PAMDAN/DBS film on the number of cycles during the film formation, the condition of film formation as in Fig. 3, the activity of these films were measured 0.2 M H₂SO₄ at 50 mVs⁻¹ scan rate.

The kinetics of the redox process of both PAMDAN and PAMDAN/DBS was performed by studying the relation between the voltammetric peak currents (Ipa and Ipc) and the scan rate (ν). A linear relationship was obtained in both cases of (Ipa - ν) and (Ipc - ν) for the two examined electrodes as shown in Fig. 6. The obtained results indicate that thin films exhibit a linear (Ip - ν) behaviour based
on models developed for thin layer cells [12,15], On the other hand, when the \(\text{PAMDAN/DBS}\) electrode is cycled in an aqueous solution containing only \(\text{DBS}\) \((1 \times 10^{-5} \text{ M})\) as shown in Fig. 7 (the doted line c) the electrode showed no activity. The activity is regenerated if \(\text{H}_2\text{SO}_4\) is added to the solution (Fig. 7b dashed line), i.e. if condition of Fig. 4 are restored. As seen in (Fig. 7,solid line) the redox response of \(\text{PAMDAN/DBS}\) is suppressed in presence of \(\text{DBS}^-\) as an electrolyte. This may be attributed to the difficult diffusion of \(\text{DBS}^-\) through the film to compensate the positive charge generated in the film during oxidation. Presence of \(\text{H}_2\text{SO}_4\) in the medium was found to slightly improve the redox response compared to \(\text{DBS}^-\) alone. This may be explained by the easier diffusion of \(\text{SO}_4^{2-}\) anions within the film compared with the bulky \(\text{DBS}^-\) due to the smaller size of the former. This was confirmed by using only \(\text{H}_2\text{SO}_4\) as electrolyte, Fig. 4.

![Figure 6.](image)

**Figure 6.** Voltammetric peak current versus scan rate of \(\text{PAMDAN}\) (curve •) and \(\text{PAMDAN/DBS}\) (curve ○) electrodes in 0.2 M \(\text{H}_2\text{SO}_4\). The film formed as in Fig. 2 and Fig. 3.

The effect of surfactant concentration during the film formation on the electroactivity of \(\text{PAMDAN/DBS}\) films was examined in Fig. 8. Clearly, the \(I_{Pa}\) increases with the increase of the initial concentration of \(\text{DBS}\) until reaching a maximum after which the \(I_{Pa}\) declines. The increase of \(I_{Pa}\) with the increase in surfactant concentration may be attributed to the increase in \(\text{DBS}^-\) content dispersed in the polymer matrix. This increase of \(\text{DBS}^-\) in the polymer leads to the increase of stability as well as the charge capacity of the film. The drop in the \(I_{Pa}\) beyond \(\text{DBS}\) concentration of \(5 \times 10^{-6} \text{ M}\) could be explained by the adsorption of \(\text{DBS}\) onto the electrode surface forming a barrier, Fig. 9a. This barrier may hinder the charge transfer [16,17], and consequently the growth of the polymer film diminishes.
Other authors attributed the depression of the electroactivity of similar systems to the formation of a barrier on the film surface which prevent the charge exchange [18,19].

**Figure 7.** Typical cyclic voltammograms of PAMDAN/DBS film electrode in different electrolytes at scan rate 50 mVs\(^{-1}\): a) (\(\longrightarrow\)) \(\text{H}_2\text{SO}_4\); b) (\(\longrightarrow\)) \(\text{DBS}+\text{H}_2\text{SO}_4\); c) (\(\cdots\)) \(\text{DBS}\). The film formed as in Fig 3.

**Figure 8.** Effect of concentration of DBS on the \(I_{Pa}\) of the polymeric film. The film formed as in Fig 3
**Figure 9.** Adsorption of DBS- on the surface of the electrode, (a) low surface coverage; (b) high surface coverage; (c) micelle formation

The variation of surface tension as a function of concentration of surfactant for pure DBS, DBS/H₂SO₄ and DBS/H₂SO₄/AMDAN was studied and the results are shown in Fig 10. The cmc values of DBS, DBS/H₂SO₄ and DBS/H₂SO₄/AMDAN are 1 x 10⁻² M, 5 x 10⁻⁴ M and 5 x 10⁻⁵ M, respectively. Clearly the cmc decreases in presence of H₂SO₄ and more decrease is noticed in presence of monomer. This may be attributed to that the presence of monomer and/or H₂SO₄ enhances the formation of micelles. The association of the hydrophobic part of DBS becomes favored as the charge of the ionic head of DBS decreases [11]. This may be achieved through, (i) interaction of protons with the –SO₃⁻ groups giving –SO₃H; (ii) complex formation between DBS⁻ and the protonated monomer (-NH₃⁺).

The effect of change of the scan rate on the anodic current of the polymer film formed in presence and absence of different concentrations of DBS during film formation is given in Fig 11. The higher $I_{pa}$ in the case of PAMDAN/DBS (1 X 10⁻⁶ M) and PAMDAN/DBS (5 X 10⁻⁶ M) may be attributed to the inclusion of DBS⁻ in the polymer matrix. As the surfactant concentration increases in the polymer matrix the $I_{pa}$ increases. The decrease of $I_{pa}$ for PAMDAN/DBS (5 X 10⁻⁵ M) may be
attributed to the enhancement of adsorption of free surfactant species at the electrode surface, Fig 9b. The higher adsorption density of surfactant species the higher retardation of charge transfer which is basically needed for the formation of the film. PAMDAN/DBS (5 X 10^-4 M) showed lower $I_{Pa}$ than PAMDAN-surfactant free. This may be attributed to the formation of micelles and hemimicelles at the electrode surface, Fig.9c. In the micellar region, the surfactant species associate into aggregates in an energetically favored process [20,21]. Such aggregates may hinder the charge transfer and hence formation of good polymer film becomes hard to establish.

![Graph](image.png)

**Figure 10.** Variation of surface tension of DBS solutions in absence and presence of H2SO4 and AMDAN monomer

The stability of PAMDAN/DBS film was tested in 0.2 M H2SO4 by cyclic voltametry over 150 cycles. Only around 5% decrease in the $I_{Pa}$ was recorded within the initial 10 cycles then no change was observed over the subsequent 140 successive scans. This implies that the polymer film formed is mechanically and electrochemically stable. This may be attributed to the nonrelease of the doped surfactant anions during the reduction of PAMDAN/DBS. The immobilization of DBS\textsuperscript{-} into the polymeric matrix through the hydrophobic part of the surfactant prevents the movement of the anions out of the polymer structure. This leads to the non mechanical distortion of the polymer matrix which sustains the stability of the film [7].
Figure 11. Effect of change of the scan rate on $I_{p_{a}}$ of the polymer film formed in absence and presence of different concentrations of DBS during film formation. The redox response of the polymeric films were measured in 0.2M H$_2$SO$_4$

On the basis of the results described above, the following scheme may describe the mechanism of the redox process of PAMDAN/DBS:

$$\begin{align*}
\text{PAMDAN}^+/\text{DBS}^- + Y^+ &\xrightarrow{\text{reduction}} \text{PAMDAN}/\text{DBS}/Y^+ + X^- \\
\text{PAMDAN}^+/\text{DBS}/Y^+ + X^- &\xrightarrow{\text{oxidation}} \text{PAMDAN}^+/\text{DBS}/Y^+/X^-
\end{align*}$$

where $Y^+$ and $X^-$ represent the cation and the anion, respectively, of the electrolyte.

According to above scheme, when the polymer is reduced to its neutral form, there is no release of the DBS$^-$ anion, but rather an insertion of the cation $Y^+$ (viz. hydrogen). However, when reoxidizing the polymer, two parallel processes occur: the first, corresponding to the cation deinsertion [step (1)] and the second, corresponding to anion (viz. sulphate) insertion [step (2)]. This implies that the surfactant remains immobilized in the polymer, as a consequence expected.
4. CONCLUSIONS

Modified electrodes resulting from electro polymerization of AMDAN in 0.2 M H2SO4 electrolyte solution in the presence of DBS showed higher $I_{pa}$ and $I_{pc}$ and low peak separation compared with PAMDN prepared in the absence of DBS. This indicated that the presence of DBS played an important role in the electrochemical response of PAMDN/DBS films. The kinetics studies of the redox process showed that there was slow ions diffusion through the polymer film than that in the liquid electrolyte. Also, the stability testing of PAMDN/DBS indicated that the polymer film is mechanically and electrochemically stable. This was attributed to the immobilization of DBS anion into the polymeric matrix.

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References

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