Int. J. Electrochem. Sci., 3 **(2008)** 1512 - 1522

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

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

Asem A. Atia[*], *Abla A. Hathoot*[**] *and Magdi Abdel-Azzem*

Chemistry Department, Faculty of Science, Menoufia University, Shebin El-Koam, Menoufia, Egypt
[*]E-mail: asemali2010@yahoo.com
[**]E-mail: ablahathoot@yahoo.com

Received: 18 September 2008 / *Accepted:* 12 October 2008 / *Published:* 17 November 2008

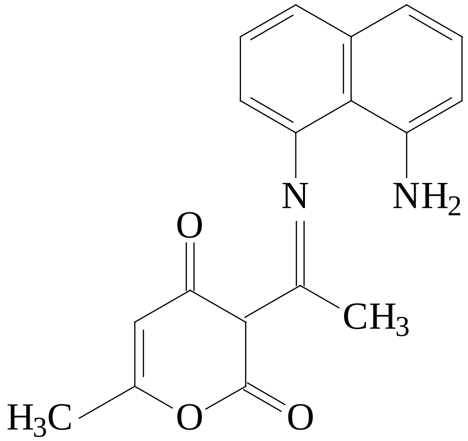
Poly 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene (*PAMDAN*) electrode films were synthesized from aqueous solutions of 0.2 M H_2SO_4 in absence and presence of dodecylbenzene sulphonate (*DBS*). The electrochemical behavior of both electrodes was investigated using cyclic voltammetry 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

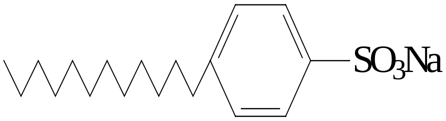
1. INTRODUCTION

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 electorsynthesis 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.



(a) 8-(3-acetylimino-6-methyl-2,4-dioxopyran)-1-aminonaphthalene (*AMDAN*)



(b) Dodecylbenzene sulphonate sodium salt (*DBS*)

Figure 1. Chemical structure of, (a) 8-(3- acetylimiro-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 elecrtrochemically grown onto platinum electrodes by cyclic voltametry (v = 50 *mV/s*) between -0.2 and 0.8 *V* (versus *SCE*) for 20 cycles in aqueous solution of 2 x 10^{-3} *M AMDAN* and 0.2 *M* H_2SO_4 at zero concentration of *DBS* (*PAMDAN*), then in presence of *DBS* at different concentration in the range of 1 x 10^{-6} to 1 x 10^{-2} *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_2SO_4 and *DBS/*H_2SO_4*/AMDAN*.

3. RESULTS AND DISCUSSION

The cyclic voltammogram of polymer growth of 2 x 10^{-3} *M AMDAN* monomer solution in 0.2 *M* H_2SO_4 was recorded as shown in Fig 2. In the first cycle, *AMDAN* electrooxidized mainly in an irreversible peak at 0.44*V* followed by another one at 0.7 *V* together with a reduction peak at -0.66*V* 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.

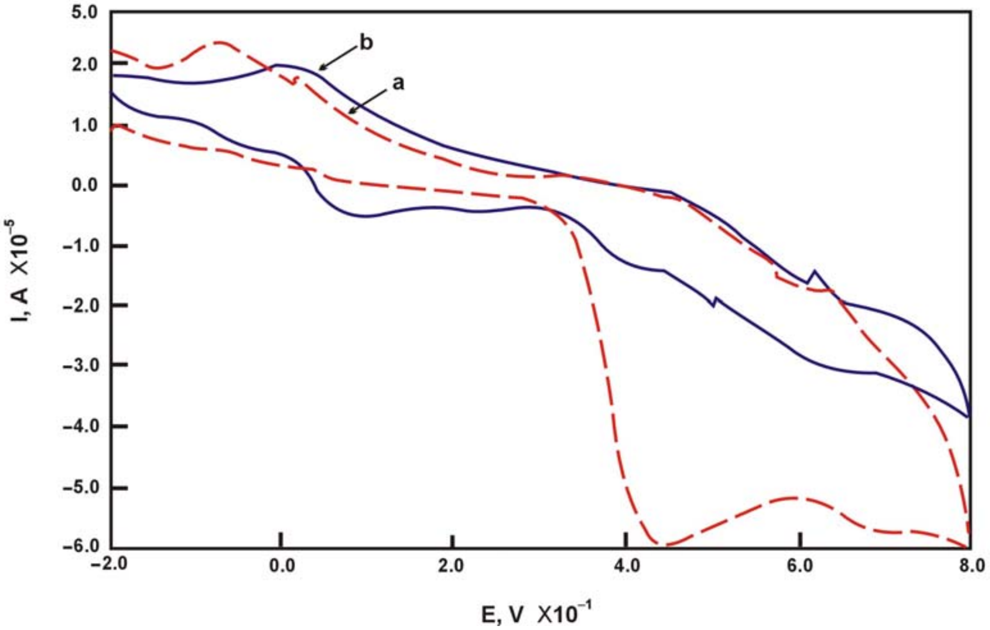


Figure 2. Typical cyclic voltammograms obtained during the growth of the film in 2×10^{-3} *M AMDAN*; In 0.2 *M* in H_2SO_4 electrolytic solution (*PAMDAN*),a) (- - -) 1st cycle,b) (—) 20th cycle; The film was prepared at $\nu = 50$ m Vs^{-1} between -0.2 and 0.8 V (vs *SCE*) for 20 cycles at Pt electrode

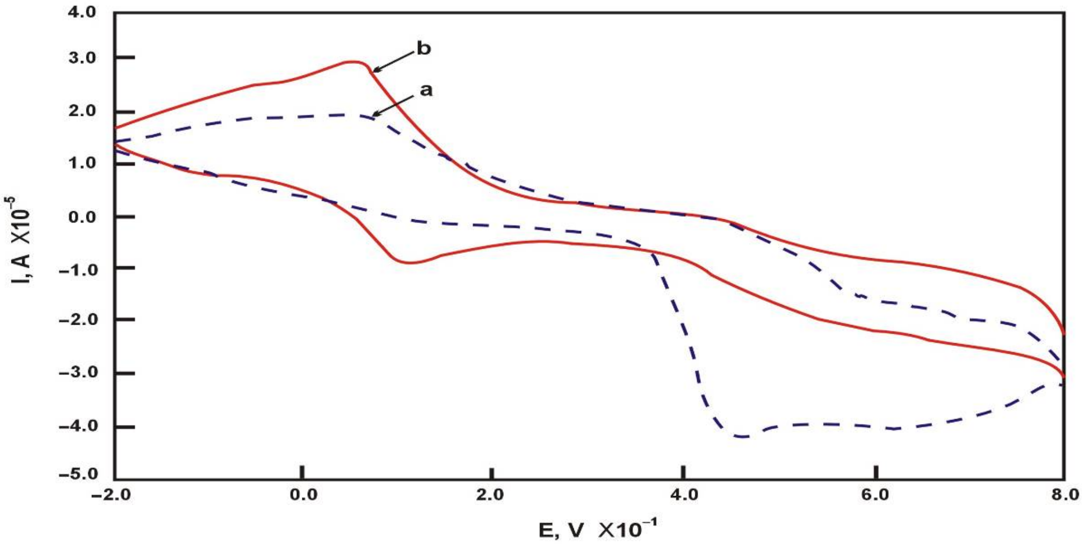


Figure 3. Typical cyclic voltammograms obtained during the growth of the film in 2×10^{-3} *M AMDAN*; In 0.2 *M* H_2SO_4 and 5×10^{-6} *M DBS* (*PAMDAN/DBS*), (- - -) 1st cycle, (—) 20th cycle. The film was prepared at ν = 50 m Vs^{-1} between -0.2 and 0.8 V (vs *SCE*) for 20 cycles at Pt electrode.

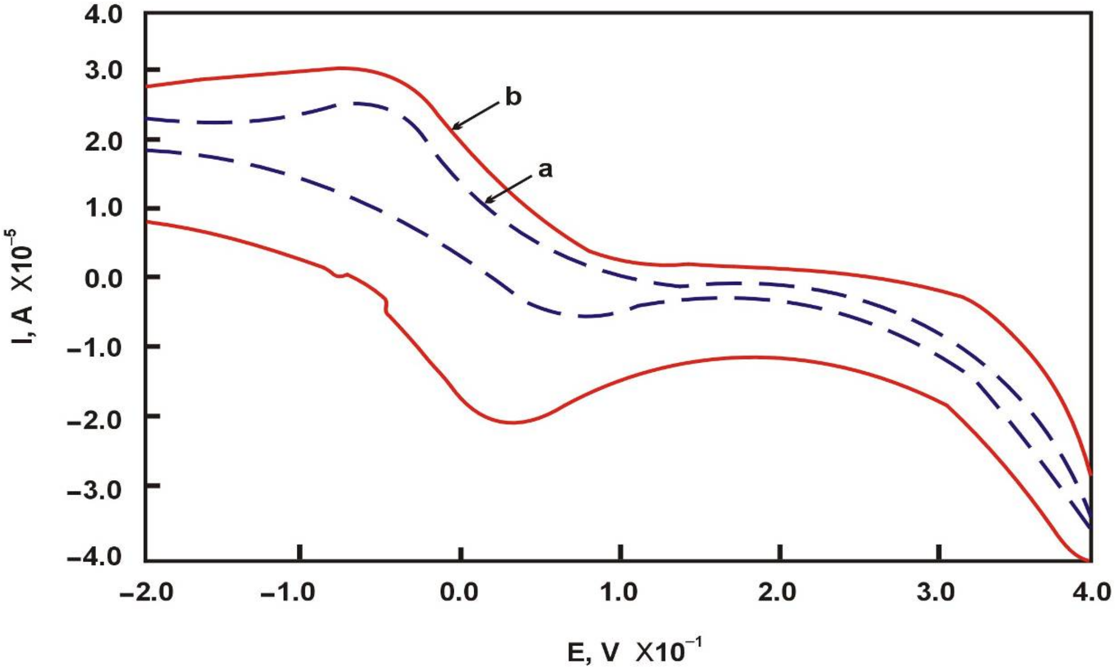


Figure 4. Voltammograms of *PAMDAN* (- - -) and *PAMDAN/DBS* (—) film electrodes in 0.2 *M* H_2SO_4 electrolyte solution. Scan rate: 50 mVs^{-1}. The film formed as in Fig.2and Fig 3 respectivly.

The above experiment was repeated in the presence of 5 x 10^{-6} *M DBS*. During the first positive potential scan, only one anodic peak was observed at 0.43*V* On the negative sweep, a reduction peak at 0.05*V* appeared. After 20 cycles, the first oxidation peak was disappeared and a new redox system at

0.1*V*and 0.05*V* 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* H_2SO_4 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 and important role in the electrochemical response of the *PAMDAN/DBS* films. The currents response (I_{pa}) of *PAMDAN/DBS* films increase gradually as the number of cycles increases during film formation from 5 to 20 cycles (Fig. 5) . Afterwards, I_{pa} 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 I_{pa} 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.

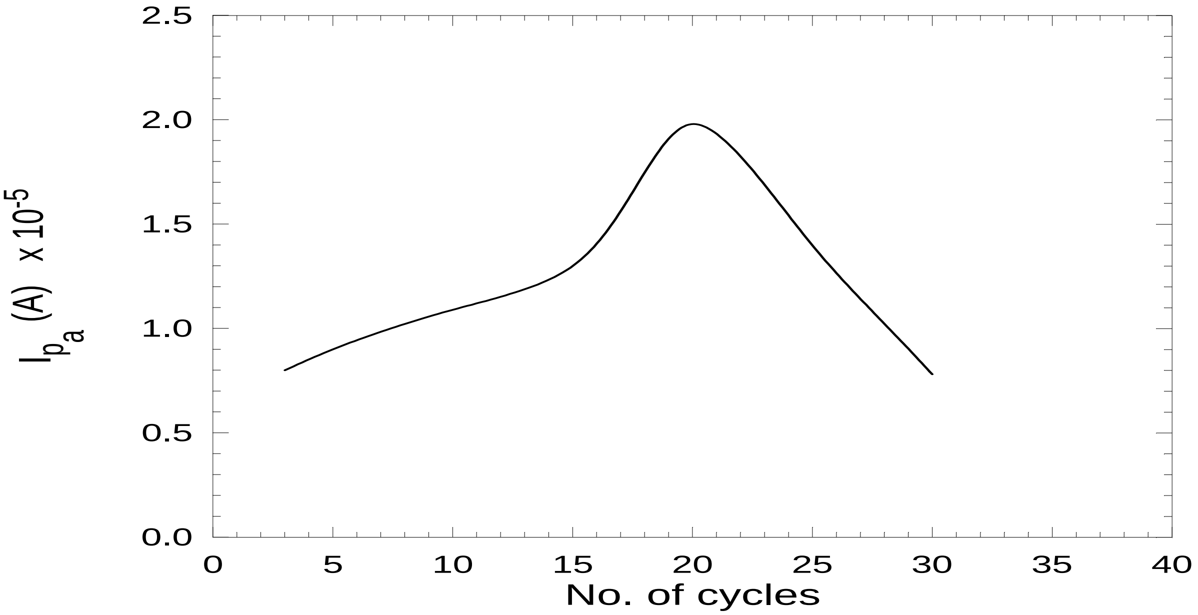


Figure 5. Dependence of the current response of *PAMDAN/DBS* film on the number of cycles during the film formation, the condition of film formation as in Fig.3, the activity of these films were measured 0.2 *M* H_2SO_4 at 50 m Vs^{-1} scan rate.

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 (υ). A linear relationship was obtained in both cases of (I_{pa}-υ) and (*Ipc*- υ) for the two examined electrodes as shown in Fig. 6. The obtained results indicate that thin films exhibit a linear (*Ip*-υ) behaviour based on models developed for thin layer cells [12,15], On the other hand, when the (*PAMDAN/DBS*) electrode is cycled in an aqueous solution containing only *DBS* (1×10^{-5} M) as shown in Fig. 7 (the doted line c) the electrode showed no activity. The activity is regenerated if H_2SO_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 *PAMDAN/DBS* is suppressed in presence of *DBS*$^-$ as an electrolyte. This may be attributed to the difficult diffusion of *DBS*$^-$ through the film to compensate the positive charge generated in the film during oxidation. Presence of H_2SO_4 in the medium was found to slightly improve the redox response compared to *DBS*$^-$ alone. This may be explained by the easier diffusion of SO_4^{2-} anions within the film compared with the bulky *DBS*$^-$ due to the smaller size of the former. This was confirmed by using only H_2SO_4 as electrolyte, Fig. 4.

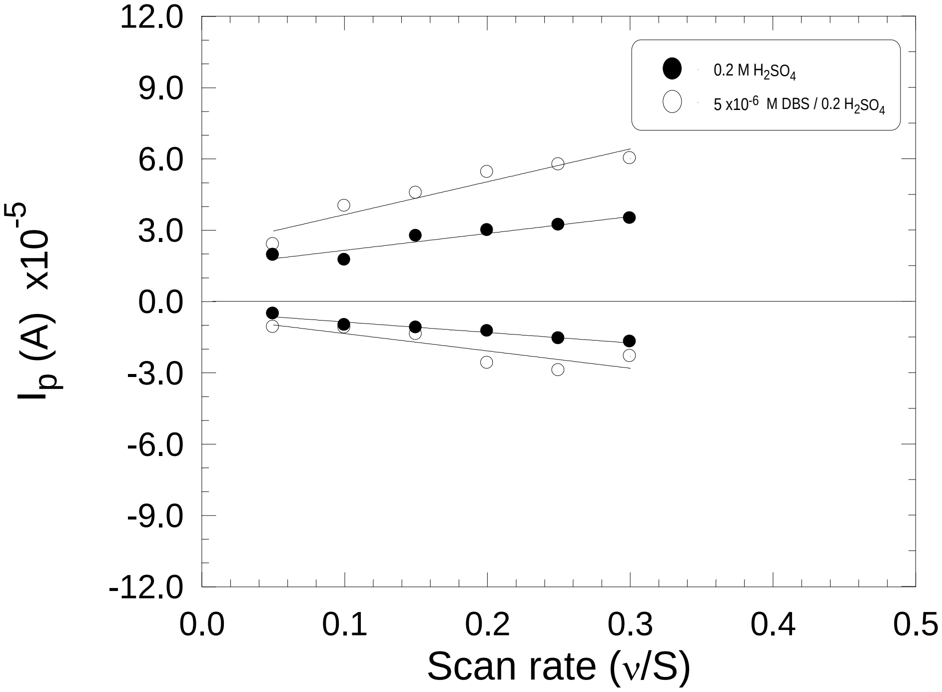


Figure 6. Voltammetrics peak current versus scan rate of *PAMDAN* (curve ●) and *PAMDAN/DBS*(curve ○) electrodes in 0.2 M H_2SO_4. The film formed as in Fig.2and Fig 3.

The effect of surfactant concentration during the film formation on the electroactivity of *PAMDAN/DBS* films was examined in Fig. 8. Clearly, the I_{Pa} increases with the increase of the initial concentration of *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 *DBS*$^-$ content dispersed in the polymer matrix. This increase of *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 *DBS* concentration of 5 x 10^{-6} *M* could be explained by the adsorption of *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].

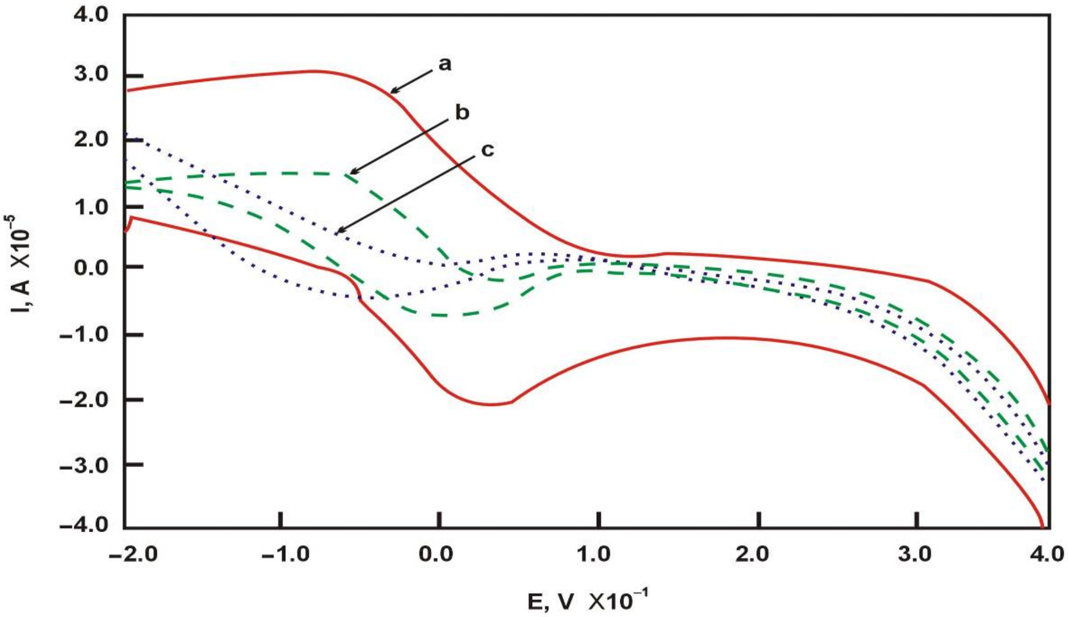


Figure 7. Typical cyclic voltammograms of *PAMDAN/DBS* film electrode in different electrolytes at scan rate 50 mVs^{-1},a**) (—)** H_2SO_4;b) (– –**)** *DBS*+H_2SO_4;c) **(…)** *DBS*.
The film formed as in Fig 3.

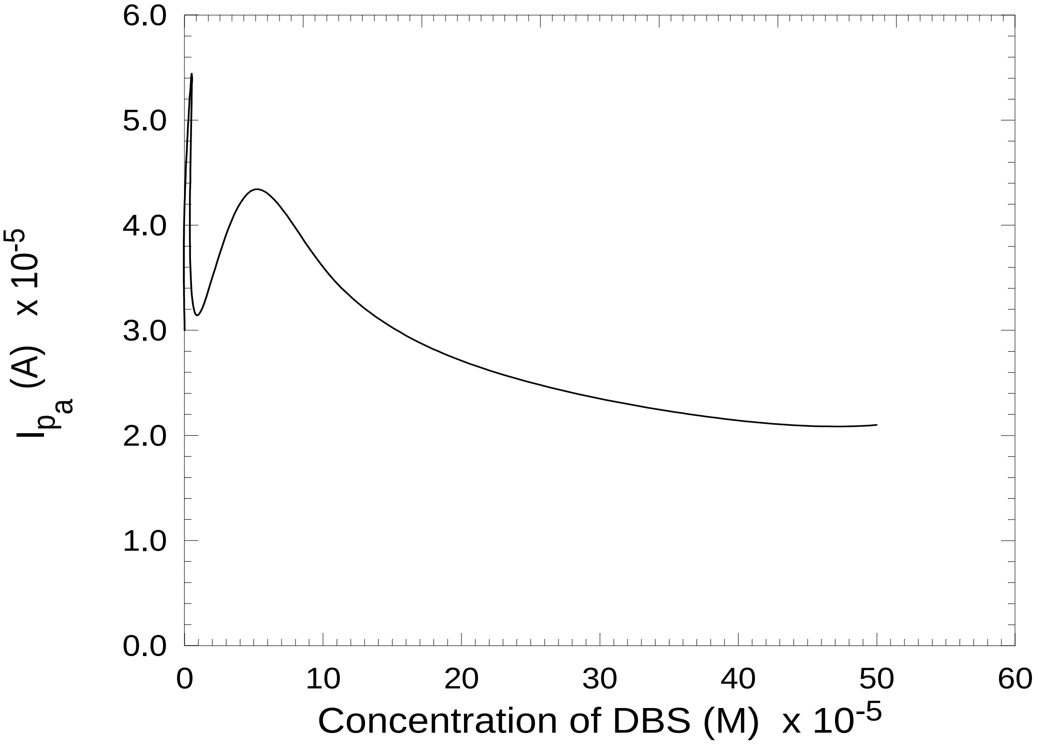


Figure 8. Effect of concentration of *DBS* on the I_{Pa} of the polymeric film.The film formed as in Fig 3

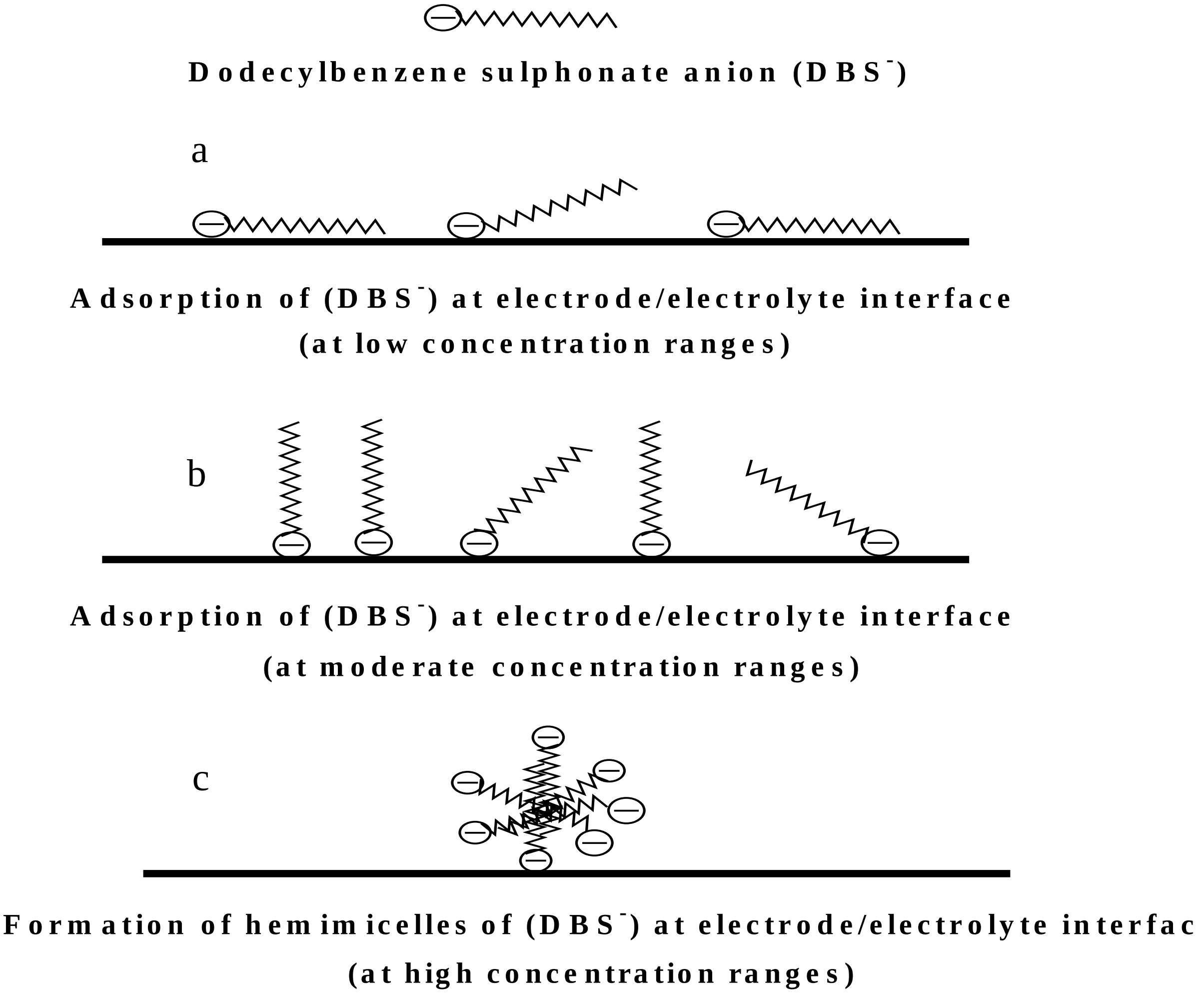


Figure 9. Adsorption of DBS- on the surface of the electrode, (a) low surface coverage; (b) high surface coverage; (c) micelle formation

The variation of surface tension as a function of concentration of surfactant for pure *DBS, DBS/*H_2SO_4 and *DBS/*H_2SO_4*/AMDAN* was studied and the results are shown in Fig 10. The *cmc* values *of DBS, DBS*/H_2SO_4 and *DBS*/H_2SO_4/*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 H_2SO_4 and more decrease is noticed in presence of monomer. This may be attributed to that the presence of monomer and/or H_2SO_4 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 $–SO_3^-$ groups giving $–SO_3H$; (ii) complex formation between *DBS*- and the protonated monomer ($-NH_3^+$).

The effect of change of the scan rate on the anodic current of the polymer film formed in absence and presence 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.

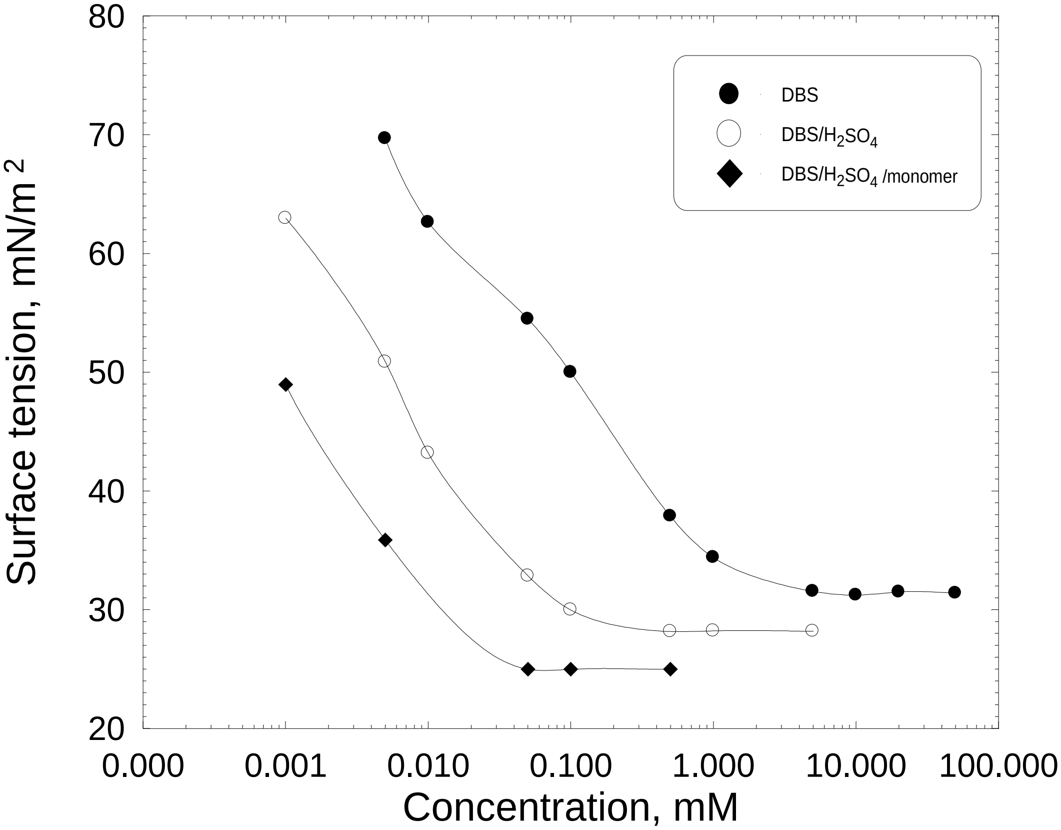


Figure 10. Variation of surface tension of *DBS* solutions in absence and presence of H_2SO_4 and *AMDAN* monomer

The stability of *PAMDAN/DBS* film was tested in 0.2 *M* H_2SO_4 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*$^-$ 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] .

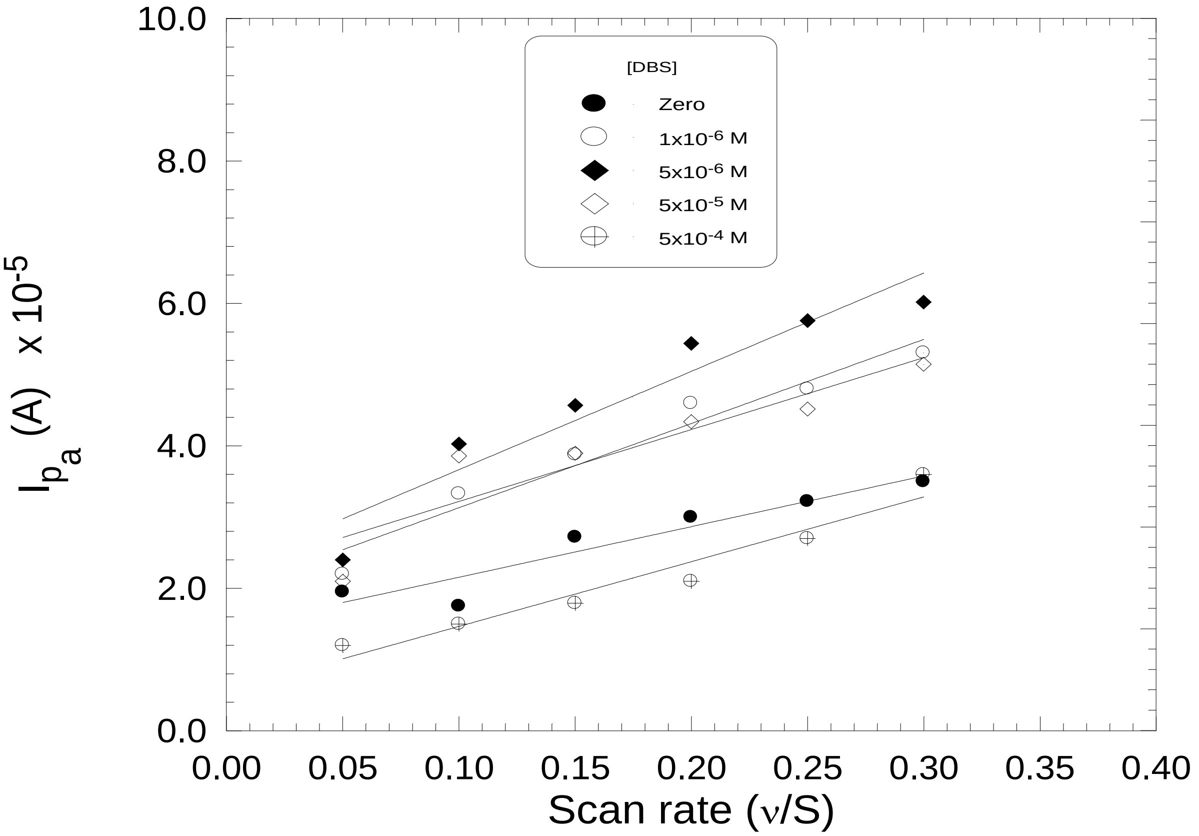
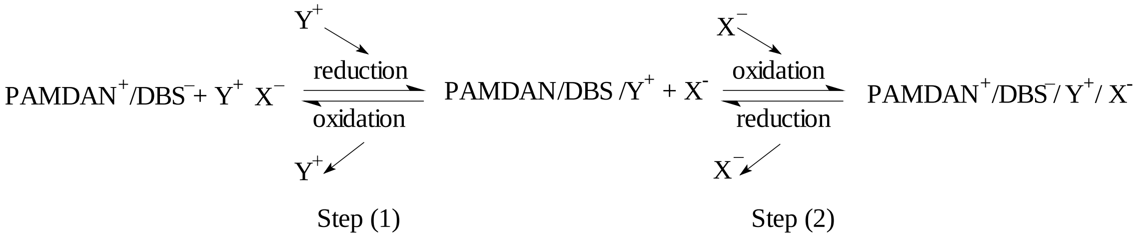


Figure 11. Effect of change of the scan rate on I_{Pa} of the polymer film formed in absence and presence of different concentrations of *DBS* during film formation.The redox response of the polymeric films were measured in 0.2M H_2SO_4

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



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* H_2SO_4 electrolyte solution in the presence of *DBS* showed higher I_{pa} and I_{pc} and low peak separation compared with *PAMDAN* prepared in the absence of *DBS*. This indicated that the presence of *DBS* played an important role in the electrochemical response of *PAMDAN/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 *PAMDAN/DBS* indicated that the polymer film is mechanically and electrochemically stable. This was attributed to the immobilization of *DBS* anion into the polymeric matrix.

ACKNOWLEDGEMENTS
The authors wish to express their thanks to Alexander Von Humboldt Foundation for scientific equipment.

References

1. H..A Abd El-Rahman, A A Hathoot, M El-Bagoury, M Abdel-Azzem, *J Electrochem Soc* 147 (1) (2000) 242
2. U.S Yousef, A.A Hathoot , M. Abdel-Azzem, *Eur Polym J* 37(2001) 1267.
3. M .Satoh, K. Kaneto , K .Yoshino *Synth Met* 14(1986) 289.
4. T .Yoda, A. Othani, T. Shimidzu, K. Honda ,*Chem Lett Japan* (1986) 687.
5. W .Wernet, M. Monkenbush, G. Wegner, *Mol Cryst Liq Cryst* 118(1985) 193.
6. NTL. Hien, B. Garcia, A. Pailleret, C. Deslouis, *Electrochim Acta* 50(2005) 1747.
7. M.A .De Paoli, S.P. Anero, P .Prosper, B .Scrosati ,*Electrochim Acta* 35(1990) 1145 .
8. C .Visy, E. Krivan , G .Peintler ,*J Elecroanal Chem* 462(1999) 1.
9. D .Myers, Surfactant Science and Technology, VCH, 1988.
10. E.H .Lucassen-Reynders, Anionic Surfactants, Marcel Dekker, 1981.
11. D.J. Shaw ,(1980) Introduction to Colloid and Surface Chemistry, Butterworths.
12. S. Panero, P .Prosperi, B .Scrosati, *J Electrochim Acta* 37(1992) 419.
13. U .Johanson, M .Marandi, T. Tamm, *J Electrochim Acta* 50(2005) 1523.
14. T .Yau, T.V. Nguyen , R .White, *J Electrochem Soc* 135(1989) 1971.
15. A.A. Hathoot ,*Eur Pol J* 36(2000) 1063.
16. C, Lagrost, M. Jouini, J .Tanquy, S. Aeiyach, J.C. Lacroix, K.I. Chane Ching, P.C. Lacae, *Electrochim Acta* 46(2001) 3985.
17. A.A. Atia, M. M .Saleh , *J Appl Electrochem* 33(2003)171.
18. K .Maksymiuk, A.S. Nyback, J .Bobacka, A .Ivaska ,*J Electroanal Chem* 430(1997)243.
19. S.B .Saidman , *Electrochim Acta* 46 (2003)1719.
20. Th.F. Tadros, Surfactants, Academic Press, 1983.
21. H .Rupprecht, T .Gu, *Colloid Polym Sci* 269(1991)506.