

Voltammetry of Aniline with Different Electrodes and Electrolytes

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The aim of the present paper is the electrochemical characterization of aniline as well as obtaining of thin polyaniline films on carbon electrodes, which can be used as analytical sensors.

The study was carried out by voltammetry in aqueous medium within the potential range of $-0.3 \leftrightarrow +1.4$ V/S.C.E., at a scanning rate of 50 mV s^{-1} , by using different electrode surfaces (Pt.E., P.C.E., Sp.C.E. and G.C.E.) and support electrolytes (H_2SO_4 , $\text{H}_2\text{SO}_4 + \text{NaClO}_4$, Na_2SO_4 , $\text{Na}_2\text{SO}_4 + \text{NaClO}_4$). Particular attention was paid to the aniline electropolymerization in neutral medium, in a low concentration ($5 \cdot 10^{-4} \text{ M}$), which was compared with that in acid medium.

Voltammetric characteristics of aniline (E_a , E_c , i_a , i_c) were estimated, the reversibility of electrode processes ($\Delta E_{(a-c)}$, S_a/S_c ratio) was appreciated and the electropolymerization mechanism was correlated with the shapes of the voltammograms thus obtained. The electropolymerization efficiency was also estimated.

INTRODUCTION

Obtaining of conducting polymers by electropolymerization has been paid a particular attention by researches in the last two decades.^{1,2}

Among these macromolecular compounds, polyaniline was much studied due to its rather easy preparation, good stability under the medium conditions as well as to its interesting redox properties associated with chain ni-

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trogens.³ It can be prepared electrochemically by aniline polymerization in aqueous solutions under constant voltage⁴ and also by cyclic voltammetry.^{5,6}

According to Simionescu and coworkers,³ the polymerization and electropolymerization of aniline can be performed at room temperature, at pH = 0.0–2.0 in the presence of acids as HCl, HF, HBr, H₂SO₄, HClO₄, CH₃COOH, Cl₃C-COOH, *etc.* which also act as doping agents for the resulting polymer. Polymerization can also proceed in neutral and in alkali media. The electrodes can be made of Pt, C, Cu, Fe, Zn, Cr, Pd, *etc.* Aniline deposition by cyclic voltammetry is advantageous due to its short exposure to the anodic potential and to reduction of the oxidized species, which did not react, during the cathodic cycle. Consequently, inclusion of the hydrolysis products into polyaniline deposits decreases and the obtained films are thicker and more conductive.⁷

According to,^{8,9} aniline polymers mainly consist of aminoimines, which may exist in different oxidation states,^{7,8} from the completely oxidized forms, the *p*-phenyleneimine, till the completely reduced one, the *p*-phenyleneamine.

Snauwaert and coworkers (cited in Ref. 7) found, by means of X-ray photoelectronic spectroscopy, that the amine/imine ratio is dependent on the electrode potential. At +0.15 V/S.C.E. the imine concentration is about 25% (protoemeraldine), increasing to 50% (emeraldine) at +0.60 V/S.C.E. and then to 80% (nigraniline) at +0.80 V/S.C.E. In conclusion, the oxidation degree of polyaniline (PA) increases as the potential becomes more positive. The 50% oxidized polymer shows the highest electrical conductivity.³ The different structures can be converted into one another by oxido-reductive treatments.

The electronic properties of polyaniline strongly depend on the redox state, the doping level and the polymer moisture content.^{10,11}

This fact would be indicative of a strong correlation between the electrochemical behaviour of the monomer (aniline) and the electronic properties of the polymer. In this connection, the present study aims to make evident the electrochemical behaviour of the aniline with different electrode surfaces (Pt.E, P.C.E., Sp.C.E., G.C.E.) and aqueous solutions, both acid and neutral (H₂SO₄, H₂SO₄ + NaClO₄, Na₂SO₄, Na₂SO₄ + NaClO₄), by cyclic voltammetry within a potential range of -0.3 ↔ +1.4 V/S.C.E. and a scanning rate of 50 mV s⁻¹.

Some aspects of the cyclic voltammetry of aniline and some of its *p*-substituted derivatives can be found in another paper.¹²

It is noteworthy that polyaniline is obtained during cyclization even within the concentration domains (about 10⁻⁴ M).

EXPERIMENTAL

The aniline was previously purified. Aqueous solutions of $5 \cdot 10^{-3}$ M concentration were prepared with twice-distilled water. Solutions of electrolytes were prepared with *p.a.* reagents and twice-distilled water.

Voltammetric runs within the $-0.3 \leftrightarrow +1.4$ V/S.C.E. potential range were made on a POLAROGRAPH of the OH-102 Radelkis type with a polarographic cell with three electrodes, at room temperature, after bubbling purified nitrogen for 10 minutes. Saturated calomel electrode (S.C.E.) was used as reference electrode and a platinum spiral as auxiliary electrode. The following working electrodes were used: platinum wire electrode (Pt.E.) of $\varnothing = 1$ mm and $l = 5$ mm., paste carbon electrode (P.C.E.) of $\varnothing = 3$ mm., prepared as described in ¹³, spectral carbon electrode (Sp.C.E.) of $\varnothing = 4$ mm., and glassy carbon electrode (G.C.E.) of $\varnothing = 2$ mm. The electrodes were carefully cleaned after each run. Cyclization within the given domain was done at 50 mV s^{-1} rate till the settling of voltammetric currents (anodic and cathodic current intensities were approximately constant).

The following solutions were used as support electrolytes: 10^{-1} M H_2SO_4 ; 10^{-1} M $\text{H}_2\text{SO}_4 + 10^{-2}$ M NaClO_4 ; 10^{-1} M Na_2SO_4 , and 10^{-1} M $\text{Na}_2\text{SO}_4 + 10^{-2}$ M NaClO_4 .

The surface area under voltammetric peaks was evaluated using a planimeter.

RESULTS AND DISCUSSION

The fact has already been accepted that the mechanism of aniline oxidation is the same in acidic, neutral and alkali media; the chemical and electrochemical polymerizations are also similar.³

The cyclic voltammograms obtained with aniline on different electrode surfaces with the same support electrolyte are depicted in Figure 1 (a, b, c, d).

The voltammetric curves are indicative of oxidation proceeding on every surface under consideration in two stages. The anodic peak situated at more positive potentials ($E_{a(2)} = +1.0$ V/S.C.E.) is particularly intense in the anodic branch of the first spinning cycle and can be attributed to the initial monomer oxidation, according to a possible mechanism described in Refs. 3, 8. According to the authors, the neutral aniline molecule is oxidized and deprotonated in the first stage, when a nitrenium cation $\text{C}_6\text{H}_5\text{NH}^+$ is formed. By the electrophilic attack of this cation on the other aniline molecule, a "head-tail" dimer (*p*-aminodiphenylamine) is formed.¹⁴

A mechanism of chemical polymerization of aniline was proposed by Wei and coworkers^{15,16} (Figure 2). The electrochemical polymerization is similar.³

In this mechanism, the dimer formation is the rate determining step, which is accompanied by the loss of an electron (e^-) and of a proton for every aniline molecule. Kinetic studies of aniline electropolymerization indicated

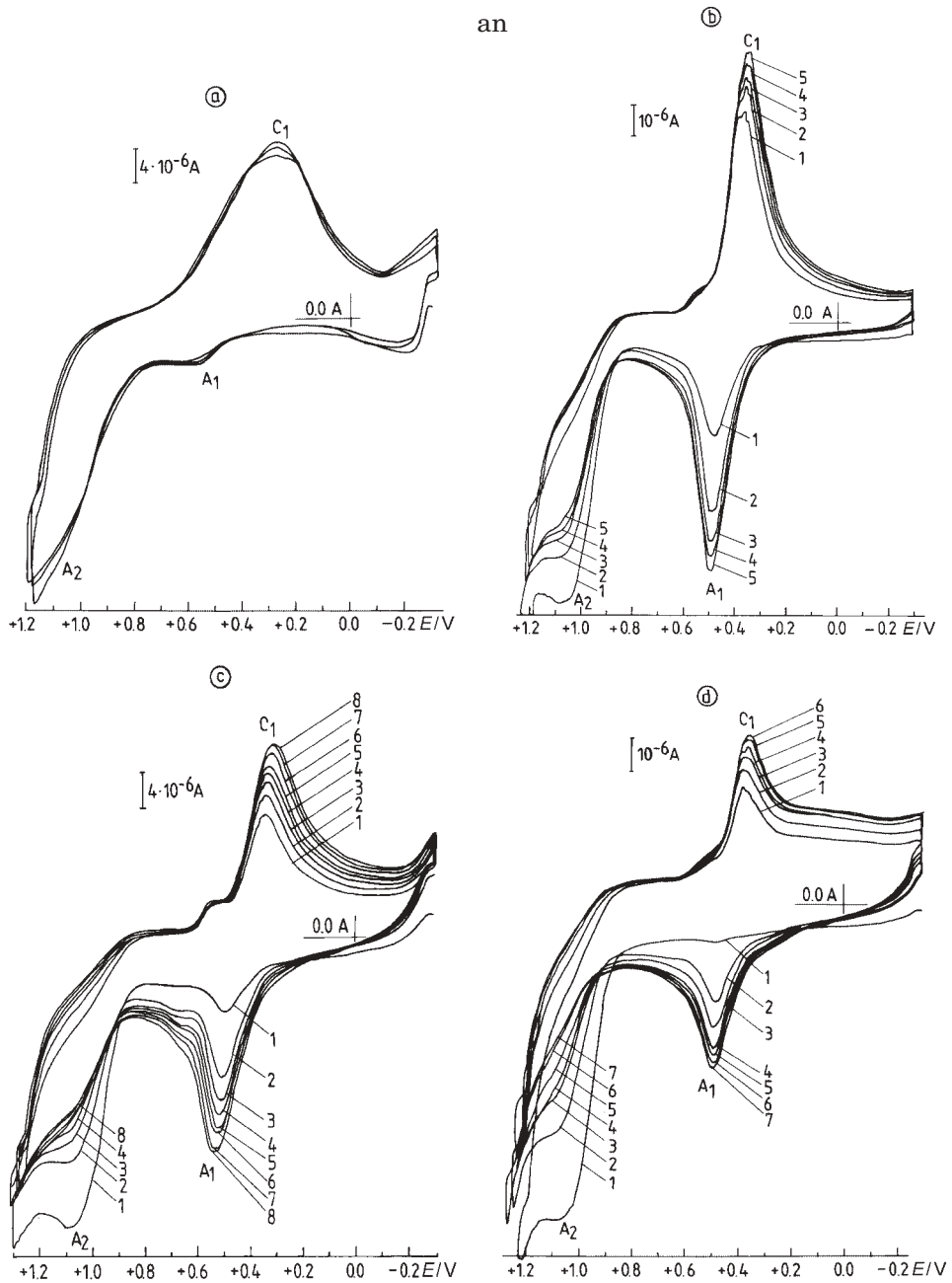


Figure 1. Cyclic voltammograms obtained with aniline on different electrode surfaces. ($c_{\text{aniline}} = 5 \cdot 10^{-4} \text{ M}$; $10^{-1} \text{ M H}_2\text{SO}_4 + 10^{-2} \text{ M NaClO}_4$; $v = 50 \text{ mV s}^{-1}$). a - Pt.E.; b - P.C.E.; c - Sp.C.E.; d - G.C.E.

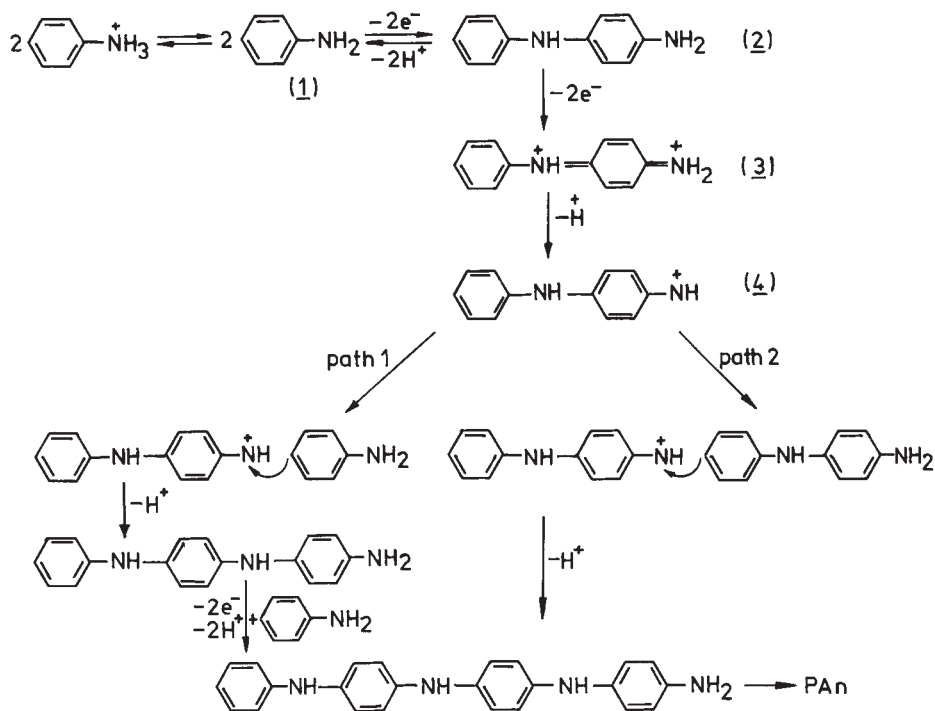


Figure 2. Proposed mechanism for the chemical polymerization of aniline^{15,16}.

increasing rate of polymer chain, of about 10^4 times higher than the initiation one.¹⁵

The dimer is then oxidized in one step to the diimine quinoiden form, with participation of two electrons,³ due to its low oxidation potential in comparison with aniline.⁴ The redox couple situated within the range of less positive potentials has a progressive evolution (intensities of voltammetric currents increase with increasing the number of scanning cycles) and might be attributed to the dimer and, subsequently, to the polymer forming on the electrode surface.

In the paper¹⁷ the authors present the mechanism of the electrooxidation of dimethylaniline in neutral medium. According to this, the initial oxidation of the monomer proceeds at $E = + 0.60$ V/S.C.E. with loss of $2e^-$. The dimer is oxidized at $+ 0.40$ V/S.C.E. and the trimer is oxidized at $+ 0.20$ V/S.C.E., also with participation of $2e^-$.

As regards the voltammograms obtained by us it might be estimated that at $E_{a(2)} \cong + 1.0$ V/S.C.E. almost all the monomer is oxidized (at least 80%), and then a redox equilibrium installs oneself, located at $E_{a(1)} \cong + 0.500 -$

+0.600 V/S.C.E. and $E_{c(1)} \cong +0.300$ V/S.C.E., corresponding to a polymer of 50 % iminoamino content.

As it can be seen from Figure 1, the influence of the electrode nature on the potential of voltammetric peaks is not significant, while the intensities of voltammetric currents are very different.

Stabilization of redox processes was rapid on Pt.E (only 3 scanning cycles were necessary) and slower on carbon electrodes (5–8 cycles).

The anodic peaks of the monomer are wider than the anodic–cathodic peaks of the polymer. This is indicative of a more difficult charge transfer in the case of the monomer than in the case of the polymer, the latter showing high conductivity.³

By taking the $\Delta E_{(a-c)}$ and S_a/S_c ratio (where S_a , S_c represents the surface area under voltammetric anodic and cathodic peaks respectively) voltammetric parameters into account, the reversibility of electrode processes may be appraised. The data can be seen in Table I.

The data in the table indicate quasireversibility of the redox process characteristic of the polymer (excepting for the Pt.E., where reduction prevails). The irreversibility degree decreases with increasing the number of scanning cycles, which is clearly evident from G.C.E.

The influence of the support electrolyte nature on the aniline voltammetric behaviour, can be appraised by comparing the cyclic voltammograms in Figure 3 (a, b, c, d).

A characteristic feature of the anodic curve shape can be seen in the first scanning cycle. Namely, in the absence of NaClO_4 in both acid and neutral media, only one peak is observable within the domain of high positive potential values, while in the presence of NaClO_4 , the anodic curve shows two peaks in the both cases.

It might be appraised that the monomer stability is higher in the absence of NaClO_4 , while the ClO_4^- ion promotes formation of the dimer, responsible for the appearance of the anodic peak during the first scanning cycle. This might be caused by the competition between the doping ions (SO_4^{2-} , ClO_4^-), whose nature influences also the electrochemical properties of the polymer.⁷ Along with cyclization, the redox couple, characteristic of the formed polymer, appears in both cases simultaneously with the monomer peak decrease (see the $i_{a(1)} / i_{a(n,c)}$ ratio).

The anodic peak potentials are more positive in acidic medium (higher stability of the compounds than in neutral medium). Maintenance of the potential values of the anodic and cathodic peaks, during cyclization, deserves mention.

In neutral medium, a tendency to modification of the shape of voltammetric curves can be noticed, especially for the cathodic branch during cyclization. Anodic peaks (to a lesser extent) and cathodic peaks (to a greater

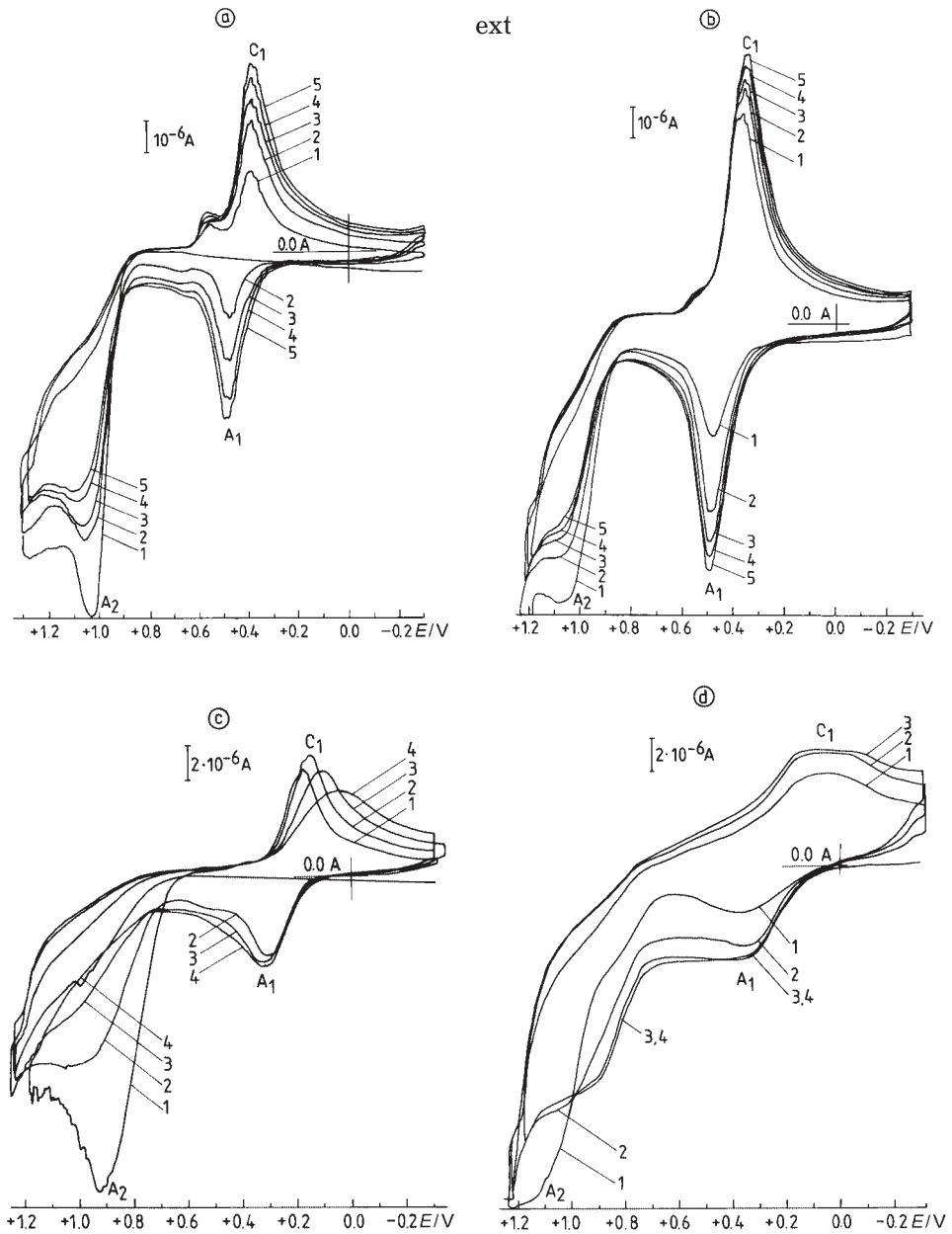


Figure 3. Cyclic voltammograms of aniline obtained with different support electrolytes. ($C_{\text{aniline}} = 5 \cdot 10^{-4}$ M; P.C.E.; $\nu = 50 \text{ mV s}^{-1}$). a = 10^{-1} M H_2SO_4 ; b = 10^{-1} M $\text{H}_2\text{SO}_4 + 10^{-2}$ M NaClO_4 ; c = 10^{-1} M Na_2SO_4 ; d = 10^{-1} M $\text{Na}_2\text{SO}_4 + 10^{-2}$ M NaClO_4). Note: Figure 3 (b) = Figure 1 (b).

TABLE I

Influence of the electrode nature on the redox process reversibility (redox couple A_1-C_1)
 ($c_{\text{aniline}} = 5 \cdot 10^{-4}$ M; support electrolyte: 10^{-1} M H_2SO_4 + 10^{-2} M $NaClO_4$; $v = 50$ mV s^{-1}).

Elec- trode	Scanning cycle (1)			Scanning cycle (n)*		
	$\Delta E(A_1-C_1)$ (V)	$\frac{S(A_1)}{mm^2}$ $\frac{S(C_1)}{mm^2}$	Process character	$\Delta E(A_1-C_1)$ (V)	$\frac{S(A_1)}{mm^2}$ $\frac{S(C_1)}{mm^2}$	Process Character
Pt.E.	0.275	0.1832	irreversible reduction	0.275	0.1872	irreversible reduction
P.C.E.	0.100	0.4235	irreversible reduction	0.125	0.8162	quasireversible process
Sp.C.E.	0.175	0.2050	irreversible reduction	0.230	0.7480	quasireversible process
G.C.E.	0.120	0.0540	irreversible reduction	0.150	0.8625	quasireversible process

* n = cycle number (Pt.E. - 3; P.C.E. - 5; Sp.C.E. - 8; G.C.E. - 7)

TABLE II

Influence of the support electrolyte nature on the reversibility of the aniline redox process
 (redox couple A_1-C_1) ($C_{\text{aniline}} = 5 \cdot 10^{-4}$ M; P.C.E.; $v = 50$ mV s^{-1})

Support electro- lyte	Scanning cycle (1)			Scanning cycle (n)*		
	$\Delta E(A_1-C_1)$ (V)	$\frac{S(A_1)}{mm^2}$ $\frac{S(C_1)}{mm^2}$	Process character	$\Delta E(A_1-C_1)$ (V)	$\frac{S(A_1)}{mm^2}$ $\frac{S(C_1)}{mm^2}$	Process Character
A	-	-	-	0.100	0.730	quasireversible process
B	0.100	0.4235	irreversible reduction	0.125	0.816	quasireversible process
C	-	-	-	0.160	0.670	quasireversible process
D	0.210	0.5277	irreversible reduction	0.230	0.728	quasireversible process

* n = cycle number; $n = 5$ (A, B); $n = 4$ (C, D)

A = 10^{-1} M H_2SO_4 ; B = 10^{-1} M H_2SO_4 + 10^{-2} M $NaClO_4$; C = 10^{-1} M Na_2SO_4 ; D = 10^{-1} M Na_2SO_4 + 10^{-2} M $NaClO_4$.

) corresponding to the polymer are shifted, which results in an increase of the interval between them and implicitly in a decrease of the reversibility of the redox process.

The charge transfer during electropolymerization is more difficult than in acid medium (peaks A_1 and C_1 are wider).

On the other hand, peak A_1 is located at lower potential values ($E_{a(1)} = + 0.350$ V/S.C.E., as compared to $E_{a(1)} = + 0.500$ V/S.C.E. in acid medium). It might be assumed that the polymers obtained in neutral medium are of a higher polymerization degree than those obtained in acid medium.¹⁷

The presence of the ClO_4^- ion makes the charge transfer more difficult (the curves have wide and less defined peaks).

The aniline reversibility characteristics on P.C.E. in the function of support electrolyte are given in Table II.

The data in Table II shows that the polymer behaves as a quasireversible system, where the presence of the ClO_4^- ion reduces the reversibility in both acid and neutral media ($\Delta E_{(a-c)}/V$ grows). However, several authors^{3,7} have evaluated the ClO_4^- ion as an advantageous doping agent.

In order to estimate the electropolymerization efficiency, the electrode surface covering during the anodic process A_1 was calculated ($\Gamma = Q / nFA$ (mol cm^{-2});¹⁸ $n = 2$, Refs. 3, 17). The experimental data are given in Tables III, IV.

It can be noticed in Table III that thin films (monomolecular layer corresponding to 10^{-10} mol cm^{-2})¹⁸ are obtained on G.C.E. during the first scanning cycle, while multi-molecular layers are obtained on Pt.E., Sp.C.E. and P.C.E.. During the last scanning cycle, the covering consists of multimolecular layers on each electrode under study. The thickest layers are obtained on Pt.E., but the redox process A_1 - C_1 is irreversible in both the first and the last scanning cycles.

TABLE III

Influence of the electrode nature on the aniline electropolymerization efficiency ($C_{\text{aniline}} = 5 \cdot 10^{-4}$ M; support electrolyte: 10^{-1} M H_2SO_4 + 10^{-2} M NaClO_4 ; $v = 50$ mV s^{-1}).

Electrode	$\Gamma_a / \text{mol cm}^{-2}$		$\Gamma_a(n) / \text{mol cm}^{-2}$
	Scanning cycle (1)	Scanning cycle (n)*	$\Gamma_a(1) / \text{mol cm}^{-2}$
Pt. E.	$2.30 \cdot 10^{-8}$	$2.700 \cdot 10^{-8}$	1.174
P.C.E.	$1.10 \cdot 10^{-9}$	$2.775 \cdot 10^{-9}$	2.523
Sp.C.E.	$7.59 \cdot 10^{-10}$	$5.175 \cdot 10^{-9}$	6.818
G.C.E.	$2.12 \cdot 10^{-10}$	$3.900 \cdot 10^{-9}$	18.396

*n = number of the cycle (Pt.E. - 3; P.C.E. - 5; Sp.C.E. - 8; G.C.E. - 7)

TABLE IV

Influence of the support electrolyte nature on the efficiency of the aniline electropolymerization process ($C_{\text{aniline}} = 5 \cdot 10^{-4}$ M; P.C.E.; $v = 50$ mV s $^{-1}$)

Support electrolyte	$\Gamma_a / \text{mol cm}^{-2}$	
	Initial scanning cycle	Final scanning cycle
A	$3.960 \cdot 10^{-10}$	$1.760 \cdot 10^{-9}$
B	$1.100 \cdot 10^{-9}$	$2.775 \cdot 10^{-9}$
C	$1.468 \cdot 10^{-9}$	$2.584 \cdot 10^{-9}$
D	$1.453 \cdot 10^{-9}$	$4.228 \cdot 10^{-9}$

A = 10^{-1} M H $_2$ SO $_4$; B = 10^{-1} M H $_2$ SO $_4$ + 10^{-2} M NaClO $_4$; C = 10^{-1} M Na $_2$ SO $_4$; D = 10^{-1} M Na $_2$ SO $_4$ + 10^{-2} M NaClO $_4$.

The data in Table IV indicate that the films obtained on P.C.E. (in the absence of NaClO $_4$) are thinner in acid medium than in neutral medium.

The ClO $_4^-$ improves the efficiency of the aniline electropolymerization in both cases to about the same extent ($\Gamma_{a(B)} / \Gamma_{a(A)} = 1.576$; $\Gamma_{a(D)} / \Gamma_{a(C)} = 1.636$). In this case, multimolecular layers are formed during the initial scanning cycle.

CONCLUSIONS

Aniline in small concentrations (about 10^{-4} M) can be characterized electrochemically by cyclic voltammetry, within the $-0.3 \leftrightarrow +1.4$ V/S.C.E. potential domain, in acid or neutral aqueous solutions, on Pt and carbon electrodes.

The nature of the electrodes does not significantly influence the potential values of the anodic and cathodic peaks, determining instead the intensity of voltammetric currents.

In our paper, we present a possibility of obtaining thin and reproducible polyaniline films on carbon electrodes, which can be used as analytical sensors for determining ions and molecules in low concentrations (inorganic and organic).

The electropolymerization process proceeds in two stages. The first stage of monomer oxidation is an irreversible process on every electrode under study, while the polymer formed by cyclization might be considered as an quasi-reversible system on carbon electrodes, and as an irreversible one, with a strong reduction character, on Pt.E. This fact is surprising because in chemical polymerization the monomer oxidation is reversible, while that of the dimer is irreversible (See Figure 2).

Electropolymerization in neutral medium can be considered more advantageous due to the lower oxidation potential (A_1) as well as to the possibility of obtaining a higher polymerization degree.

The presence of the ClO_4^- ion improves the electropolymerization efficiency in both acid and neutral media.

This study points to the conclusion that good results can be obtained starting from diluted aqueous solutions (10^{-4} M) of monomer subjected to electropolymerization by cyclic voltammetry within the potential range of $-0.3 \leftrightarrow +1.4$ V/S.C.E., on P.C.E. in both acid (10^{-1} M H_2SO_4) and neutral (10^{-1} M Na_2SO_4) media, in either the presence or the absence of the ClO_4^- ion.

The polyaniline conducting films of desired thickness can be obtained by careful selection of the working conditions (monomer concentration, electrode type, nature of the support electrolyte, number of scanning cycles).

REFERENCES

1. R. W. Murray, *Acc. Chem. Res.* **13** (1980) 135–141.
2. M. E. G. Lyons (Ed.), *Electroactive Polymer Electrochemistry* Part. 1: *Fundamentals*; Part 2: *Application*, Plenum Press, New York, 1994.
3. C. Simionescu, I. Cianga, and M. Grigoras, *Roum. Chem. Quartely Reviews* **3** (1995) 3–13.
4. D. M. Mohilner, R. N. Adams, and W. J. Argersinger Jr., *J. Am. Chem. Soc.* **84** (1962) 3618–3625.
5. E. M. Genies, A. A. Syed, and C. Tsintavis, *Mol. Cryst. Liq. Cryst.* **57** (1984) 2254–2260.
6. C. Q. Cui, L. H. Ong, T. C. Tan, and J. Y. Lee, *Synth. Metals.* **58** (1993) 147–151.
7. S. Pruneanu, E. Veress, J. Marian, and L. Oniciu, *J. of Materials Sci.* 1997, in press.
8. C. Simionescu, I. Cianga, and A. Farcas, *Rev. Roum. de Chimie* **39** (1994) 333–338.
9. C. Simionescu, M. Grovu-Ivanoiu, I. Grigoras, Al. Duca, and I. Cocarla, *Angew. Makromol. Chem.* **239** (1996) 1–12.
10. A. G. MacDiarmid, L. S. Huang, and B. D. Humphrey, *Synth. Met.* **18** (1987) 393–395.
11. W. W. Foke, G. C. Wnek, and Y. Wel, *J. Phys. Chem.* **91** (1987) 5913–5917.
12. D. Bejan and Al. Duca, *Bul. I. P. Iasi*, **XXXIX(XLIII)**, fasc. **1–4** (1993) 23–31.
13. Al. Duca and D. Bejan, *Rev. Roum. de Chimie* **36** (1991) 439–453.
14. M. Breitenbach and K. H. Hackner, *J. Electroanal. Chem.* **29** (1971) 306–310; *ibid* **33** (1971) 45–47; *ibid* **43** (1971) 267–272.
15. Y. Wei, X. Tang, Y. Sun, and W. Focke, *J. Polym. Sci., Part A: Polym. Chem.* **27** (1989) 2385–2390.
16. Y. Wei, R. Hariharan, and S. A. Patel, *Macromolecules* **23** (1990) 758–761.
17. G. Hambitzer and J. Heitbaum, *Anal. Chem.* **58** (1986) 1067–1070.
18. R. G. Murray, *Electroanalytical Chemistry*, vol 13, Marcel Dekker, Inc., New York and Basel, 1984, p.192.
19. Al. Duca and D. Bejan, unpublished data.

SAŽETAK**Voltamperometrija anilina s različitim elektrodama i elektrolitima***Doina Bejan i Alexandru Duca*

Svrha je ovog rada elektrokemijska karakterizacija anilina i dobivanje tankih polianilinskih filmova na ugljikovim elektrodama koje bi se mogle rabiti kao analitički senzori.

Primijenjena je voltamperometrija s linearnom promjenom napona u vodenom mediju, u području potencijala od -0.3 V do $+1.4$ V (prema S.C.E.), s brzinom od 50 mV/s, koristeći se platinskom i različitim grafitnim elektrodama te mijenjajući osnovne elektrolite (H_2SO_4 , $H_2SO_4 + NaClO_4$, Na_2SO_4 , $Na_2SO_4 + NaClO_4$). Posebna pažnja bila je posvećena elektropolimerizaciji anilina u neutralnom mediju pri niskoj koncentraciji ($5 \cdot 10^{-4}$ M), kao i usporedbi s onom u kiselom mediju.

Određene su voltamperometrijske osobine anilina (potencijali i vršne struje anodnih i katodnih odziva), procijenjena je reverzibilnost elektrodnih procesa (razlika vršnih potencijala anodnih i katodnih odziva, odnos količine naboja u anodnom i katodnom procesu), a mehanizam elektropolimerizacije uspoređen je s oblicima dobivenih voltamograma. Određena je djelotvornost elektropolimerizacije.