

**ELECTRODE PROCESSES OF NEUTRAL RED  
ON GLASSY CARBON AND INDIUM TIN OXIDE (ITO)  
ELECTRODES IN AQUEOUS BUFFERED SOLUTIONS**

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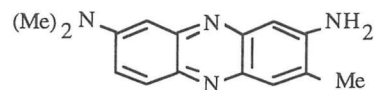
**SUMMARY**

*The electrode processes of Neutral Red (3-amine-7-dimethylamine-2-methyl-phenazine) have been studied voltammetrically on Glassy Carbon (GC) and on Indium Tin Oxide (ITO) electrodes in buffered aqueous solutions. Multicycle voltammetric treatment of neutral red yields a water insoluble surface film.*

**Key words:** voltammetry of Neutral Red, electrode reaction mechanisms of Neutral Red on GC, Neutral Red electrode reactions on ITO

**INTRODUCTION**

Neutral Red (3-amine-7-dimethylamine-2-methyl-phenazine monohydrochloride) has long been used as a pH indicator due to the fact that its red-yellow colour change in aqueous media [1-4].



Neutral Red, NR

The oxidized form of NR shows different protonation equilibria [5] and in solutions of  $\text{pH} > 0$  it only exists as a monoprotonated (Red,  $\lambda_{\text{max}} = 530 \text{ nm}$ ) form and an unprotonated (Yellow,  $\lambda_{\text{max}} = 450 \text{ nm}$ ) one. On the other hand, two protonation possibilities of reduced form have been reported [6] where for  $\text{pH} < \text{pK}_{\text{a}2} = 4.4$  the diprotonated ( $\text{NRH}_4^{2+}$ ) ions have been identified as a predominant form whereas in the range  $\text{pK}_{\text{a}2} < \text{pH} < \text{pK}_{\text{a}1} = 6.3$  the monoprotonated  $\text{NRH}_3^+$  ones have been noted in majority. Suzuki *et al.* [7] detected two redox systems in acid aqueous solutions on mercury electrode. The first reversible wave of polarographic reduction of  $\text{NRH}^+$  to the respective form  $\text{NRH}_2$  has been observed. The second wave, which was less reversible, was attributed to the reduction of a fluorescent compound produced by a chemical change of the first electroreduction product. Halliday and Matthews [2] have detected one or two waves dependently on different electrode materials. Electroreduction mechanisms of phenazines in non-aqueous media and on various electrode materials have been discussed by several authors [8-12]. The aim of this work is to describe the electrochemical behaviour of **neutral red** on Glassy Carbon (GC) and on Indium Tin Oxide (ITO) electrodes.

## EXPERIMENTAL

Voltammetric experiments were carried out with a three electrode cell by means of a BELPORT potentiostat equipped with a linear wave generator BELPORT and a RIKEN-DENSHI X-Y recorder. For electrolysis under controlled potential the working and auxiliary electrodes were separated using the electrolytic bridge. As supporting electrolytes the various ionic strength solutions of  $\text{K}_2\text{SO}_4$  buffered by means of Britton-Robinson (GC electrode) and citric/citrate buffers (ITO electrode) were used. The pH value and temperature of solutions were controlled by means of a CRISON 501 pH-meter and a HETO-CB7, respectively.

Spectroscopic measurements were carried out by means of an Uvikon 930 KONTRON spectrophotometer.

A foil of Pt ( $A = 4 \text{ cm}^2$ ) was used as counter electrode. A Hg/Hg<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>(sat.) electrode was used as reference electrode. Glassy Carbon (GC, METROHM) and Indium Tin Oxide glass (ITO, 30  $\Omega/\text{cm}^2$ , GLASSTRON) were applied as the working electrodes.

Before each experiment the GC electrode ( $A = 0.07 \text{ cm}^2$ ) was cleaned with 2M KOH., then in H<sub>2</sub>SO<sub>4</sub> (conc.) and 2M H<sub>2</sub>SO<sub>4</sub>, and rinsed with deionized water (Milli-Q PLUS MILLIPORE). After the cleaning the GC electrode was polished with Al<sub>2</sub>O<sub>3</sub> (METROHM) and then rinsed with water. The ITO electrode ( $A = 0.4 \text{ cm}^2$ ) was pretreated in acetone and dried in nitrogen stream. Neutral Red chlorhydrate (PANREAC, for microscopy) was used.

The voltammetry on the GC electrode was performed in NR solutions with concentrations from  $c_{\text{NR}} = 0.5 \times 10^{-4}$  up to  $4 \times 10^{-3}$

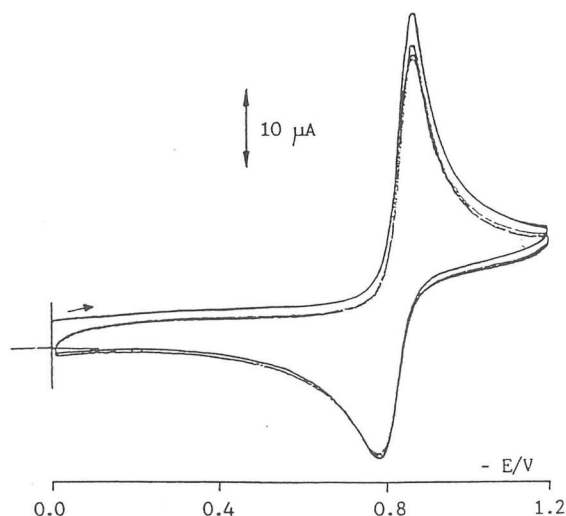


Fig. 1. Voltammogram of NR ( $c_{NR} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ; supp. electrolyte: acetic/acetate buffer,  $I = 0.1 \text{ M}$ , pH 5.03,  $T = 298 \text{ K}$ ) on Glassy Carbon electrode ( $v = 100 \text{ mVs}^{-1}$ )

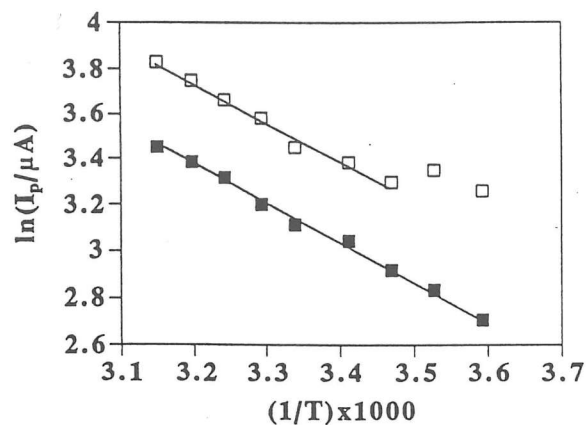


Fig.2. Temperature dependence of voltammetric current peaks of NR ( $c_{NR} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) on GC electrode ( $v = 100 \text{ mV s}^{-1}$ ) in Britton - Robinson buffer ( $I = 0.1 \text{ M}$ , pH 5.03 ); cathodic peaks (□):  $y = 9.1666 - 1.6971x$  ( $r = 0.9937$ ); anodic peaks (■):  $y = 8.7023 - 1.666x$  ( $r = 0.9981$ )

$\text{mol} \cdot \text{dm}^{-3}$  in the aqueous solutions with Britton-Robinson buffer and in the solutions in the mixed water-DMF solvents. In experiments with the ITO electrode the solution of NR was prepared in the supporting electrolyte with citric/potassium citrate buffer. All reagents (*p.a.*, PANREAC) were used without additional purification.

## RESULTS AND DISCUSSION

The cyclic voltammograms of **Neutral Red** on GC (glassy carbon) electrode are shown in Fig. 1.

For both anodic and cathodic processes the dependence of the respective peak currents on temperature are presented in Fig.2. The linear plots of  $\ln i_p$  vs  $(1/T)$  show an Arrhenius behaviour. The apparent activation energies obtained from plots are equal to  $14.5 \text{ kJ mol}^{-1}$  and this value lies within a diffusion controlled processes energy range. However, the adsorption of  $\text{RNH}^+$  on the electrode is made evident at lower temperatures.

The measured peak potential/pH dependencies show the shift of the respective  $E_{p,a}$  and  $E_{p,c}$  peak potential values to a more negative potential range with an increasing pH (Fig.3). Figure 3 clearly illustrates the preprotonation chemical step of neutral red. The dependence of cathodic potential peak values as a function of pH shows two linear plots with crossing point indicating  $\text{pK}_a = 6.7$  according to potentiometric results [3,4]. Below this value the oxidized species of NR are protonated and then the charge transfer takes place. In basic solutions NR is directly reduced since  $E_p$  remains nearly constant with pH changes at  $\text{pH} > 6.7$  as occurs in other organic substances. Three

TABLE 1

Voltammetric peak potential values of Neutral Red (NR) ( $c_{NR} = 1.2 \times 10^{-3} M$ , ref. Hg/Hg<sub>2</sub>SO<sub>4</sub>, K<sub>2</sub>SO<sub>4</sub>(sat), /mV) on stationary Glassy Carbon electrode in Britton-Robinson buffer (I = 0.1M, pH 5.03) and  $W^c = |E_{p,c} - E_{p/2,c}|$ , and  $W^a = |E_{p,a} - E_{p/2,a}|$  / mV.

$\nu$ / mVs <sup>-1</sup>	$-E_{p,c}$	$-E_{p/2,c}$	$W^c$	$-E_{p,a}$	$-E_{p/2,a}$	$W^a$
30	810	776	34	764	799	35
40	803	771	32	759	794	35
50	797	767	30	750	787	37
60	804	776	28	755	799	44
70	809	772	37	756	792	36
80	810	772	38	753	797	44
90	802	769	33	753	785	32
100	804	765	39	741	782	41
120	811	777	34	744	787	43
130	814	776	38	741	785	44

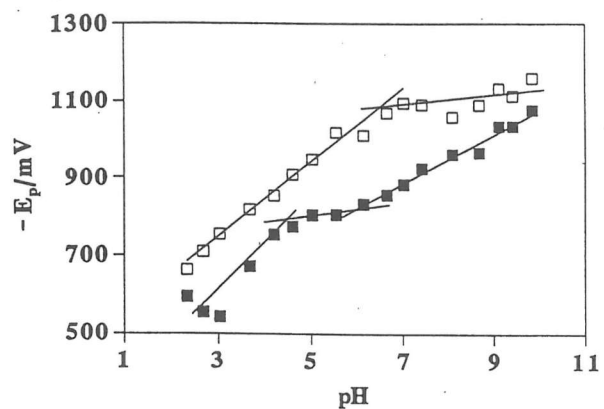


Fig.3. pH dependencies of voltammetric peak potentials of NR ( $c_{NR} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ ) on GC electrode ( $\nu = 100 \text{ mV s}^{-1}$ ) in Britton-Robinson buffer (I = 0.1 M, T = 298 K); cathodic (□), anodic (■)

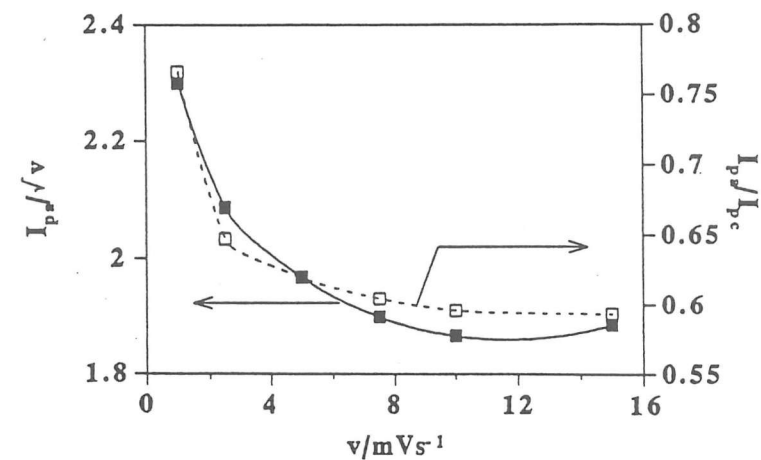
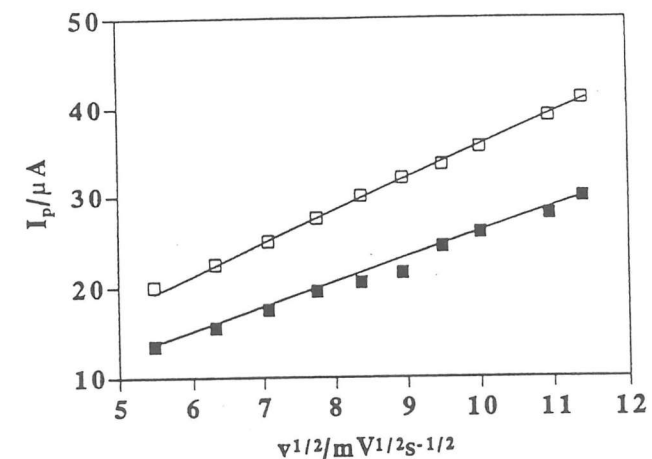


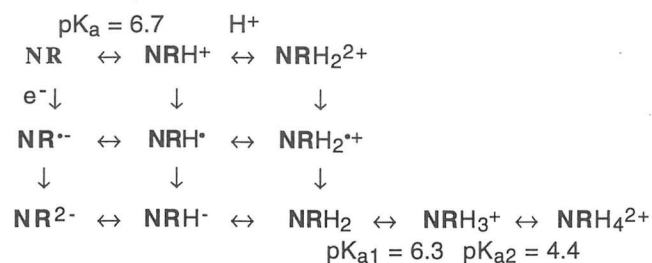
Fig.4. The current peaks as the functions of sweep rate [14]; cathodic (□) ( $r = 0.9993$ ), anodic (■) ( $r = 0.9957$ ); GC electrode ( $c_{NR} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ , Britton-Robinson buffer of I = 0.3 M, pH 4.5)

straight lines of anodic peak potential  $E_{p,a} = f(\text{pH})$  indicate two crossing points which are close to  $\text{pK}_{a1} = 6.3$  and  $\text{pK}_{a2} = 4.4$  for NR reduced species according to Nikolskii's data [6].

The half width (Table 1) of the cathodic peak  $W_{1/2,c}$  and  $W_{1/2,a}$  the anodic peak implies the quasi-reversible two-electron process [13]. The anodic and cathodic peak currents linearly depend on the scan rate functions (Fig. 4a) with different slopes, and the Nicholson-Shain [13] current functions (Fig. 4b) prove the process to be a two-electron, quasi-reversible, controlled by diffusion and coupled to a chemical reaction

The current peak of the first anodic scan presented in Fig.1 decreases slightly when the ionic strength of solution increases as corresponds to the reduction of an charged specie (Table 2), however the respective peak potential values remain constant.

The electrochemical mechanism associated to the Ic/Ia couple can be illustrated by means of a square type scheme [8,10,14,15]:



Where the stable reduced acidic species (in aqueous solution),  $\text{NRH}_3^+$  and  $\text{NRH}_4^{2+}$ , must be dissociated before the re-oxidation. For this reason the electrochemical reoxidation of the species mentioned above is slightly affected by the overall concentration of acetic acid in the

TABLE 2

The voltammetric peak potentials/ mV/ of NR on GC electrode ( $c_{\text{NR}} = 1.2 \times 10^{-3}$  M) in Britton-Robinson buffer (pH 5.03) of various ionic strength

I/M	$-E_{p,c}(\text{I})/\text{mV}$	$-E_{p,a}(\text{I})/\text{mV}$	$\Delta E_p(\text{mV})$	$I_{p,c}(\text{I})/\mu\text{A}$	$I_{p,a}(\text{I})/\mu\text{A}$	$I_{p,a}/I_{p,c}$
0.156	811	741	70	31	23	0,74
0.279	818	735	83	31	20	0,65
0.402	828	741	87	31	18	0,58
0.525	834	745	89	31	17	0,55

TABLE 3

The voltammetric peak potentials /mV/ of NR on GC electrode ( $c_{\text{NR}} = 1.2 \times 10^{-3}$ ,  $v = 100 \text{ mVs}^{-1}$ ) in Britton-Robinson buffer of  $I = 0.3 \text{ M}$  with various concentrations of acetic acid ( $c_{\text{H}}$ ).

$C_{\text{H}}/\text{M}$	$-E_{p,c}(\text{I})/\text{mV}$	$-E_{p,a}(\text{I})/\text{mV}$	$\Delta E_p(\text{mV})$	$I_{p,c}(\text{I})/\mu\text{A}$	$I_{p,a}(\text{I})/\mu\text{A}$	$I_{p,a}/I_{p,c}$
0,064	825	749	76	26	20	0,77
0,128	822	739	83	30	18	0,61
0,208	825	726	99	30	17	0,56
0,288	825	723	102	31	17	0,55

buffered solution ( $c_H$  in Table 3). When the buffer capacity increases the dissociation reactions of  $\text{NRH}_3^+$  and  $\text{NRH}_4^{2+}$  species should be inhibited since the process is checked thermo-dynamically and kinetically.

The adsorption of phenazine on mercury electrode was already described by Laitinen [16] in  $\text{NaClO}_4$  aqueous solution. When the adsorbed compact film of oxidized species was formed, the slope of the graph  $I_p=f(c)$  changes abruptly when  $c = c_m$ . The relations between the current peaks of the first cycle and concentration of **NR** in the solution are shown in Fig. 5. The straight lines crossing point of the cathodic current peak dependence shown in Fig. 5a indicates a  $c_m$  concentration of about  $1.2 \cdot 10^{-4}$  M of **NR** which illustrates the boundary concentration.

Therefore, the maximum values of the surface concentration of **Neutral Red** covering the GC electrode surface ( $\Gamma'_m$ ) can be approximately calculated from the equation (10,16):

$$\Gamma'_m = 0.74 (D_{\text{ox}})^{1/2} c_m t_1^{1/2} \quad (6)$$

where  $c_m \approx 1.2 \cdot 10^{-4}$  mol.dm<sup>-3</sup> is the experimental value (Fig. 5a) and  $t_1$  is the time assigned by voltammetric scan rate. Diffusion coefficient ( $D_{\text{ox}}$ ) of **NR** oxidized form was calculated on the basis of experimental results and equals  $3 \cdot 10^{-6}$  s cm<sup>-2</sup>. Finally, the approximate value of the surface area covered by **NR** oxidized specie ( $\Gamma'_m$ ) of the order  $10^{-11}$  mol×cm<sup>-1</sup> has been calculated and this approach corresponds to the flat lying specie area about 50-60 Å<sup>2</sup>. The self association of neutral red causes the non linear dependence on  $c$  of  $i_p$  in

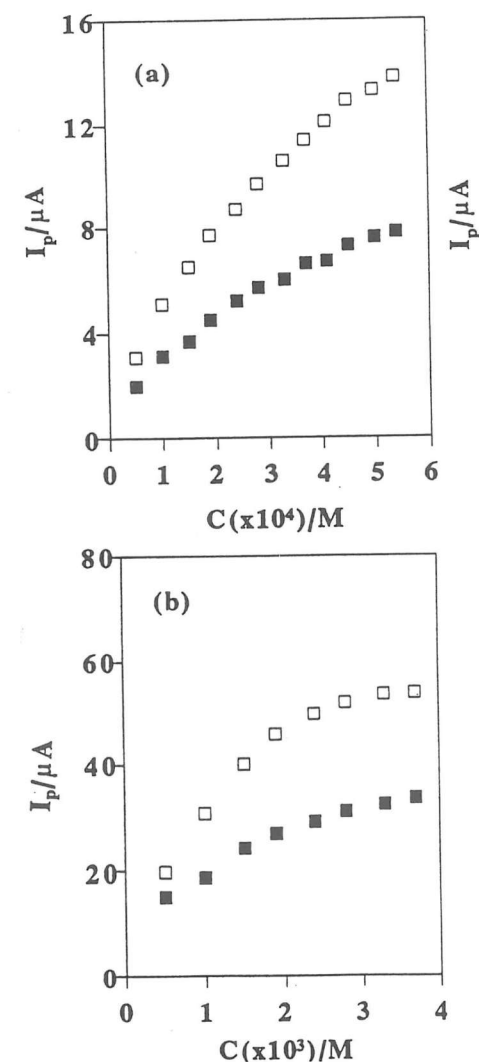


Fig.5. Current peak dependencies on **NR** concentration in solutions on GC electrode ( $v = 100 \text{ mV s}^{-1}$ , Britton-Robinson buffer of  $I = 0.3 \text{ M}$ , pH 4.5); cathodic ( $\square$ ), anodic ( $\blacksquare$ )

concentrate solutions (Fig. 5b) as is common in many organic substances in aqueous solution.

Figure 6 illustrates the formation of a new irreversible redox couple ( $II^c/II^a$ ) in the potential peaks  $E_{p,c} = -0.5$  and  $E_{p,a} = -1.4$  V (versus Hg/Hg<sub>2</sub>SO<sub>4</sub> electrode) and, in consequence, the decreasing of the respective current peaks of NR redox processes. The thickness of this film increases slowly (in the long term voltammetric treatment) This latter type form of covering surface film is characterized by new ( $II^c/II^a$ ) irreversible couple and the redox processes ( $I^c/I^a$ ) are successively checked. In the single sweep oscillographic polarograms of NR in solutions of various pH (pH 3-6) presented by Suzuki and Sawada [7] the second irreversible wave was recorded (on drop mercury electrode). This second peak may be compared with our  $II^c$  peak in Fig. 6.

The ( $II^c/II^a$ ) couple is not recorded when DMF is added to the solution since the reaction products are soluble in water-DMF mixed solvent. The shift of  $E_p$  values in the mixed solvent (Table 4) can be interpreted on the basis of the solvation activity transfer coefficient of proton from water to the mixed water-DMF solvent. This solvent effect causes the shift of the standard potential of reactions with participation of solvated proton [17].

The experiments on ITO electrode were carried out in K<sub>2</sub>SO<sub>4</sub> electrolyte with citric/citrate buffer, since HAc/Acetate system has caused some trouble with stability of supporting electrolyte due to the catalytic reduction of acetic acid during the long term voltammetric measurements. The first cycle voltammogram on ITO electrode is shown in Fig.7 and the analysis of the obtained current peaks functions can let

TABLE 4

Influence of the composition of the mixed water-DMF solvent on peak potentials of NR on GC electrode ( $v = 50 \text{ mVs}^{-1}$ ). Ratio of the current peaks  $(I_{pa}/I_{pc})^{\text{water}}$  and  $(I_{pa}/I_{pc})^{\text{solv.}}$  are equal to  $0.8 \pm 3\%$ . Solution parameters as in Table 3

$c_{\text{DMF}}/\text{Vol.}\%$	$-E_{p,c}$	$-E_{p,a}$	$\Delta E_p$
0	797	767	70
8	798	724	74
20	815	730	85
28	842	757	85
40	879	791	88

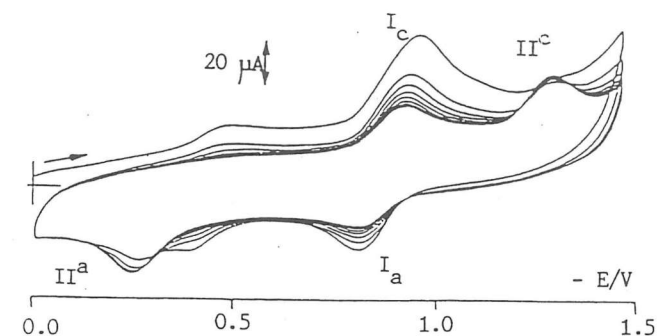


Fig.6. Multicycle voltammogram of NR ( $c_{\text{NR}} = 1.2 \times 10^{-3} \text{ mol dm}^{-3}$ , Britton-Robinson buffer of  $I = 0.1 \text{ M}$ , pH 6.1) on GC electrode ( $v = 100 \text{ mV s}^{-1}$ )

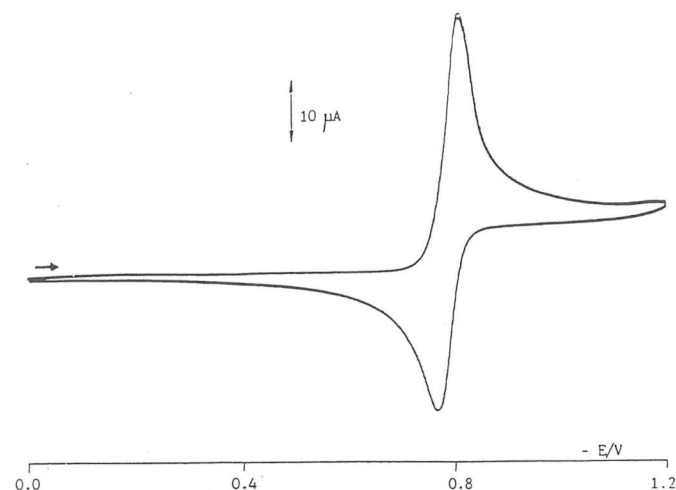


Fig. 7. Voltammogram of NR ( $c_{NR} = 2.5 \times 10^{-4} \text{ mol dm}^{-3}$ ,  $I = 0.22$  M citric/citrate buffer, pH 4.4) on ITO electrode ( $v = 20 \text{ mV s}^{-1}$ )

us conclude that they illustrate the same mechanisms that this described above on GC electrode.

Eventually, in order to obtain the electrochromic surface film the ITO electrodes have been treated in a long term voltammetric studies and by the chronoamperometric technique under controlled potential. The colour changes of ITO surface were not observed. Both experimental ways provide a new surface layer with  $\lambda_{\text{max}} = 380 \text{ nm}$ . Nevertheless, at pH = 4.7, the solution of oxidized specie shows a red colour ( $\lambda_{\text{max}} = 530 \text{ nm}$ ) and the reduced species an orange colour ( $\lambda_{\text{max}} = 480 \text{ nm}$ ) that are related with the  $\text{RNH}^+$  and  $\text{RNH}_3^+$  species, respectively. The couple IIc/IIa corresponds to the new phase formed on the ITO electrode ( $\lambda_{\text{max}} = 380 \text{ nm}$ .) This water-insoluble surface layer hindered the I<sup>c</sup>/I<sup>a</sup> process. In spite of the fact that the I<sup>c</sup>/I<sup>a</sup> process is quasi-reversible, the existence of a secondary II<sup>c</sup>/II<sup>a</sup> process hinders the application of NR in electrochromic devices(18) based on the ITO transparent electrode.

## REFERENCES

1. C.J. Drumond, F. Grieser and T.H. Healy, *J.Chem. Soc. Faraday Trans. I.*, 85 (1989) 552
2. C.S. Haliday and D.B. Matthews, *Austr. J.Chem.*, 36 (1983) 507
3. "The Merck Index", 11th Edition, Merck & Co., Inc. 1989
4. E. Baumgartner, R. Fernandez-Prini and D. Turin, *J.Chem. Soc. Faraday Trans. I.*, 70 (1974) 1518
5. P. Bartels, *Z. Phys. Chem.* 9 (1954) 74
6. a) B.P. Nikolskii, V.V. Paltchevskii, L.A. Polanskaya and V.V. Boriskin, *Dokl. Akad. Nauk SSSR*, 193 (1970) 352;  
b) B.P. Nikolskii, V.V. Paltchevskii, L.A. Polanskaya and A.G. Rodichev, *Dokl. Akad. Nauk SSSR*, 194 (1970) 1334
7. M. Suzuki and S. Sawada, *Denki Kagaku*, 38 (1971) 249
8. Y. Mugnier, L. Roullier and E. Laviron., *Electrochim. Acta*, 36 (1991) 803
9. D.N. Bailey, D.K. Roe and D.M. Hercules, *J.Electrochem. Soc.*, 116 (1969) 190
10. E. Laviron, *J.Electroanal. Chem.*, 52 (1974) 355
11. E. Laviron and Y. Mugnier, *J.Electroanal. Chem.*, 111 (1980) 337
12. R.C. Kaye and H.I. Stonehill, *J.Chem. Soc.*, (1952) 3240
13. R.S. Nicholson and I. Shain, *Anal. Chem.*, 36 (1964) 706
14. E. Laviron and I. Roullier, *J.Electroanal. Chem.*, 57 (1983) 7
15. E. Laviron, *J.Electroanal. Chem.*, 146 (1983) 15
16. H.A. Laitinen and B. Mosier, *J.Am.Chem.Soc.*, 80 (1958) 2363
17. H. Scholl and K. Sochaj, *Electrochim. Acta*, 34 (1989) 915
18. A. Roig. Doctoral Thesis. Universitat of Valencia (1994)



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**INFLUENCE OF HALIDE IONS ON THE ELECTROCHEMICAL  
BEHAVIOUR OF MAGNESIUM AT HIGH CONCENTRATIONS**

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**SUMMARY**

Magnesium, one of the lightest nonferrous metals assumes great importance due to many attractive structural, chemical and electrochemical features. The influence of the halide ions at concentrations ranging from 0.1 M to 2.0 M on the corrosion behaviour of primary magnesium has been investigated by galvanostatic polarisation and atomic absorption spectroscopy (AAS). The corrosion kinetic parameters namely open circuit potential (OCP), corrosion potential ( $E_{\text{corr}}$ ), corrosion current ( $I_{\text{corr}}$ ) and Tafel constants ( $b_a$  and  $b_c$ ) have been calculated from polarisation experiments. These data are interpreted to bring out the effects of the halide ions and their concentration on the corrosion of magnesium in these media. The amount of magnesium anode dissolved and estimated by the instrumental method has been compared with the electrochemical weight loss. The dissolution rate in the former is found to be more than in the latter. Suitable explanations have been forwarded for the excess dissolution of magnesium. The change in  $p^{\text{H}}$  observed during the polarisation at high current densities has also been investigated and explained suitably in this paper.

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