Polyaniline, Poly-N,N-dimethylaniline and Poly-N, N-diethylaniline coatings for brass Protection

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ABSTRACT *The Polymers, such as polyaniline, poly-N,N-dimethylaniline and poly-N,N-diethylaniline were chemically deposited on a brass surface with an anodic oxidation by potentiostatic method. The tests for corrosion protection of the polymers coated and uncoated brass substrate were investigated in 0.1M NaCl solution by using potentiostatic polarization. Tafel polarization measurements showed, the studied polymers coating have ability to protect the brass against corrosion. Some conditions, applied potential, electrolyte composition, electro-polymerization time and monomer type, of polymer prepared potentiostatically affect on the corrosion parameters, i_0 (exchange current), I.E.% (inhibition efficiency), and P (porosity) of the polymers coated brass in aggressive medium of 0.1M aqueous solution. The all corrosion and electro-polymerization experiments were investigated at 30oC in all electrolytes.*

Introduction

Corrosion of metals has been a persisting problem in society and, hence, it is an important area of research. The metal corrosion involves the transfer of electrical charge in aqueous solution at the metal-electrolyte interface. Corrosion protection is often afforded by isolating metals from the corrosive environment using polymer coatings. Practical applications of conductive polymers have received considerable interest as corrosion protective coating on oxidizable metals in most recent times[1-5]. This because these polymers are chemically stable, environmentally viable, and have good corrosion resistance[6]. Mengoly et al.[7] was the first to examine the protective behavior of polyaniline on stainless steel and then in 1985, DeBerry[8] showed that the electrochemically synthesized polyaniline act as corrosion protective layer on stainless steel in 1.0M H_2SO_4 . Since then, several research groups[9-13] have systematically investigated the electrochemical synthesis of various conducting polymers on oxidizable metals for corrosion protection purposes.

In our present work, we investigated the corrosion protection of polyaniline, poly-N,N-dimethylaniline, and poly-N,N-diethylaniline coatings brass in 0.1M NaCl aqueous solution. we studied also the effects of the polymers coating brass prepared under some conditions, such as applied potential, electrolyte composition, and polarization time against corrosion in the same aggressive medium. This because these conditions exhibit influence on the properties of the coating polymer and, hence, effects on the brass corrosion protection[14].

Experimental

Material and Sample Preparation:

The brass working electrode is a disk with surface area $0.1662571 Cm^2$. The brass was cut as a cylindrical rode of 65% copper and 35% zinc, and mounted into glass tube of appropriate diameter with epoxy resin. The disk surface was polished prior to any experiment with 600 grit SiC paper, rinsed with distilled water and polished with an acetone-saturated paper towel to remove any grease and produce a relatively scratch free, smooth, shiny surface[15].

The Electrolyte Media:

All chemicals were of analytical grade. Bi-distilled water was used to prepare all solutions, 0.5M aniline in 1.0M of H_2SO_4, HCl, and HNO_3. We prepared also another solutions, 0.5M of N,N-dimethylaniline, and N,N-diethylaniline in 1.0M H_2SO_4. The experiments were carried out at 30oC in all the tested electrolytes.

The Electrolytic Cell and Measured Potentials:

A conventional three-electrode/one-compartment glass cell consisting of a brass disk, a platinum wire, and Ag/AgCl electrode, were used as working, counter, and reference electrodes respectively. The all potentials measured with respect to Ag/AgCl reference electrode.

Synthesis of Polymer Coating on Brass:

The polymers coatings were potentiostatically deposited on a brass, in solutions 0.5M monomers in 1.0M of H_2SO_4, HCl, and HNO_3, using a potentiostat Model PST006 from Voltalab-Radiometer analytical with software Model voltamaster 4. Some conditions affecting electrochemical polymerization such as applied potential, electrolyte composition, polarization time, and monomer type were written in tables (1-5) to exhibit influence on the properties of the polymer coating.

Corrosion Experiments:

The potentiostatic polarization experiments (E-Volt versus i-Amper) were carried for uncoated and polymer coated brass in aggressive medium of 0.1M NaCl aqueous solution.

Results and discussion

Figures (1-11) show a relation between the applied potentials (E-Volt) versus log current (i-Amper) according to the follow Tafel equation (1),

$$\eta = a + b \log I \qquad (1)$$

Where , η is the over-voltage ; more positive and negative potentials with respect to the free corrosion potential ($E_{corr.}$), a is the intercept of Tafel line with the applied potential, b is the anodic and cathodic Tafel slope depends on the polarization values with respect to $E_{corr.}$; Tafel constants (B_a, B_c).

Corrosion potentials ($E_{corr.}$) and the exchange-i_o (corrosion-$i_{corr.}$) currents density for the experiments of figures (1-11) determined by the extrapolation of the linear portions of the anodic and cathodic Tafel curves of polymer coated and uncoated brass. The anodic (B_a) and cathodic (B_c) Tafel slopes were calculated also from the figures (1-11).

A polarization resistance (R_p) for the polymer coated brass could be estimated by the expression(2) [16],

$$R_p = B / i_{corr.} \qquad (2)$$

Where, $B = B_a B_c / 2.303(B_a + B_c)$

The corrosion inhibition efficiency (I.E.%) was evaluated from the measured $i_{corr.}$ values obtained from Tafel polarization method using the relationship (3).

I.E.% = ($i_{corr.} - i\'_{corr.}$ / $i_{corr.}$) x 100   (3)

where $i_{corr.}$ and $i\'_{corr.}$ are the corrosion current density without and with coared polymer[17]. The porosity in the coating is very important parameter to determine whether a coating is suitable or not to protect the substrate against corrosion. In order to calculate the porosity of the polymer, we have used the follow relationship (4) [18],

P = {R_p(uncoated) / R_p(coated)} x $10^{\Delta E_{corr.}/B_a}$ (4)

Where P is the total porosity, R_p(uncoated) and R_p(coated) denote the polarization resistance for uncoated and coated brass, respectively. $\Delta E_{corr.}$ is the difference between corrosion potentials of coated and uncoated brass by volt and B_a the anodic Tafel slope for uncoated brass substrate.

The all parameters of $E_{corr.}$, $i_{corr.}$, B_a, B_c, B, R_p, I.E.%, and P obtained from Tafel curves of figures (1-11) were listed in tables (1-5).

Table (1): Corrosion parameters of uncoated and coated brass by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1M-H_2SO_4 at 750 mV with difference times, in aggressive medium of 0.1 M NaCl aqueous solution.

Time of polyaniline formation	B_a V/decade	B_c V/decade	B Volt	i_o μA	R_p KΩ	$E_{corr.}$ Volt	I.E.% of polymer coating	P of polymer coating
Uncoated brass	0.061	0.073	1.44×10^{-2}	176.90	81.57	-0.344	-	-
0.5 min.	0.193	0.203	4.3×10^{-2}	83.01	5.18×10^2	-0.200	53.08%	36.13%
1.0 min.	0.154	0.075	2.19×10^{-2}	41.87	5.23×10^2	-0.228	76.33%	12.44%
5.0 min.	0.098	0.098	2.13×10^{-2}	3.98	5.35×10^3	-0.374	97.80%	0.0473%

Table (1) of figures (1-4) offers the effect of polyaniline coating thickness, formed by potentiostatic polarization of 0.5M aniline in 1.0M H_2SO_4 at 750mV with difference time, on brass corrosion resistance in 0.1M NaCl aqueous solution. It is essential to note that the polyaniline coating thickness and the brass corrosion resistance increase with increase the time of polyaniline potentiostatic polarization and the I.E.% of polyaniline coating respectively.

There is a good correlation between porosity and thickness of the coating, it shows that the porosity in the coating decreases with increase in thickness of the polyaniline coating. The lower values of the porosity in polyaniline coatings permit an improvement of the I.E.% of polyaniline coating

against brass corrosion by hindering the access of the corrosive chloride ions to the brass substrates[18]. The diffusion of corrosive chloride ions must occur through the pores of polyaniline coating, for the initiation and continuation of the electrochemical process[19]. It seems that the coating thickness significantly affects the corrosion protection properties of the polyaniline coating. It is essential to note that the corrosion current values of coated brass were found to be lower than uncoated brass and also decrease with increase the time of polyaniline preparation (enhancement of polyaniline thickness). This case was simply related to physical barrier behavior of polyaniline coating between the corrosive environment and underlying brass[20], and also due to improvement its inhibition properties against corrosion respectively.

Table (2): Corrosion parameters of uncoated and coated brass by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1M-H_2SO_4 at difference potentials and constant time equals 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Potential of potentiostatic polarization	B_a V/decade	B_c V/decade	B Volt	i_o μA	R_p KΩ	$E_{corr.}$ Volt	I.E.% of polymer coating	P of polymer coating
Uncoated brass	0.061	0.073	1.44×10^{-2}	176.90	81.57	-0.344	-	-
710 mV	0.361	0.236	6.20×10^{-2}	91.35	6.78×10^2	-0.219	48.40%	13.47%
730 mV	0.219	0.190	4.42×10^{-2}	10.00	4.42×10^3	-0.315	94.40%	0.055%
750 mV	0.098	0.098	2.13×10^{-2}	3.98	5.35×10^3	-0.374	97.80%	0.0473%

Table (2) of figures (1,4-6) displays the relation between i_o, I.E.%, and P calculated in 0.1M NaCl solution with respect to the applied potentials of polyaniline electro-polymerization in a solution of 1.0M H_2SO_4 and 0.5M aniline for 5.0 minutes on brass electrode surface. It clears that the porosity and the I.E.% of polyaniline coated brass decreases and increases, respectively with increase the electro-polymerization applied potentials of aniline on brass surface potentiostatically. This means that the applied potential has a very strong influence on the outcome of the polymerization. In the other word, the

applied potential of electro-polymerization exhibits influence on the properties of the prepared polyaniline[14]. Table (2) tells us also that the corrosion current values of coated brass decreases with increase the applied potentials of polyaniline prepared potentiostatically on brass surface, this confirms to us that the applied potential is prerequisite to affect on the corrosion protective coatings. So, there is ideal electro-polymerization potential has a very strong influence on the properties of coating polymer and, hence increases its protection to brass against corrosion.

Table (3): Corrosion parameters of uncoated and coated brass by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1M of difference solvents at 750 mV and constant time equals 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Solvent of polyaniline preparation	B_a V/decade	B_c V/decade	B Volt	i_o μA	R_p KΩ	$E_{corr.}$ Volt	I.E.% of polymer coating	P of polymer coating
Uncoated brass	0.061	0.073	1.44×10^{-2}	176.90	81.57	-0.344	-	-
1.0 M H_2SO_4	0.098	0.098	2.13×10^{-2}	3.98	5.35×10^3	-0.374	97.80%	4.73×10^{-2}%
1.0 M HCl	0.139	0.069	2.00×10^{-2}	19.98	1.00×10^3	-0.282	88.70%	84.70×10^2%
1.0 M HNO_3	0.062	0.066	1.39×10^{-2}	0.65	2.14×10^4	-0.295	99.60%	2.40×10^{-2}%

Table (3) of figures (1,4,7,8) displays P, I.E.%, and i_o values of polyaniline coating brass in 0.1M NaCl solution, formed by potentiostatic polarization of 0.5M aniline in 1.0M of difference solvents, H_2SO_4, HCl, and HNO_3 at constant potential equals750mV for 5.0 minutes. We note that the porosity, inhibition efficiency, and the corrosion current of coating brass depend on the electrolyte type[14] of polyaniline prepared potentiostatically. The porosity and corrosion current values decrease but the inhibition efficiency values increase in the order of HCl, H_2SO_4, and HNO_3. These results mean that the polyaniline coating brass prepared potentiostatically in HNO_3 is more protective barrier between brass and NaCl aggressive medium than the others. This may be to the packing efficiency of the polyaniline coating brass prepared in HNO_3 is the greatest.

Table (4): Corrosion parameters of uncoated and coated brass by poly-N,N-dimethylaniline film, formed by potentiostatic polarization of 0.5 M N,N-dimethylaniline in 1M-H_2SO_4 at difference potentials at constant time equals 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Potential of potentiostatic polarization	B_a V/decade	B_c V/decade	B Volt	i_o μA	R KΩ	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated brass	0.061	0.073	1.44×10^{-2}	176.90	81.57	-0.344	-	-
710 mV	0.424	0.282	7.35×10^{-2}	123.07	5.98×10^2	-0.223	30.40%	13.14%
750 mV	0.382	0.243	6.45×10^{-2}	27.37	2.36×10^3	-0.255	84.50%	0.9946%

Table (4) of figures (1,9,10) offers the affecting applied potentials of the electrochemical polymerization of N,N-dimethylaniline, in 1.0M H_2SO_4 on brass surface, on the corrosion protection properties of poly-N,N-dimethylaniline in NaCl corrosive medium. These results clear that the corrosion parameters, i_o, I.E.%, and P of poly-N,N-dimethylaniline and polyaniline coated brass behave the same trend with respect to the applied potential of electro-polymerization. This confirms that the applied potential is essential prerequisite to affect on the peculiarities of coating polymer[14].

Table (5): Corrosion parameters of uncoated and coated brass by difference polymers film formed by potentiostatic polarization of 0.5 M corresponding monomer in 1.0 M-H_2SO_4 at 750 mV and constant time equals 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Type of coating polymer	B_a V/decade	B_c V/decade	B Volt	i_o μA	R KΩ	E_{corr} Volt	I.E.% of polymer coating	P of polymer coating
Uncoated brass	0.061	0.073	1.44×10^{-2}	176.90	81.57	-0.344	-	-
Polyaniline	0.098	0.098	2.13×10^{-2}	3.98	5.35×10^3	-0.374	97.80%	4.73×10^{-2}%
Poly-N,N-dimethylaniline	0.382	0.243	6.45×10^{-2}	27.37	2.36×10^3	-0.255	84.50%	99.46×10^{-2}%
Poly-N,N-diethylaniline	0.094	0.707	3.60×10^{-2}	10.49	3.43×10^3	-0.204	94.10%	4.69%

Table (5) of figures (1,4,10,11) offers the corrosion parameters, P, I.E.%, and i_o of difference polymers (polyaniline, poly-N,N-dimethylaniline, and poly-N,N-diethylaniline) coating brass in 0.1M NaCl aggressive medium, formed by potentiostatic polarization of 0.5M corresponding monomer in 1.0M H_2SO_4 at 750mV for 5.0 minutes. It shows that the corrosion parameters of polymer coating depend on the polymer category under the same condition of electro-polymerization. This may be to the adhesion differences of polymers to brass surface. The porosity values of polymers coating brass decrease in the order poly-N,N-diethylaniline, poly-N,N-dimethylaniline, and polyaniline. This case was simply related to the packing efficiency of each polymer, which depends on the size of monomer unit in polymer chain. It is essential to note also that the I.E.% and i_o values of polymers coated brass increase and decrease respectively in the order poly-N,N-dimethylaniline, poly-N,N-diethylaniline, and polyaniline. The inhibition efficiency and the corrosion current values of poly-N,N-dimethylaniline contrary with its value of porosity with respect to the other polymers. This is due to the oxidation of poly-N,N-dimethylaniline coated brass, without degradation during the corrosion experiment, from leucoemeraldine to pernigraniline form. Therefore the increase in the corrosion current of poly-N,N-dimethylaniline coated brass include the oxidation of polymer film rather than the pure dissolution current of the underling brass surface [21-24].

Our observed experimental results of figures (1-11) and tables (1-5) suggest that a low porosity of the polymer coating without oxidation and a strong adhesion to the substrate are prerequisites for excellent corrosion protective coatings.
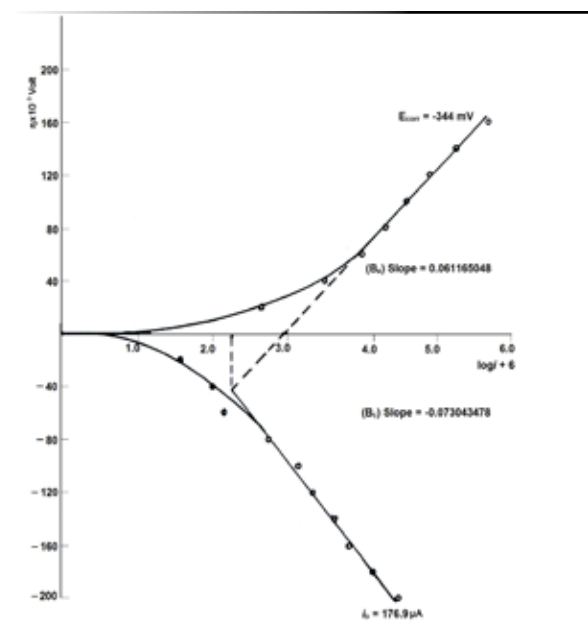

Fig. (1): Tafel plot of potential (E-Volt) versus log current (i-Amper) of uncoated brass in aggressive medium of 0.1 M NaCl aqueous solution.
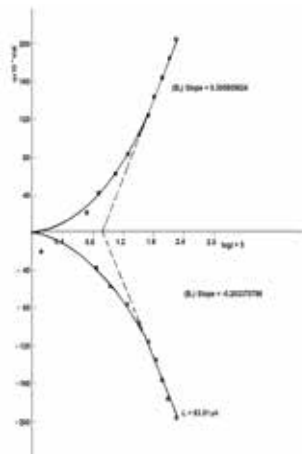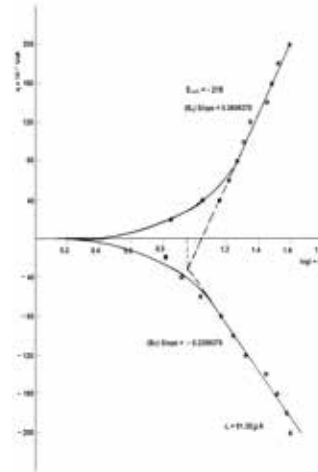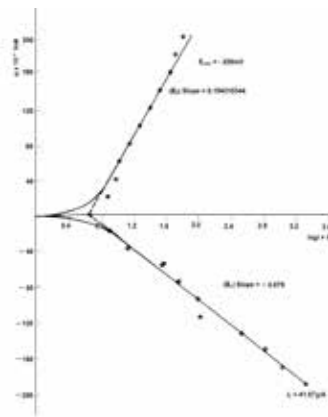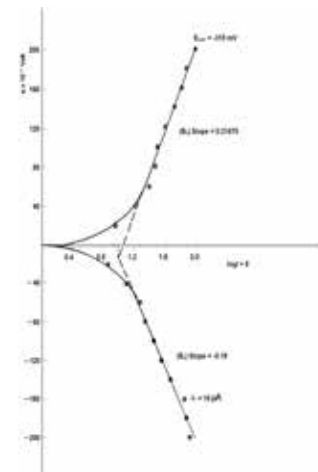
Fig. (2): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M H2SO4 at 750 mV for 0.5 minute, in aggressive medium of 0.1 M NaCl aqueous solution
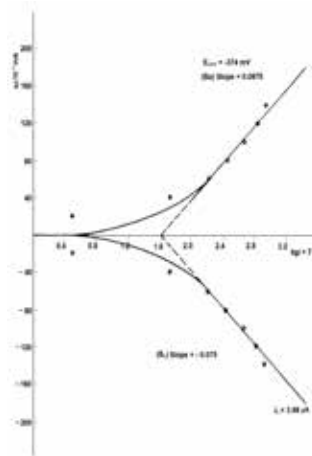

Fig. (5): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M H2SO4 at 710 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Fig. (3): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M H2SO4 at 750 mV for 1.0 minute, in aggressive medium of 0.1 M NaCl aqueous solution
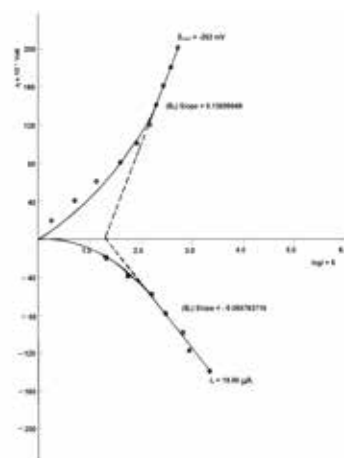

Fig. (6): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M H2SO4 at 730 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.
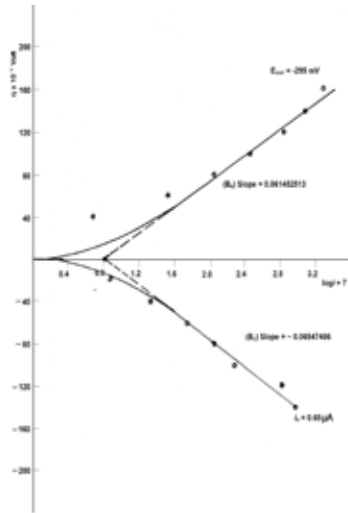

Fig. (4): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M H2SO4 at 750 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Fig. (7): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M HCl at 750 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution

Fig. (8): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by polyaniline film, formed by potentiostatic polarization of 0.5 M aniline in 1.0 M HNO3 at 750 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.
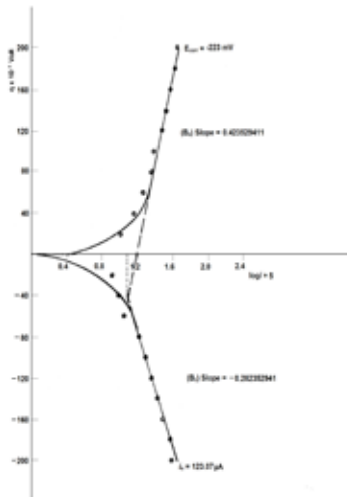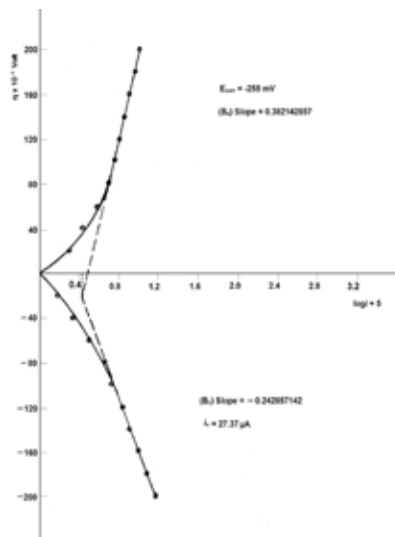

Fig. (9): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by poly-N,N-dimethylaniline film, formed by potentiostatic polarization of 0.5 M N,N-dimethylaniline in 1.0 M H2SO4 at 710 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Fig. (10): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by poly-N,N-dimethylaniline film, formed by potentiostatic polarization of 0.5 M N,N-dimethylaniline in 1.0 M H2SO4 at 750 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.
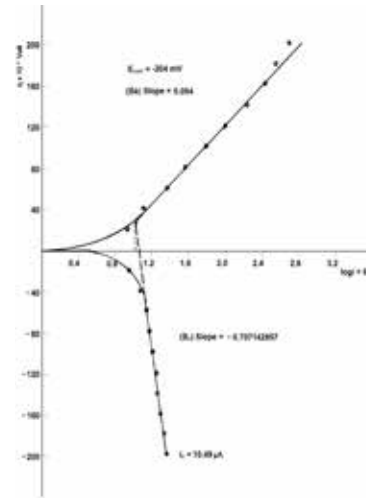

Fig. (11): Tafel plot of potential (E-Volt) versus log current (i-Amper) of brass coated by poly-N,N-diethylaniline film, formed by potentiostatic polarization of 0.5 M N,N-diethylaniline in 1.0 M H2SO4 at 750 mV for 5.0 minutes, in aggressive medium of 0.1 M NaCl aqueous solution.

Conclusions
The following conclusions can be drawn from this work:

1. The corrosion resistance of polyaniline, poly-N,N-dimethylaniline, and poly-N,N-diethylaniline coated brass was higher than of uncoated brass.
2. The polymer coatings hindered the attack of the corrosive ions on brass surface.
3. The corrosion parameters, i_o, I.E.%, and P of polymers coated brass in 0.1M aqueous solution depend on, applied potential, time of electro-polymerization, polymer type, and electrolyte composition of polymer prepared potentiostatically.
4. The decrease in the porosity (P) values calculated from polarization studies for all polymers coated specimens revealed the higher inhibition efficiencies of these polymers.
5. The increase in the corrosion current (i_{corr}.) of poly-N,N-dimethylaniline coated brass than the other polymers is due to the oxidation of polymer film rather than the pure dissolution current of underling brass surface.
6. Our observed experimental results suggest that a low porosity of the polymer coating without degradation is prerequisite for excellent corrosion protective coatings.

REFERENCE 1- G. Bereket, E. Hur, Y. Sahin, Prog. Org. Coat. 54 (2005) 63. | 2- T. Zhang, C.L. Zeng, Electrochim. Acta 50 (2005) 4721. | 3- M.M. Popovic,B.N. Grgur, Synth. Met. 143(2) (2004) 191. | 4- N.A. Ogurtsov, A.A. Pud, P. Kamarchik, G.S. Shapoval, Synth. Met. 143(1) (2004) 43. | 5- Sonal Patil, S.R. Sainkar, P.P. Patil, Appl. Surf. Sci. 225 (2004) 204. | 6- Kunal G. Shah, Gouri S. Akundy, and Jude O. Iroh J. Appl. Polym. Sci. 85 (2002) 1669. | 7- G. Mengoli, M. Munari, P. Bianco, S. Misiani, J. Appl. Polym. Sci. 26 (1981) 4247. | 8- D.W. DeBerry, J. Electrochem. Soc. 132 (1985) 1022. | 9- J.I. Martins, M. Bazzaoui, T.C. Reis, E.A. Bazzaoui, L.I. Martins, Synth. Met. 129 (2002) 221. | 10- M. Bazzaoui, L.I. Martins, E.A. Bazzaoui,T.I. Martins, Electrochim. Acta 47 (2002) 2953. | 11- S.R. Moraes, D.H. Vilca, A.J. Motheo, Prog. Org. Coat. 48 (2003) 28. | 12- A.M. Fenelon, C.B. Breslin, Electrochim. Acta 47 (2002) 4467. | 13- A.M. Fenelon, C.B. Breslin, Surf. Coat. Technol. 190 (2005) 264. | 14- Kunihiko Imanishi, Masaharu Satoh, Yutaka Yasuda, Rikio Tsushima, Shuzo Aoki, J. Electroanal. Chem. 242 (1988) 203. | 15- E.A. Joorg and O.F. Devereux, Corrosion 52 (1996) 953. | 16- D.E. Tallman, Y. Pae, and G.P. Bierwagen, Corrosion 55 (1999) 779. | 17- C. Jeyaprabha, S. Sathiyanarayanan, and G. Venkatachari, J. Appl. Polym. Sci. 101 (2006) 2144. | 18- Sudeshna Chaudhari, A.B. Gaikwad, and P.P. Patil, Current Applied Physics 9 (2009) 206. | 19- R. Mazeikiene, A. Malinauskas, Polymer Degradation Stability 75 (2002) 255. | 20- Tunc Tüken, Birgül Yazici, and Mehmet Erbil, Materials Chemistry and Physics 99 (2006) 459. | 21- P. Herrasti, P. Ocôn, A. Ibanez and E. Fatâs Journal of Applied Electrochemistry 33 (2003) 533. | 22- J. R. Santos, L.H.C. Mattoso and A.J. Motheo, Electrochim. Acta 43 (1998) 309. | 23- P. Herrasti and P. Ocôn, Appl. Surf. Sci. 172 (2001) 276. | 24- L.F. DElia, R.L. Ortiz, O.P. Marquez, J. Marquez and Y. Martinez, J. Electrochem. Soc. 148 (2001) 297. |