The Inhibitive Effect of BTA on The Corrosion of Copper Rotating Cylinder Electrode in Oxygenated 0.1M H_2SO_4 Under Controlled Conditions of Mass Transfer

Dr.Sh.A.Sameh* , Dr.I.K.Salih* , Dr.S.H.Alwash & Dr.A.A.Alwasity***

Received on:25/2/2008
Accepted on:3/9/2009

Abstract

The inhibitive action of benzotrizole (BTA) on the corrosion of copper in oxygenated 0.1M sulfuric acid solution has been investigated using the rotating cylinder electrode to provide turbulent conditions. Potentiostatic polarization measurements were carried out at different temperatures of 283,288,293 and 298K and various speeds of rotation, 100,200,300 and 400 rpm.

In general, BTA, at concentration of 0.01M, effectively inhibits the corrosion of copper in oxygenated 0.1M sulfuric acid solution. Moreover, BTA effectively inhibits the anodic dissolution of copper and the cathodic reactions ,i.e., HER and oxygen reduction reaction. Therefore, BTA acts as a mixed inhibitor in oxygenated solutions.

The overall percentage of inhibition efficiency is about 98% . This indicates that a Cu-BTA film is developed on the copper electrode surface which about 98% of the corrosion rate . The overall inhibition efficiency is neither affected by the turbulent flow rate , nor by the temperature increases.

The corrosion rate is temperature dependent only, which indicates that the corrosion of copper in inhibited oxygenated 0.1M sulfuric acid solutions is under activation control.

Keywords: : BTA inhibitor , Corrosion inhibition of copper using BTA , BTA as corrosion inhibitor of copper in acid.

تأثير المثبط بنزوترايزول على تاكل قطب اسطواني دوار من النحاس في محلول حامض الكبريتيك 0.1مولاري مشبع بالاوكسجين في ظروف انتقال كتلة معينة

الخلاصة

اجريت دراسة لفعالية البنزوترايزول (C6H5N3) كمثبط للتآكل في حماية النحاس من التآكل في محلول حامض الكبريتيك ذو التركيز 0.1مولاري مشبع بالاوكسجين عند ظروف جريان مضطرب بأستخدام منظومة القطب الاسطواني الدوار.

اجريت تجارب الاستقطاب بالمجهاد الساكن في درجات حرارة مختلفة 283 :، 288 ،293، 298كلفن وبسرع متفاوتة 400 :،300،200، 100دورة بالدقيقة.

اظهرت النتائج ان البنزوترايزول ذو التركيز 0.01مولاري اعاق حركية ذوبان انود النحاس والتفاعلين الكاثوديين :تفاعل تحرر الهيدروجين وتفاعل اختزال الاوكسجين مما تترتب عليه اعاقة تآكل النحاس في محلول حامض الكبريتيك المشبع بالاوكسجين. لذا فأن

*** Chemical Engineering Department, University of Technology/Baghdad**
**** Collage of Engineering, University of Baghdad /Baghdad**

https://doi.org/10.30684/etj.28.6.13
2412-0758/University of Technology-Iraq, Baghdad, Iraq

سلوك مثبط التآكل من النوع المزدوج في محاليل مشبعة بالاوكسجين.
ان النسبة المئوية لفاعلية الاعاقة الكلية بحدود % 98ويعود سبب ذلك لتكون حاجز من البنزوترايزول -نحاس على سطح قطب النحاس الذي ادى بدوره الى اعاقة معدل التآكل بنسبة .% 98.ومن النتائج المتحققة ..عدم تأثر فعالية الاعاقة الكلية بزيادة كلاً من معدل الجريان المضطرب ودرجات الحرارة ...وان معدل التآكل يتأثر بدرجة الحرارة فقط ... وهذا يعني ان تآكل النحاس في حامض الكبريتيك ذو التركيز 0.1مولاري مشبع بالاوكسجين ومثبط بالبنزوترايزول محكوم بطاقة التنشيط.

Introduction

Corrosion inhibitor is a chemical substance which , when added in small concentration to an environment effectively decreases the corrosion rate of the metal exposed to such environment . In a sense, an inhibitor can be considered as a retarding catalyst[1] .

The corrosion of copper and brass in sulfuric acid solutions may be inhibited using thiourea, quinoline and azoles, but the most effective inhibitor being benzotrisole (BTA)[2,3].

Allam et.al, conclude that a concentration of 10-3 M BTA was not enough to prevent general corrosion of Cu10Ni alloy in a sulfide polluted salt water.[4]

The most effective and efficient concentration of BTA in acid solutions, as a corrosion inhibitor was 0.01M[2].

Benzotrizole ($C_6H_5N_3$) is a nontoxic heterocyclic organic compound, having the structural formula [6] :

Antonijevic and Petrovic suggest that the presence of nitrogen atoms in triazole ring enables bounding with copper and is a basis for inhibitive effect of BTA.[5]

Many investigators [6-13] studied the inhibitive action of BTA on the corrosion of copper in sulfuric acid solutions under various conditions.

It was generally agreed that BTA inhibits the anodic dissolution of copper , but the mode of action of this

organic compound on the cathodic processes is in dispute.

However, Tohala[14] reported that in deaerated acid solution ,BTA inhibits both the anodic and cathodic reactions .Moreover, in oxygenated acid solution, BTA inhibits the anodic dissolution of copper and oxygen reduction reaction .[15]

In general, it was accepted that Cu-BTA film is developed on that metal surface during immersion or electrochemical polarization [6-8, 14-20].

The thickness of the film is in dispute[8,11,17]. However Tohala[14] reported that in deaerated solutions this film was reduced upon the application of a large cathodic overpotential .Moreover ,in oxygenated solution, a thick film of Cu-BTA is developed which covers the whole electrode surface and good protection of the metal is achieved.

The effect of the flow on corrosion inhibition of copper in sulfuric acid solution, using BTA as inhibitor is very scarce . Ross and Berry[9] showed that the effect

of turbulence in reducing inhibitor efficiency is oxygen dependent. In the absence of oxygen , the efficiency of 0.01 M BTA to inhibit the corrosion of copper in flowing 10% sulfuric acid solution, was unaffected by increasing the acid flow rate up to a Reynolds number (Re)= 10000. However in oxygenated solutions, the inhibition efficiency decreased , firstly as the flow rate increased. Secondly, further big decrease occurred, as the oxygen concentration increased.

The effect of the increasing temperature on the inhibited acid-metal reaction is highly complex, as the result of [21].

1- Increasing the rate of uninhibited acid-metal reaction[22,23].
2- Change of the fraction of the metal surface covered by adsorbed inhibitor.
3- Considerable changes in the effectiveness of the covered surface.
4- Decomposition or rearranging of some inhibitor molecules.

Machu[24] reported that inhibition becomes more effective with increasing temperature due to an increase in the surface area of metal covered by inhibitor molecules as the temperature increases[25].

To summarize, BTA is effectively used as corrosion inhibitor of copper in sulfuric acid solutions. It acts as a mixed inhibitor in oxygenated solutions.

The purpose of the present work is to investigate the inhibitive action of BTA on the corrosion of copper in oxygenated 0.1 M sulfuric acid solution at different bulk temperature and various flow rates. A turbulent flow was employed, by using the rotating cylinder electrode (RCE) which is of industrial importance. An 0.01M BTA in the acid solution was used, which represents the most effective and efficient concentration[2].

Experiment

The apparatus used in this work consisted of the following main parts, a supporting frame work, RCE assembly, polarization cell, constant temperature bath, a potentiostat and supplying unit of oxygen.

The RCE assembly, shown in Fig.(1), consisted of :

1 A rotating cylinder and electrode shaft (RCE).
2 A driving shaft, bearing unit and slip ring unit (the electrode mounting).
3 Motor and speed controller (the driving unit).

The design provided for a cylinder which was detachable from the electrode shaft, having the following dimensions :

ro = 15 mm
ri = 18 mm
h = 20 mm

The specimens were cut and turned down to shape and size from 50mm diameter rod of high purity copper having total purity of Cu = 99.85%.

The composition of copper being, given in Table (1)[26].

Before each test the electrode surface was prepared by grinding on successive grades of emery paper of 400, 800 and 1000 grit respectively.

Then , the specimen was washed with distilled water, rinsed with acetone, dried with clean tissue paper and kept in a desiccator over

silica gel before use[27] .

The electrochemical tests were carried out in a polarization cell , which consists of a cylindrical glass vessel of a capacity of 2.5L.Three electrodes cell was used.The working electrode was in a cylindrical form. Saturated calomel electrode (SCE) was used as a reference electrode with Luggin capillary tip placed at 1-2 mm from the working electrode surface [28] . Platinum counter electrode was used as an auxiliary electrode. Bulk temperature control was achieved by using a constant temperature bath supplied with a refrigerating cooler.

The test solution (0.1M H_2SO_4) was prepared from analar grade concentrated sulfuric acid diluted with distilled water. Benzotrizol (BTA) (M.wt.= 119.13) of analar grade was used as an inhibitor at a concentration of 0.01M.

The experiments were carried out to determine the polarization curves (cathodic and anodic) of copper in oxygenated 1000 ml of 0.1M H_2SO_4 solution containing 0.01 M BTA .The experiments were made under isothemal condition , at four test solution bulk temperature ; viz : 283 , 288 , 293 and 298 K and under turbulent flow conditions at four controlled rotating speeds i.e., 100 , 200 , 300 and 400 rpm. Each experiment involved electrochemical polarization of copper electrode from – 0.9 v to + 1.6 v with manual scan rate of 20×10-3 v/min , using Wenking potentiostat (Wenking LT 87).

Prior to every experiment, oxygen was allowed to bubble into the solution at a rate of 300 ml /min for a period of 30 min to ensure complete oxygen saturation of the solution.

Thereafter , and at the start of the electrochemical polarization , the gas rate was reduced to 25 ml /min.

The detailed design of the apparatus and experiments work were described else where[29].

Results and Discussion

The potentiostatic polarization curves for oxygenated inhibited solutions are shown in Figs (2-5).

1-The cathodic region

In a previous work [30] , similar to the present one , but in uninhibited solutions, the cathodic curves showed clearly the presence of the limiting current density (i_L) of the oxygen reduction reaction. The cathodic curves of Figs. (2-5) show the absence of the i_L of the oxygen reduction reaction. This result indicates the inhibition of the oxygen reduction reaction , using BTA , and contradicts the suggestion made by other workers[6,10] who reported that BTA has no effect on the oxygen reduction reaction. On the other hand, the result is in agreement with that reported by Tohala[14] .

Table (2) shows the values of the cathodic current density at a cathodic potential of -300 mv , at different bulk temperature and various speeds of rotation . The table shows that the cathodic current density is temperature dependent only. This result indicates that the cathodic reaction is under activation control. Moreover, any value of the cathodic current density in Table (2) is much lower than the corresponding value in an uninhibited oxygenated solutions , see Table (3)[30] and lower than the corresponding value in uninhibited

dearated solutions , see Table (4) [30] . It may be recalled that values of the cathodic current density, at potential of -300 mv, in uninhibited oxygenated solutions are much higher than the corresponding values in uninhibited deaderated solutions (see Tables 3 and 4).This was attributed to the presence of another cathodic reaction, i.e., oxygen reduction reaction in addition to the hydrogen evolution reaction (HER) [30]. Therefore, the present results indicate that BTA inhibited both the HER and oxygen reduction reaction in this region of the cathodic curve. The inhibition of HER is in agreement with the results of the workers[6,10] .

The inhibition efficiency in this region of the cathodic curve (-300 mv) , was calculated using cathodic current density values in Tables (2 and 3) for inhibited and uninhibited oxygenated solutions respectively, and the following equation :

$$\% \text{ efficiency} = (i_{un} - i_{in})/i_{un} * 100 \quad \ldots..(1)$$

Where i_{in} and i_{un} represent the inhibited and uninhibited current density values respectively. The results are given in Table (5) . The table shows excellent inhibition in the cathodic region . The percent of inhibition efficiency ranged from 95.8 to 98 for the experimental temperatures and flow rates used. The results indicate that, in the cathodic region,a Cu – BTA film is developed which inhibits both the HER and oxygen reduction reaction. This film has covered 96–98% of the electrode surface and was not affected by flowrate and / or temperature increases. The current density values that increased with increasing temperature (see Table 2), are very small and do not represent more than (2-4)% of the total values in uninhibited solutions. It is suggested that the cathodic reactions, which are represented by these small values of current densities, are taking place on the uncovered area of the electrode surface , i.e., not covered by Cu –BTA film.

It worths to show that 100-400 rpm, in this work , represent turbulent flow rates equivalent to Re = 13500 – 53600. Therefore, in the present work , turbulence has no effect at all on the inhibition efficiency in the cathodic region.

To summarize , BTA has excellent inhibition of the cathodic reactions, i.e., HER and oxygen reduction reaction. The inhibition efficiency ranged from 96 to 98%. Turbulence has no effect on the inhibition efficiency which remained almost constant over the flow rate range employed.

2-The Anodic Region

The anodic current density values were taken at a specific overpotential of 60 mv ΔE , instead of at a specific anodic potential . This was because of the difficulty in the latter case due to the short anodic region (see Figs. 2-5). The results are given in Table (6). The table shows that the anodic current density is temperature dependent only.

This results indicate that anodic dissolution of copper in inhibited solution is under activation control. The corresponding values of the anodic current density , in uninhibited oxygenated solution at a specific anodic overpotential of 60 mv ΔE , are given in Table (7) [30,

The inhibition efficiency in the anodic region at overpotential 60 mv ΔE , was calculated using the anodic density values in Tables (6 and 7) and Eq. (1). The results are given in Table (8). The table shows excellent inhibition in the anodic region which is in agreement with other workers[4,6,12] . The percentage of inhibition efficiency ranged from 97.3 to 98.4 for the experimental temperatures and flow rates used. The results indicate that a Cu – BTA film is developed on copper surface which inhibited about 97 % of the anodic reactions. Moreover , the inhibition efficiency was not affected by turbulent flow rates employed ,i.e., Re = 13500 – 53600 .

To summarize , BTA has excellent inhibition of the anodic dissolution of copper in acid solution . The inhibition efficiency ranged from 97.3 to 98.4 % . Turbulence has no effect on the inhibition efficiency. The anodic dissolution of copper in inhibited solution is under activation control.

The Corrosion Rate

The corrosion current density values , at different bulk temperatures and various speeds of rotation , found by Tafel extrapolation method[31] , are given in Table (9). The table shows that the corrosion rate is temperature dependent only. The results, indicate that the corrosion of copper in inhibited oxygenated acid solution is under activation control.

The corrosion rate values in Table (9) are much lower than the corresponding values in uninhibited oxygenated solution(see Table 10)[30]. The overall inhibition efficiency was calculated using the corrosion rate values in Tables (9 and 10) and Eq.(1). The results are given in Table (11). The overall percentage of inhibition efficiency ranged from 97.8 to 98.2 for experimental temperatures and flow rates used .

The results indicate that a Cu-BTA film is developed on the copper electrode surface inhibited about 98% of the corrosion rate which is in agreement with previous results[6 - 8 , 14 -17] . Moreover, turbulent flow rates employed , i.e., Re = 13500 – 53600 , have no effect on the inhibition efficiency. This results contradicts the work of Ross and Berry who reported that inhibition efficiency decreased as the flowrate increased, especially , under turbulent conditions . The reasons for this big difference between the previous work 7 and the present results can be explained as follows : The RCE system offers several advantages over the flow in pipe system 30 which was employed by Ross and Berry[7]

1 The RCE provides quantified hydrodynamic mass transfer conditions.
2 The concentration of material and reaction rates are uniform over the entire cylinder surface.
3 The RCE system easy to set up accurately.
4 There are no problems of entry length and concentration profile build – up.
5 It is easy to control accurately and the results obtained should be highly reproducible.

Conclusions

In general , BTA, at concentration of 0.01 M , effectively inhibits the corrosion of copper in oxygenated 0.1 M sulfuric acid solution . BTA

effectively inhibits the anodic dissolution of copper and the cathodic reactions, i.e., HER and oxygen reduction reaction. The limiting current density, observed in uninhibited oxygen acid solutions disappears in presence of BTA , which confirms that BTA inhibits the oxygen reduction reaction . Therefore , BTA acts as a mixed inhibitor in oxygenated solutions.

The overall percentage of inhibition efficiency is about 98 for the experimental temperatures and flow rates used. The results indicate that a Cu – BTA films is developed on the copper electrode surface which inhibits about 98% of corrosion rate . Moreover , the overall inhibition efficiency is neither affected by the turbulent flow rate employed ,i.e., Re = 13500 - 53600 , nor by the temperature increase.

The corrosion rate is temperature dependent only , which indicates that the corrosion of copper in inhibited oxygenated 0.1 M sulfuric acid solution is under activation control.

References

[1] Fontana, M.G. and Greene, N.D.,Corrosion Engineering, Mc Graw – Hill, N.Y. (1978).

[2] Mayanna, S.M. and Setty , T.H.Y , Corros. Sci, 15, 627 (1975) .

[3] Francis , P.E. and Dolphin , A.S. Br .Corrosion J.,19.181 (1984).

[4] Allam, N.K., Ashour , E.A. Hegazy. H.S & Ateya B.G., The Journal of Corrosion Science and Engineering (JCSE) vol.5 , preprint 3 , conference corrosion science in the 21st century held at UMIST in July (2003).

[5] Antonijevic ,M.M and Petrovic, Int. J. Electrochem. Sci. , 3 , 1-28 (2008).

[6] Polling ,G.W.,Corros. Sci., 10,359 (1970).

[7] Cotton , J.B.,Proc., 2nd. Intr. Congr. On metallic Corrosion, NACE, N.Y. (1965).

[8] Mansfield ,F., Smith ,T. and Parry, E.P., Corrosion ,27, 289 (1971).

[9] Ross ,T.K. and Berry, M.R.,Corrosion Sci., 11,273(1971)

[10] Altura , D. and Nobe, K., Corrosion ,28 ,345 (1972).

[11] Chin, R.J.,Altura , D. and Nobe,K, ibid,29,189 (1973).

[12] Lim , A.S., M.Sc. Dissertation ,UMIST (1974)(see Ref.12).

[13] Kakoszka , C.L., ibid , UMIST (1974))(see Ref.12).

[14] Tohala,N.H.,Ph.D.Thesis,UMIST(1976).
Ashraf T. Al-Hinai and Kwadwo Osseo- Asare ,The Electrochemical Society (ECS) , vol.6 , Issue 5, may(2003)

[15] Allen , J.A., Trans. Faraday Soc., 48, 273 (1952).

[16] Chandwick , D. and Hashemi , T., Corrosion Sci., 18,39 (1978).

[17] Allam , N.K., Ashour , E.A. and Hegazy , H.S., Corrosion Science , 2280 – 2292 , Vol. 47 (2005).

[18] Milic, S.M. and Antonijevic , M.M, Corrosion Science , 51, 28-34 (2009)

[19] Qun-Jie Xu and Guo- ding Zhou, Anti-Corrosion Methods and Materials, vol.55 , Issue 6 , 303-307(2008).

[20] Nathan , C.C.,Corrosion inhibitors , NACE , Texas (1973).

[21] Shams El-Din, A.M.,El – Dahshan ,M.E. and Haggag , H.H., Desalination , 215 - 226 , Vol . 172 (2005).

[22] Rajappa , Shanthamma

Kampalappa , and Venkatesha Thimmappa V.,Turk.J. Chem., 189 – 196 , Vol. 27 (2003).
[23] Machu , W., Korrrosion U. Metallschutz , 14 , 324 (1938).
[24] Putilova , J.N.,Balezin ,S.A. and Barranik , V.P., Metallic Corrosion Inhibitors, Pergmon Press , Oxford (1960).
[25] Central Organization for Standardization and Quality Control ,Jadirya , Baghdad .
[26] Annual Book of ASTM Standards , Part 10, G 31 (1980).
[27] Annual Book of ASTM Standards , Part 10, G 59 (1980).
[28] Al- Wasity , A.A., M.Sc. Thesis , University of Technology (1999).
[29] Sameh , Sh.A., Salih , I.K., Alwash , S.H. and Al- Wasity A.A. "The Corrosion of Copper in Dearated and Oxygenated 0.1 M H2SO4 under controlled conditions of Mass Transfer, Engineering and Technology, 27, 5, P. 993(2009).
[30] Stern , M. and Geary , A.L., J.Electrochem. SOC. 104 , 56 (1957).
[31] Alwash , S.H., Ph.D. Thesis , UMIST (1977).

Nomenclatures

h Cylinder height m
i_{in} Inhibited current density A/m^2
i_L Limiting current density A/m^2
i_{un} Uninhibited current density A/m^2
Re Reynolds number Dimensionless
ri Cylinder inside radius m
ro Cylinder outside radius m
HER Hydrogen evolution reaction
RCE Rotating cylinder electrode
rpm Rotation per minute
SCE Standard calomel electrode

Table (1) The composition of copper (wt%)

Sn	Zn	P	Fe	Si	Mn	As	Sb	Al	S	Cu
0.0485	0.020	0.036	0.003	0.003	0.01	0.005	0.004	0.007	0.009	remainder

Table (2) The cathodic current density of oxygenated inhibited solutions , at – 300 mv, µA/cm ^{2}.

Temp, K	r.p.m.			
	100	200	300	400
283	2.6	3.1	2.6	3.1
288	4.0	4.0	4.2	4.2
293	8.4	7.0	6.3	7.4
298	12.0	11.0	11.0	12.0

Table (3) The cathodic current density of oxygenated uninhibited solutions , at – 300 mv, µA/cm ^{2}.

Temp, K	r.p.m.			
	100	200	300	400
283	98	100	99	100
288	180	200	200	190
293	200	290	300	310
298	330	340	340	350

Table (4) The cathodic current density of deaerated uninhibited solutions , at – 300 mv, µA/cm ^{2}.

Temp, K	r.p.m.			
	100	200	300	400
283	13	13	13	13
288	22	23	22	23
293	35	35	35	36
298	47	47	47	47

Table (5) The precent inhibition efficiency of cathodic region.

Temp, K	r.p.m.			
	100	200	300	400
283	97.3	96.9	97.4	96.9
288	97.8	98.0	97.9	97.8
293	95.8	97.6	97.9	97.6
298	96.4	96.7	97.7	96.6

Table (6) The anodic current density of oxygenated inhibited solutions , at 60 mv ΔE, µA / cm^2

Temp, K	r.p.m.			
	100	200	300	400
283	4.0	4.1	4.0	4.2
288	6.1	6.2	6.0	6.1
293	11.2	11.3	11.0	11.4
298	20.2	20.1	20.0	20.2

Table (7) The anodic current density of oxygenated uninhibited solutions , at 60 mv ΔE, μA / cm^2

Temp, K	r.p.m.			
	100	200	300	400
283	159	159	163	163
288	370	340	360	370
293	580	550	590	580
298	740	740	750	750

Table (8) The percentage inhibition efficiency of anodic region.

Temp, K	r.p.m.			
	100	200	300	400
283	97.5	97.4	97.5	97.4
288	98.4	98.2	98.3	98.3
293	98.1	98.0	98.1	98.0
298	97.3	97.3	97.3	97.3

Table (9) The Corrosion rate of oxygenated inhibited solutions, μA / cm^2.

Temp, K	r.p.m.			
	100	200	300	400
283	0.13	0.13	0.13	0.13
288	0.20	0.21	0.21	0.21
293	0.26	0.25	0.27	0.27
298	0.43	0.42	0.41	0.43

Table (10) The Corrosion rate of oxygenated uninhibited solutions μA cm^2

Temp, K	r.p.m.			
	100	200	300	400
283	7.0	7.1	7.0	7.2
288	9.4	9.5	9.4	9.4
293	12.2	12.0	12.1	12.0
298	20.0	19.0	20.0	20.0

Table (11) Overall inhibition efficiency

Temp, K	r.p.m.			
	100	200	300	400
283	98.1	98.2	98.1	98.2
288	97.8	97.8	97.8	97.8
293	97.8	97.9	97.8	97.8
298	97.8	97.8	98.0	97.9

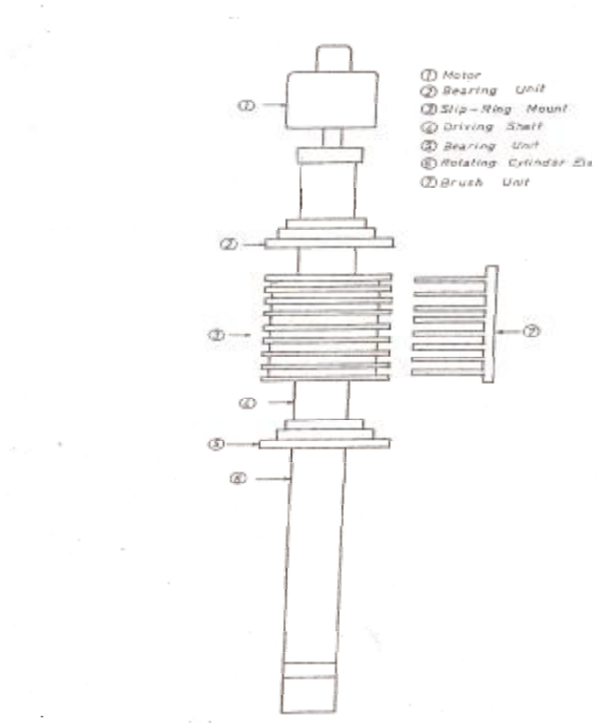

Figure (1) The Rotating Cylinder Electrode Assemply

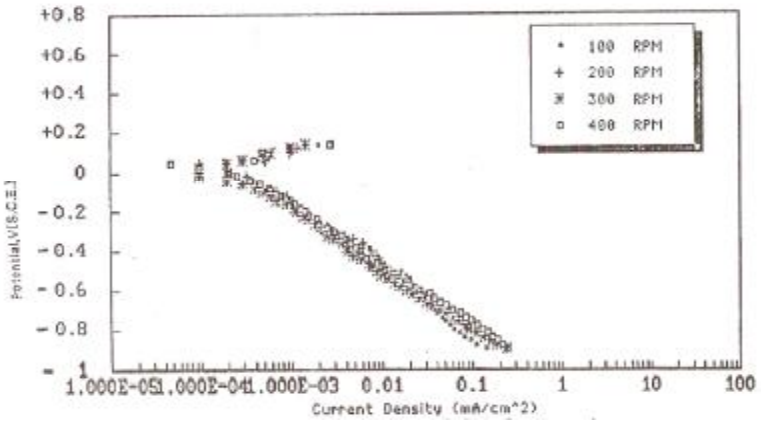

Figure (2) Potentiostatic Polar. Curve of Inhibited Oxygenated Sol., Temp.283K

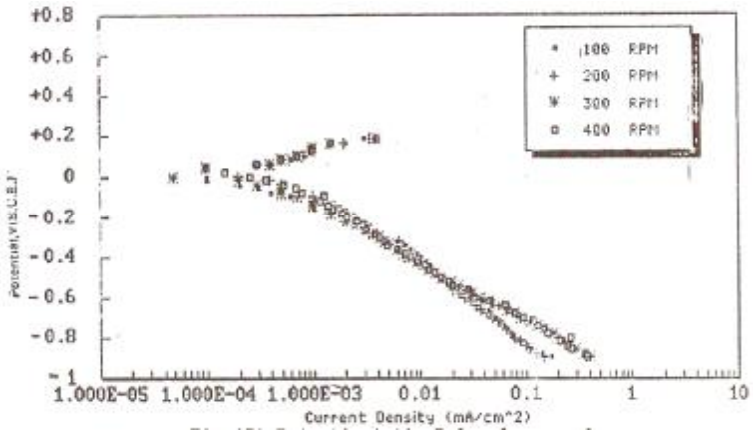

Figure (3) Potentiostatic Polar. Curve of Inhibited Oxygenated Sol., Temp.288K

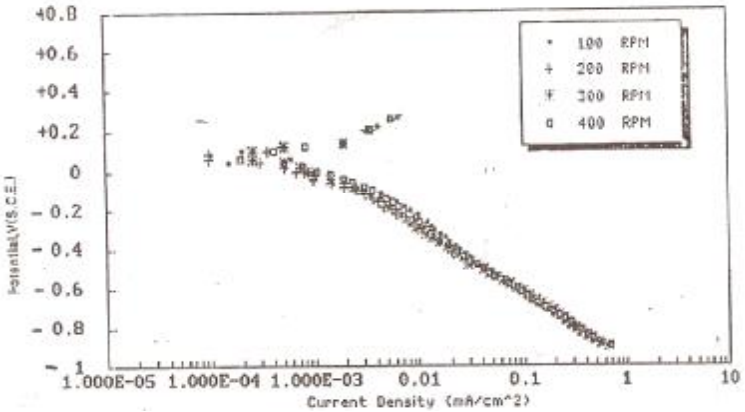

Figure (4) Potentiostatic Polar. Curve of Inhibited Oxygenated Sol., Temp.293K

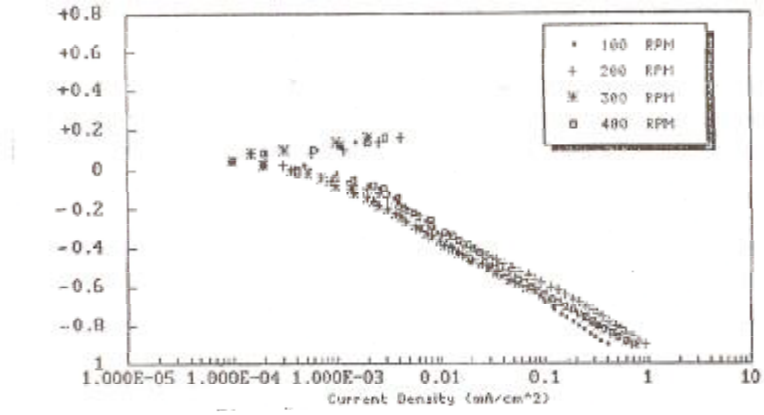

Figure (5) Potentiostatic Polar. Curve of Inhibited Oxygenated Sol., Temp.298K