

Protection Of Cooling Water System In Motors Cars From corrosion using Sodium Nitrite and Sodium hexametaphosphate

Ahmed H.Ali

Department of Chemistry, College of Science/ Al-Muthana, Al-Qadissiya University

Qhatan A.Yousif

Department of chemistry, College of Education, Al-Qadissiya University

(NJC)

(Received on 15/11/2006) (Accepted for publication on 25/3/2007)

Abstract

This research is included the investigation of electrochemical behaviour of Carbon-Steel in natural aerated solution of cooling system for motor cars and performance of sodium nitrite (SN) and sodium hexametaphosphate (SHMP) inhibitors blend for inhibiting of such corrosion process under controlled conditions of mass transfer . To achieved such control , under turbulent flow a rotating cylinder electrode (R.C.E.) system was designed to provide quantified hydrodynamics .

Potentiostatic polarization measurements under isothermal conditions were carried out at (313 , 323 , 333 , 343 , 353 , 363 and 373) K by using uninhibited solution and flow rates of (100 , 200 , 300 and 400) r.p.m. at each temperature . Corresponding experiments for inhibited solution under the same conditions .

The results show that the limiting current density is increased with increasing the temperature range and flow rate in uninhibited and inhibited solution . Also , the corrosion potentials are generally shifted to the more positive direction with increasing temperature and flow rate , whereas such potentials are shifted in less

positive direction by using mixture from inhibitors . Increasing in limiting current density (i_L) with rate the rotation is obey Levich equation . The interpretation that it is introduced in this study about the corrosion potential in uninhibited solution are independence on the theory of mixed potential .

The mechanism of inhibition by using these inhibitors have been shown and discussed .

)

(

300 200 100) ()

(400

373 313

Introduction

Corrosion is the degradation of a metal by an electrochemical of a set redox it's environment⁽¹⁾. Usually, the corrosion process consists of a set redox reaction which are electrochemical in nature. Thus, the metal is oxidized to corrosion products at anodic sites and some species are reduced at cathodic sites⁽²⁾. Carbon-steel has been widely employed as a construction material in many applications such as down hole tubular, flow lines, process facilities in general and in transmission pipelines. Effective corrosion control by the use of inhibitors therefore provides an economic option for the design and operation of oil and gas fields⁽³⁾. Corrosion inhibitors can be generally defined as a chemical substance, when added, in a small concentration to an environment, effectively decrease the corrosion rate of material exposed to such environment^(4,5). The influence of organic compounds containing sulphur and azote⁽⁶⁻¹²⁾ 2-Mercapato-benzothiazol (MBT) has studied in hydrochloric acid solutions for the protection of Carbon-Steel and iron using a concentration of 1%^(13,14). Most of earlier studies of Carbon-Steel corrosion were carried out in solution of NH_4NO_3 (62.5%) and NH_3 (23.7%)^(15,16) but there are a few data for neutral aerated solution under controlled conditions.

The aim of the present work is to investigate the role played by sodium nitrite (SN) and sodium hexametaphosphate (SHMP) on corrosion inhibition of carbon-steel that is its most widely used as engineering material while the solution sulphate and chloride ions content under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range from

313 to 373 K and flow rates of 100, 200, 300, 400 r.p.m.

Experimental Method

The chemical formula and some details of compounds for this study are given in table (1).

The effects of these compounds in table (1), on the corrosion rate of carbon-steel in neutral aerated solution of cooling system of motors cars at different values of temperatures and controlled conditions of mass transfer for carbon-steel has been chosen as the working electrode to be investigated in this work having the following composition: 0.1611% C, 0.369% Mn, 0.043% Si, 0.0225% Ni, 0.0162% S, 0.033% Cr, 99.38% Fe that it is obtained by the spectrophotometer analysis.

All measurements were made under isothermal condition with various controlled conditions of flow using a unit with rotating electrode in the form of cylinder to obtain turbulent flow condition various value of temperature were employed laminar and turbulent flow is made by a Rotating Cylinder Electrode (R.C.E.)⁽¹⁵⁻¹⁸⁾

The Rotating Cylinder Electrode (R.C.E.) assembly used in this study consists from the following items :-

1-The rotating cylinder electrode shaft .

2-A driving shaft , bearing unit and slip-ring (together described) later as the electrode mounting .

3-A driving unit (motor and speed controller) .

4-The working electrode(rotating cylinder) . The rotating cylinder comprise a carbon – steel cylinder with the following dimensions :

$$r_0 = 15\text{mm} , \quad r_1 = 8\text{mm} , \quad h = 20\text{mm} .$$

Thus , the surface area of specimens was 18.535cm^2 . The specimen were cut and turned down to shape and size from a 50mm diameter rod of carbon-steel . The inside surface of each specimen was provided with screw thread to facilitate its attachment to and removed from the electrode shaft at the beginning and end of each experiment . All specimens were vacuum annealed at 873K for (1h) after they were allowed to cool at room temperature while under vacuum⁽¹⁵⁾.

5-The polarization cell is consist of cylinder glass reaction vessel (1.47mm (diameter) x 180mm(high)) has capacity 2.5liters , Lugging capillary probe that it is include the reference electrode (Saturated Calomel Electrode , SCE) , the working electrode , thermometer and spring to cooling water glass coil . Potentiostat

experiments were carried out at a range of temperatures from 313 to 373K with controlled of flow at 100 , 200 , 300 and 400 r.p.m. from R.C.E. .

In all measurements have been used the potentiostat type Wenking LT.78 " media in Germany " and water bath type HAAKW13 with thermostat type JULABO-EM to keep the temperature constant at $\pm 0.1^{\circ}\text{C}$ until the solution is reached constant temperature . The Platinum electrode was used as an auxiliary electrode , which is prepared from a high purity rod stock .

Result and discussion

The present work aims to study the corrosion of carbon-steel in close recirculating cooling water (without hardness) that is used in motor cars and inhibition by using mixture from sodium nitrite (SN) and sodium hexametaphosphate (SHMP) under controlled conditions of mass transfer . The most convenient method to present the results is to split into three sections uninhibited solution , inhibited solution and mechanism of inhibition . Each section then comprises the results of potentiostatic experiments carried out under

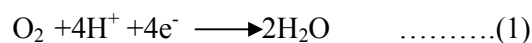
the control conditions at various electrolyte bulk temperature and flow rate .

A-Uninhibited Solution :

The electrochemical quantities (limiting current density and corrosion potential) of carbon-steel in the absence of inhibitor under flow rate from 100 r.p.m. to 400 r.p.m. over the temperature range from 313K to 373 K are summarized in table (2)

Table (2), shows that the increasing of temperatures leads to increase the limiting current density (i_L) of oxygen reduction reaction and corrosion potential (i_{corr}) also. At any temperature it is observed that it is the limiting current density of the oxygen reduction and corrosion potential are increased when the rotating cylinder electrode rate is increased from 100 r.p.m. to 400 r.p.m. . The relationship between the rate of rotation of the working electrode and the limiting current density (i_L) of oxygen reduction over the temperature range from 313 to 373K given in figure (1) . The straight line obtained clearly indicates the phenomenon of increasing current with rate of rotation whereby the system is noticed to obey Levich equation⁽¹⁹⁾ . Hence , the electrochemical behaviour of the carbon-steel

in the media under dynamic conditions is well within the prescription of the equation . This behaviour as already documented in literatures ^(19,20) . The oxygen reduction reaction on the metal surface by four electrons to form two water molecules as shown in (equations(1))⁽¹⁸⁾ .



The relationship between limiting current density (i_L) of oxygen reduction reaction and the temperature are given in figure (1) . The linearity relationship indicates the attribution to increase in mass transfer coefficient which will leads to increase in oxygen flux arriving at the cylinder surface and decrease in resistance that hinder the transfer of oxygen , especially , the diffusion boundary layer thickness . The results show a reasonable agreement with four electrons process at temperature between 313K and 373K when the Eisenbery theory is applied ⁽⁴⁾ . This means that the limiting rate of charge transfer of oxygen reduction on the rotating cylinder electrode is a four electrons process (see equation 2) . The results are agreement with reported by Samch⁽¹⁶⁾ , Taleb⁽¹⁷⁾ , Hasen⁽²¹⁾ , Ali⁽¹⁸⁾ .

In spite of the oxygen concentration is decrease in test solution when the temperature

is increased , but the limiting current density of oxygen reduction reaction is increased because the oxygen diffusion coefficient is increased and the kinematics viscosity of the solution is decreased over the temperature range from 313 to 373K.

At a constant bulk temperature , the results in table (2) shows that the corrosion potential (E_{corr}) increase as the flow rate increase . The anodic kinetics (dissolution of metal) is not mass transfer dependent while the oxygen reduction reaction is the limiting values of mass transfer controlled . Thus , it may be suggested that the corrosion potential lies within the transition zone of the oxygen reduction reaction between full charge transfer and mass transfer controlled in which the oxygen reduction reaction is mass transfer affected . This may be explain the increase in the corrosion potential as the flow rate is increased as shown in figure (2) . At a constant flow rate , the results in table (2) shows that the corrosion potential shifts to more positive values with increasing temperature because the cathodic kinetics (oxygen reduction reaction at a corrosion potential) increases as temperature increase . But , the oxygen reduction reaction at the corrosion potential was assumed to be in a

transition zone , i.e., not yet fully mass transfer controlled . Thus , if the cathodic kinetics is stimulated to a greater extent than anodic kinetics with temperature then the corrosion potential will rise with increasing temperature as shown in figure (3) .

B-Inhibited Solution :

Potentiostatic experiments were carried out on rotating cylinder electrode (R.C.E.) , using formulated inhibitor blend of NaNO_2 and $(\text{NaPO}_3)_6$ at various flow rates and temperatures for carbon – steel in aerated neutral media are shown in figure (4) .

The limiting current density (i_L) values of oxygen reduction reaction and corrosion potential (i_{corr}) at various flow rates and temperatures are given in table (3) . The general detection from the results that it is given in table (3) and figure (4) and independent on the Eisenbery theory ⁽⁴⁾ the limiting rate of charge transfer of oxygen reduction reaction on the rotating cylinder electrode is a two electron process (see equation 1) . The results in table (3) show that the limiting current density is increase with increasing temperature at a constant flow rate , also at a constant bulk temperature the limiting current density

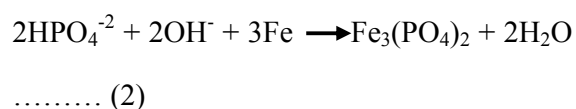
increase with increasing flow rate . These increases are much lower than that in uninhibited solution (see table 2) , at a constant bulk temperature increase as the flow rate increase . The increase in the flow rate acts to erode the formed layer , increase the metal ion transfer from the metal surface to the solution and the oxygen diffusion from the solution to the metal surface . In contrast , at a constant flow rate , the limiting current density is increased with increasing bulk temperature that it is effect cause to stimulate the anodic dissolution of iron , these results are in agreement with those obtained by Ross (22) .

The formulated inhibitor blend contains sodium nitrite as an anodic inhibitor and sodium hexametaphosphate as a cathodic inhibitor . The latter will partially inhibit the oxygen reduction reaction .Therefore , the lower values of the limiting current density of the oxygen reduction reaction are obtained in an uninhibited solution . The corrosion potential values at the various flow rates and temperature for the carbon – steel that it is given in table (3) are shifts to the less positive direction (to active direction) , in spite of the use of NaNO_2 as is anodic inhibitor (23) that it should be shift to noble direction . And more

than that used $(\text{NaPO}_3)_6$ as cathodic inhibitor (24) which it expected to effect on the corrosion potential and shift the potential strongly toward the negative value .Therefore , the role of $(\text{NaPO}_3)_6$ and NaNO_2 as an inhibitors that it are effects on the corrosion potential by the net shift of the mixed inhibitors to shift in the less positive direction . It is well known that the corrosion process can be described in terms of the theory mixed potentials (5) . A mixed potential system is a chemical reaction which can be divided into coupled electrochemical reaction , i.e., one or more anodic reactions acting in parallel with one or more cathodic reaction which operate in the absence of an external source of current . Hence , expect that the corrosion potential of carbon steel is under mixed control of anodic and cathodic partial process .

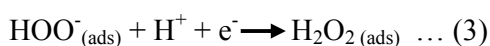
C-Mechanism of inhibition :

A possible mechanism by which the inhibitive action of polyphosphate take place is the formation of protective layer of iron phosphate on the metal surface according to the following reaction ,(equation (2)) (24) .

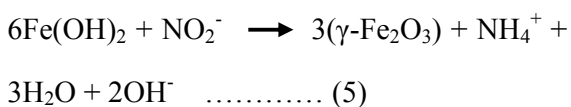
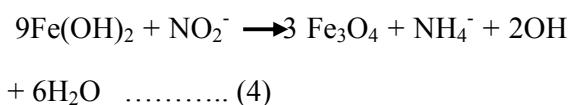


The above reaction take place in two steps , the first being stimulation of anodic

dissolution process . The free Fe^{+2} ions stimulate the hydrolysis of the polyphosphate mainly to HPO_4^{-2} and then to PO_4^{-3} which together with the hydroxyl ions , OH^- , appeared on the surface upon reduction of oxygen in equation (3) , takes part in the second step , i.e., the formation of protective layer of iron phosphate .



Polyphosphate partially amalgamate with films appearing on the metal surface and improve their protective properties . Since these films consist mainly of $\gamma\text{-Fe}_2\text{O}_3$, they do not hamper the heat transfer and they protect the metal against corrosion ⁽²⁴⁾ . The NaNO_2 inhibitor will take major part in inhibiting the anodic dissolution reaction of iron , as it is good anodic inhibitor . The protective oxide formed on the treated metal surface with nitrite consists mainly of Fe_3O_4 and $\gamma\text{-Fe}_2\text{O}_3$ ^(25,26) . It is possibly formed through the adsorption of the nitrite ion followed by an oxidation step . The overall reaction is one or both of the following reaction ⁽²⁵⁾ .



So, the presence of sodium nitrite is very important with sodium hexametaphosphate to form a thin film from $\gamma\text{-Fe}_2\text{O}_3$ according to equation (5) in addition to the formation $\gamma\text{-Fe}_2\text{O}_3$ in the presence the latter inhibitor , but in small amount . The PO_4^{-3} ions will fill in the voids and accelerate film growth , i.e., formation of $\text{Fe}_3(\text{PO}_4)_2$ (see equation 2) . In this manner prevent diffusion of Fe^{+2} from the metal surface . Therefore , the anodic dissolution will reduced .

Conclusion :-

Limiting current density (i_L) is increased with increasing the temperature range and flow rate in uninhibited and inhibited solution . Generally , The corrosion potentials are shifted to the more positive direction with increasing temperature and flow rate , whereas such potentials are shifted in less positive direction by using mixture from inhibitors . Increasing in limiting current density (i_L) with rate the rotation is obey Levich equation . The potentials of corrosion in uninhibited solution are interpretation on the theory of mixed potential . The presence of sodium nitrite is very important with sodium hexametaphosphate to form a thin film from $\gamma\text{-Fe}_2\text{O}_3$. The PO_4^{-3} ions will fill in the voids and accelerate film growth from $\text{Fe}_3(\text{PO}_4)_2$

.In this manner prevent diffusion of Fe^{+2} from dissolution will reduced .
the metal surface . Therefore , the anodic

Table (1) . Chemical formula and some details of compounds for this study

<i>Name</i>	<i>Structure</i>	<i>Company</i>	<i>Concentration (ppm)</i>
sodium nitrite (SN)	NaNO_2	BDH	100
sodium hexametaphosphate (SHMP)	$(\text{NaPO}_3)_6$	BDH	500

Table (2):- The values of limiting current density (i_L) of oxygen reduction reaction and corrosion potential (E_{corr}) in uninhibited solution for Carbon-Steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K and flow rates of (100 , 200 , 300 , 400) r.p.m.

Temperature (K)	Solution flow rate (r. p. m.)							
	100		200		300		400	
	i_L Am^{-2}	E_{corr} mV_{SCE}	i_L Am^{-2}	E_{corr} mV_{SCE}	i_L Am^{-2}	E_{corr} mV_{SCE}	i_L Am^{-2}	E_{corr} mV_{SCE}
313	1.76	600	1.98	730	2.30	760	3.60	780
323	2.61	625	2.89	750	3.29	770	4.65	810
333	3.44	650	3.80	770	4.28	785	5.70	850
343	4.27	680	4.71	785	5.27	805	6.75	855
353	5.10	690	5.62	810	6.26	835	7.80	870
363	5.93	720	6.53	830	7.25	845	8.85	910
373	6.76	810	7.44	860	8.24	875	9.90	920

Table (3):- The values of limiting current density (i_L) of oxygen reduction reaction and corrosion potential (E_{corr}) in inhibited solution for Carbon-Steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K and flow rates of (100 , 200 , 300 , 400) r.p.m.

Temperature (K)	Solution flow rate (r.p.m.)							
	100		200		300		400	
	i_L Am ⁻²	E_{corr} mV _{SCE}	i_L Am ⁻²	E_{corr} mV _{SCE}	i_L Am ⁻²	E_{corr} mV _{SCE}	i_L Am ⁻²	E_{corr} mV _{SCE}
313	1.53	430	1.64	620	1.98	720	2.67	760
323	2.34	515	2.53	680	2.76	750	3.43	790
333	2.81	580	3.33	720	3.51	780	3.90	830
343	3.93	620	3.98	750	4.04	810	4.54	840
353	4.03	650	4.96	760	5.21	830	5.77	860
363	5.12	690	5.97	790	6.02	845	6.58	880
373	5.94	780	6.42	820	7.03	860	8.18	910

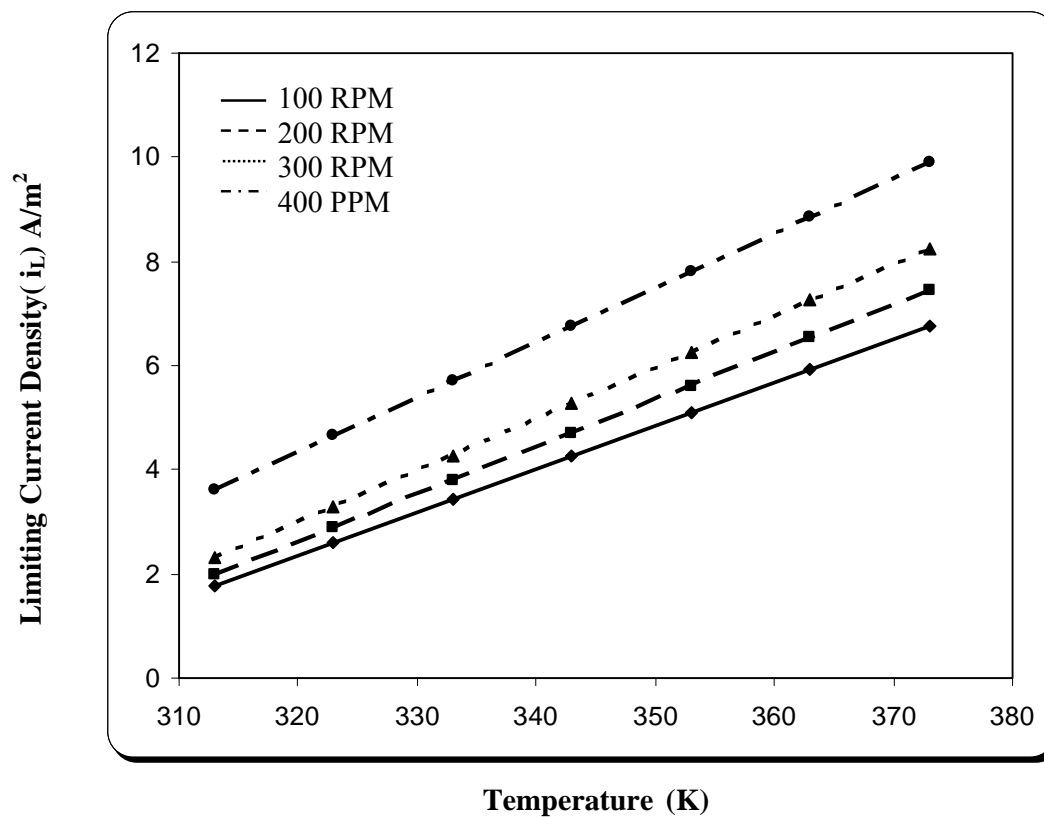


Figure (1):- The variation of limiting current density (i_L) of oxygen reduction reaction in uninhibited solution for carbon-steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K and flow rates of (100 , 200 , 300 , 400) r.p.m

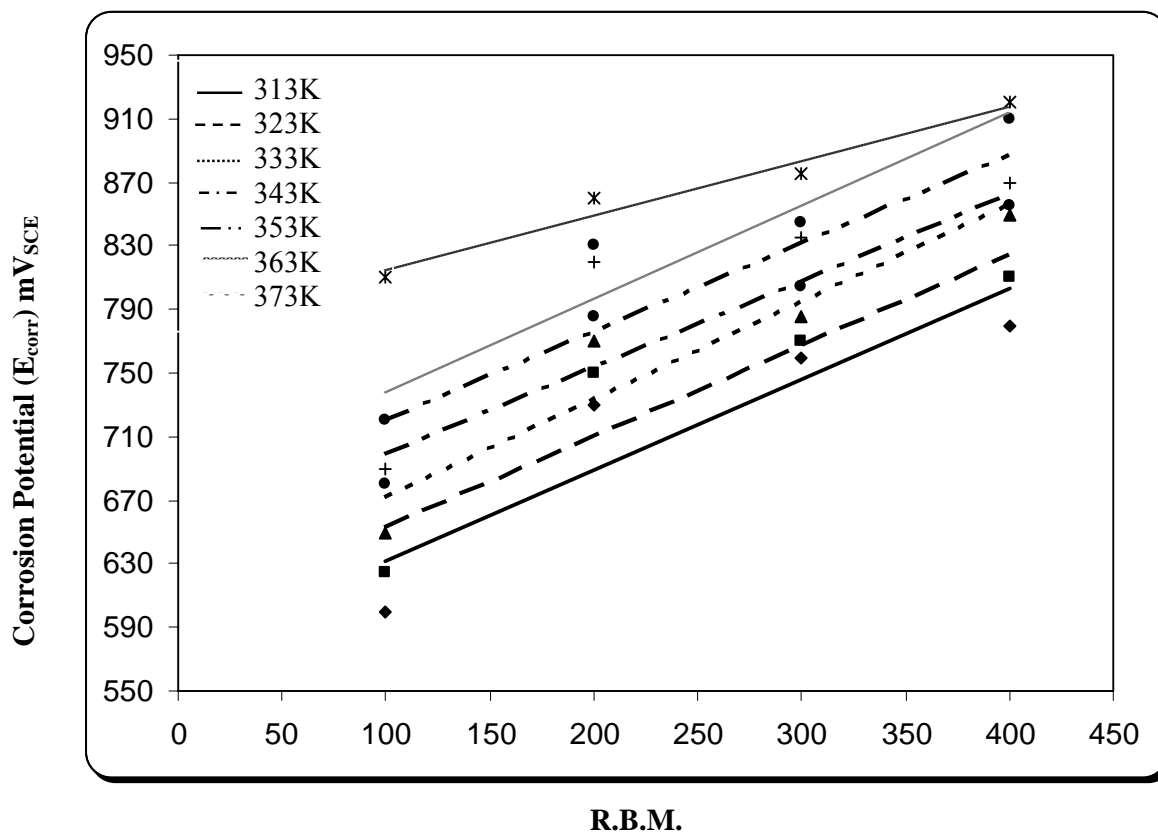


Figure (2):- The variation of corrosion potential (E_{corr}) and flow rates of (100 , 200 , 300 , 400) r.p.m in uninhibited solution for carbon-steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K

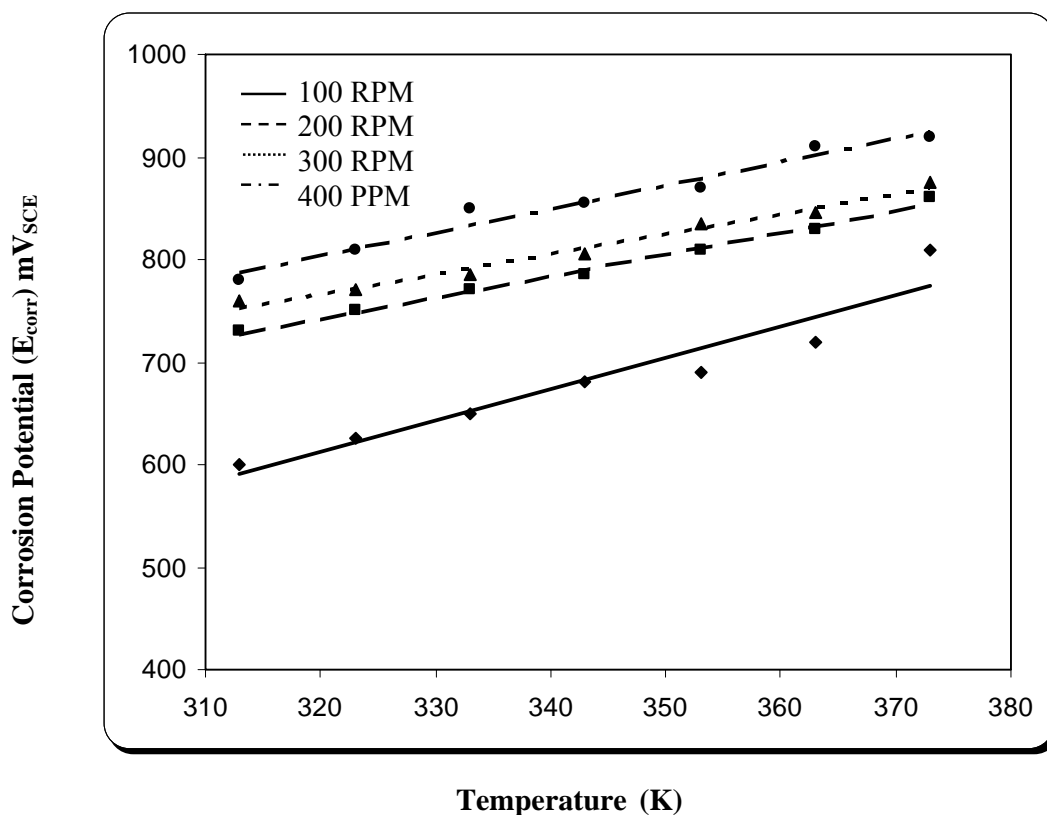


Figure (3):- The variation of corrosion potential (E_{corr}) in uninhibited solution for Carbon-Steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K and flow rates of (100 , 200 , 300 , 400) r.p.m.

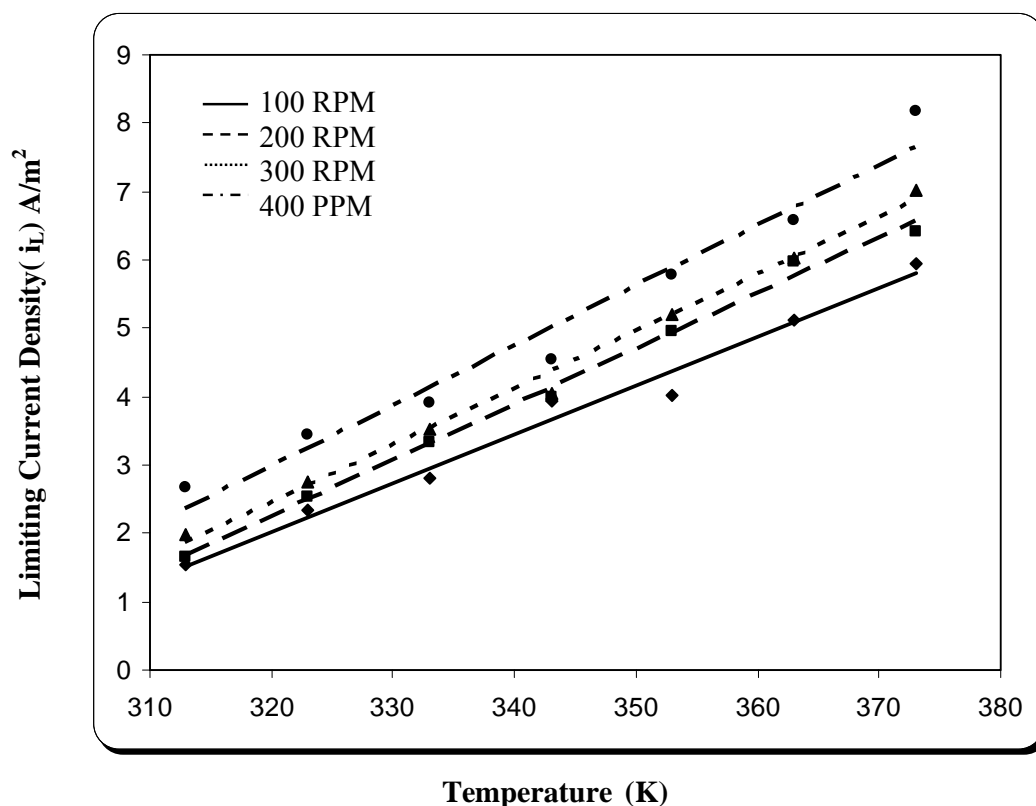


Figure (4):- The variation of limiting current density (i_L) of oxygen reduction reaction in inhibited solution for carbon-steel under controlled conditions of mass transfer in neutral aerated solution of cooling system for motors cars over the temperatures range (313-373)K and flow rates of (100 , 200 , 300 , 400) r.p.m.

Reference

- 1- Kenneth R. Trethewey and John Chamberlain “ *Corrosion for science and engineering* “, Longman Singapore publishers LTd 1996 .
- 2- A.M.Farhan , Ph.D. , *thesis* , college of science , university of Baghdad , June , 2000 .
- 3- B.Ridd “ *Corrosion* “ , LTd Scotland , from internet network , 2005 .
- 4- H.H.Uling and R.W.Revic “ *Corrosion and corrosion control* “ 3rd ed. , Jon Wiley , New York , 1985 .
- 5- M.G.Fontan and N.D.Green “ *Corrosion Engineering* “ Mc-Grow Hill , New York , 1987 .
- 6- B.Abd.El.Nabey , E.Khamis “ *Surf.Coat.Technol.*”, 1989, **28**, 83.
- 7- E.Stupisek-Lisac and K.Salaster *J.furac.Corr.Sci.* 1988 , **28** , 1189 .

- 8- J.M.Sykes , *British Corr.J.* , 1990 , **25** , 175 .
- 9- P.Chaterjee and M.K.Banerjee , *Indian J.Technol.* , 1991 , **29** , 191
- 10- S.Arab and B. Abd-El-Nabey , *Ind.J.Chem.*, 1991 , **2** , 23 .
- 11- G.Schmitt , *British Corr.J.*, 1984 , **19** , 165 .
- 12- S.Reugamani and S.Muralidharan , *J.Appl.Electrochem.*,1994 , **24** , 355 .
- 13- L.Oniciu , “*Metal Corrosion – Fundamental Aspects and anti-corrsion protection* “ E.S.E.Bucharest , 1986 .
- 14- M.Constantinescu , “*Corrosion Inhibitor* “ , Ed.Tech.,Bucharest , 1979
- 15- L.H.VanValck , “*Elements of Materials science* “ , 2nd ed. , Addison Westry Amsterdam , 1964 .
- 16- S.A.Sameh , Ph.D., *Thesis* , Chemical Engineering , University of Technology , 1994 .
- 17- M.M.Taleb , Ph.D., *Thesis* , Chemical Engineering , University of Technology , 1995 .
- 18- A.H.Ali, M.Sc. *Thesis* , Chemical Engineering , University of Technology , 2002 .
- 19- T.Hurlen and P.G.Londe , *J.Electroanal.Chem.*,1984,**18**,511.
- 20- F.P.Berger and K.L.Hau.*Int.J.Heat Mass transfer* 1977 , **20** , 1185
- 21- E.A.Hasen,” Ph.D., *Thesis* , Chemical Engineering , University of Technology , 1988 .
- 22- T.K.Ross and B.L.Hitchen , *Corrosion Science* , 1961 , **1** , 15 .
- 23- C.L.Joseph, *Proc.Third Eur. Symp. Inhib.*, 1970, **19**, 791 .
- 24- I.L.Rosenfield , “*Corrosion Inhibitor* “ , McGraw Hill , New York , 1981 .
- 25- A.Marshall , “*Corrosion Inhibitor for use in natural water system* “ London , Oyez Scientific and service Ld,1983 .
- 26- M.Cohan , *Corrosion Sci.* , 1976 , **4** , 46 .