

Polarographic Studies for the Corrosion of Carbon Steel in Hydrochloric Acid Solutions

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Abstract:

The present work deals with the quantitative corrosion determination of carbon steel in hydrochloric acid by the use of polarographic and weight loss technique.

The polarographic peak obtained at (-0.27 v) in 0.1 M hydrochloric acid was used for the determination of iron and a calibration was ranged (10^{-5} – 10^{-3}) M.

To confirm the obtained results a weight loss measurement were carried out, its results are in good agreement with that of the polarographic measurements. The research included in addition to that a kinetic study of corrosion reactions of iron in hydrochloric acid. Reaction rates were calculated at different temperature, and apparent energies of activation have been calculated from corrosion rates and Arrhenius plots.

Keywords: polarography, corrosion, carbon steel, and weight loss.

Introduction:

Corrosion of metals has been observed in many ways by many workers⁽¹⁻⁵⁾ and numbers of organic and inorganic compounds were known to inhibit the corrosion of metals and hence are extensively used⁽⁶⁻¹¹⁾.

Several polarographic methods have been used for the determination⁽¹²⁾ and micro determination⁽¹³⁾.

Corrosion studies by polarographic technique where ever possible, simple, sensitive and rapid method, yield highly reliable and reproducible results with a high order of accuracy.

This paper describes a differential pulse polarographic determination of iron in 0.1 M hydrochloric acid solutions and a measurement of the peak obtained at -0.27 volt were used.

A detailed kinetic study of corrosion reactions of carbon steel in different concentrations of hydrochloric acid solutions of (0.5 – 3) M, metal dissolution rate were calculated over the temperature range (300 – 318) K by the weight loss method.

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Experimental work:

Part 1:

The carbon steel specimen (obtained from ministry of industry) had the following composition as revealed by emission spectroscopic analysis:

Element	C	Si	Mn	Ni	Fe
%	0.05	0.4	0.61	0.04	98.9

The surface of the carbon steel were first polished then rinsed with distilled water before being immersed in the corrosive medium.

The net area of carbon steel exposed was 30 cm² and the average weight was 4 grams.

Solutions were prepared from twice distilled water and analar grade hydrochloric acid, the volume of the acid solutions used in each experiment was 75 ml. The temperature was adjusted electrically to $\pm 0.01^{\circ}\text{C}$ by using "Haake – Fk Thermostat, Germany". The experiments were done uniformly for duration of 8 hours.

Corrosion kinetic studies of carbon steel in (0.5 – 3) M *HCl* where followed as weight loss measurements at regular time intervals of (1 – 8) hours at a constant temperature 300 K and constant atmospheric pressure. A weight losses were determined using sensitive balance ($\pm 10^{-4}$ g) "Sartorius BP 301S, ISO 9001".

Similar experiments were done with all solutions at various temperatures 308, 313, and 318 K.

Part 2:

Differential – pulse polarograms were determined using a "174 A Polarographic analyzer of Princeton Applied Research, Princeton, New Jersey, USA". In conjunction with stand equipped with mechanical drop timer. A three – electrode system were used, the working electrode being a dropping – mercury electrode (DME), the reference electrode a saturated calomel electrode, and a Hg pool electrode as a counter electrode^(14, 15, 16).

The following conditions were applied: potential scan rate 10 mv./sec, voltage range 0.75 v., modulation amplitude 50 mv., drop time 0.5 sec., and current range (0.1 – 1) μA . All polarographic measurements were carried out at room temperature (22°C). The solution was deaerated by passing through it a stream of nitrogen gas for 15 min.

A number of solutions, containing known concentrations of iron as Fe^{3+} were prepared, and the differential pulse polarogram were recorded in the presence of 0.1 M hydrochloric acid as supporting electrolyte.

Results and Discussion:

Polarographs:

It is well known that Ferric ion gives a well defined polarographic peak appears at (-0.24) – (-0.34) volt versus saturated calomel electrode in different supporting electrolyte ⁽¹⁷⁾. The differential pulse polarogram for Fe^{3+} in 0.1 M HCl solution as supporting electrolyte gave one well-defined peak at a potential of -0.27 volt as shown in figure 1-a.

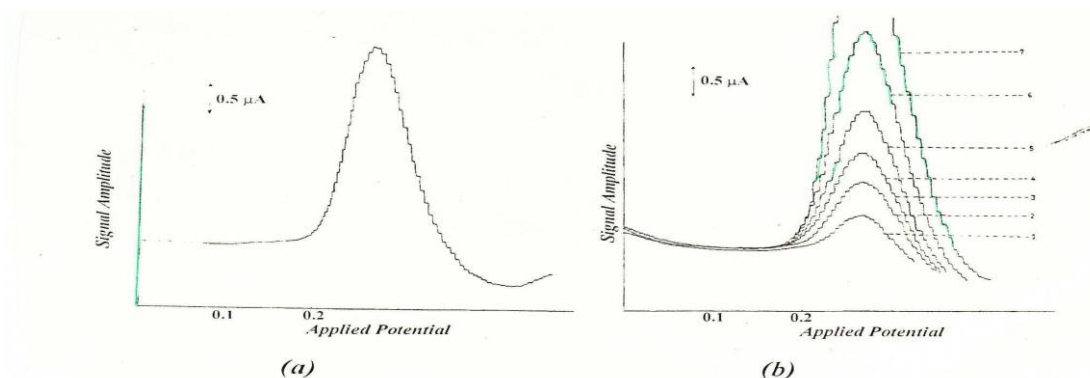


Figure (1) differential pulse polarograms of:

- a) Fe^{3+} in 0.1 M HCl.
- b) Different concentration of Fe^{3+} in 0.1 M HCl.

A series of ferric ion solutions having the concentration ranging from (10^{-3} to 10^{-5} M) were prepared by the oxidation of Fe^{2+} to Fe^{3+} using nitric acid and heating ⁽¹⁶⁾ (figure 1 – b).

The obtained results for the variation of the measured peak current (I_p) with concentrations of Fe^{3+} shows a linear relation. Table (1) tabulates all the results obtained that cover the calibration range. While figure (2) shows the calibration graph using simple equation of first degree, were constructed by a plot of peak current in (μA) versus concentration of Fe^{3+} in mg/l, and the correlation coefficient (C.C.), coefficient of determination (C.O.D.) and the percentage linearity were summarization in table (2).

Table (1): Variation of Fe^{3+} concentrations versus peak current I_p (μA) using differential pulse polarography.

Peak current $I_p, \mu A$	Conc. Mol / L * 10^{-4}	Conc. Mg / L, [Fe^{+3}]
0.256	4	1.12
0.205	3.2	0.9
0.154	2.4	0.67
0.103	1.6	0.45
0.052	0.8	0.225
0.026	0.4	0.112
0.013	0.2	0.056

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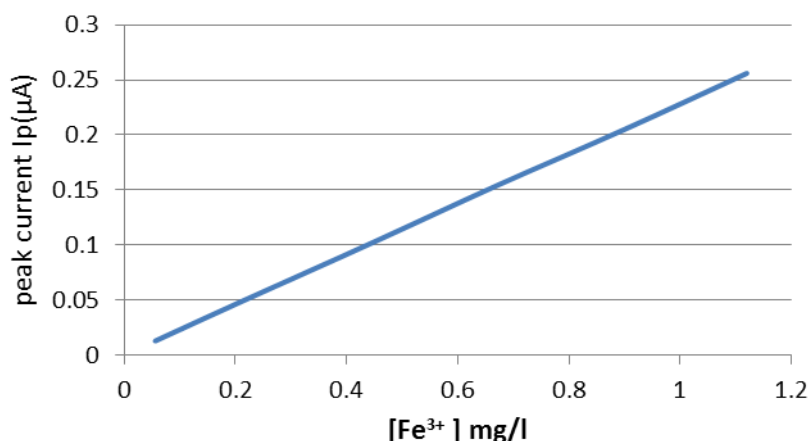


Figure (2): linear calibration graph for the variation of I_p with concentration.

Table (2): summary of linear regression for the variation of peak current with Fe^{3+} concentration using first degree equation of the form $y = a + bx$.

Concentration mg/l	Linear range	Correlation coefficient (r^2)	Percentage linearity ($r^2\%$)
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The corrosion of iron in carbon steel specimens was determined after inserting the specimens in different concentration of HCl (0.5 – 3) M for eight hours, by the use of two methods: polarographic peak current with the same procedure as for standard, and the weight loss method.

Table (3) indicates the peak current (I_p) and the weight loss calculated according to the initial volume (75 ml).

Table (3): peak current (I_p) and weight losses of carbon steel at different temperature by differential pulse polarography.

Concentration of HCl								
Temp./ K	0.5 M HCl		1 M HCl		2 M HCl		3 M HCl	
	Δw Mg*10 ⁻³	I_p μ_A *10 ⁻³	Δw Mg*10 ⁻³	I_p μ_A *10 ⁻³	Δw Mg*10 ⁻³	I_p μ_A *10 ⁻³	Δw Mg*10 ⁻³	I_p μ_A *10 ⁻³
300	3.2	14.6	4.5	20.5	4.7	21.5	10.3	47
308	6.8	31.5	9.0	41	12.7	58	19.3	88
313	10.0	45.5	12.9	59	17.4	80	25.9	119
318	15.0	68	18.0	82.3	26.0	118	37	169

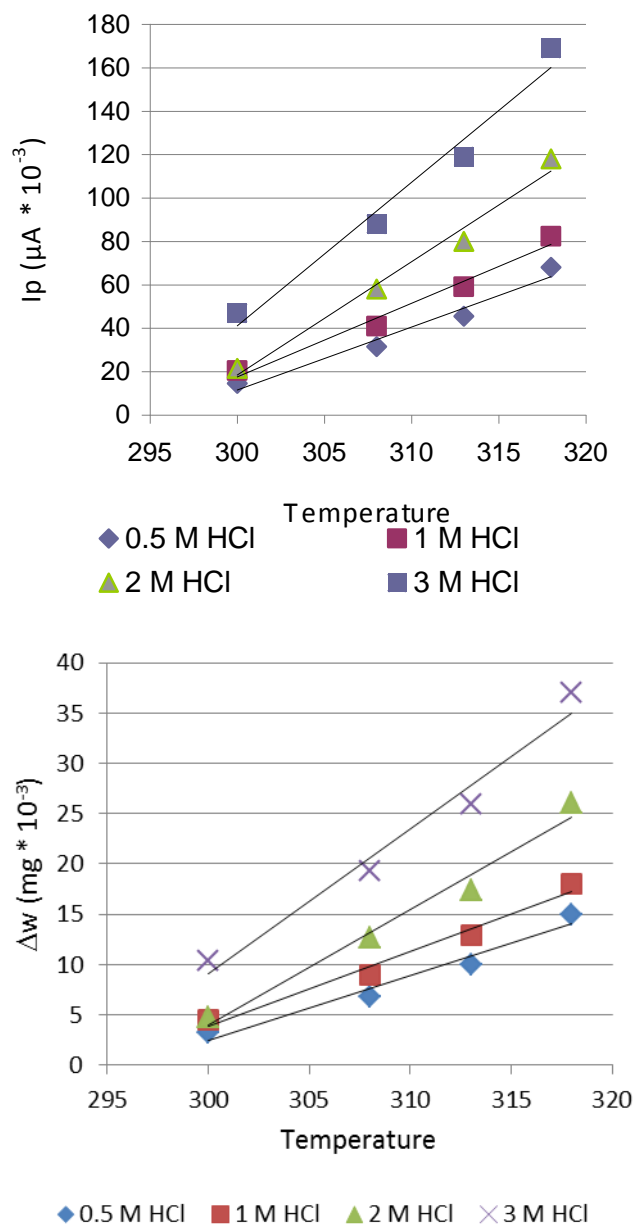


Figure (3): peak current and weight loss against temperature using DP polarographic method.

Weight loss vs. time curve:

By the application of weight loss method, data are plotted for weight of metal dissolution against time in hours for 0.5 M to 3 M acid concentrations at various temperatures (300 – 318) were presented in Table (4) and figure (4).

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Table (4): weight loss in different time and different temperature by the weight loss method.

Temp.	0.5 M $\Delta w/g$	1 M $\Delta w/g$	2 M $\Delta w/g$	3 M $\Delta w/g$	Time (hour)
300 K	0.00047	0.00082	0.00118	0.002	15
	0.001177	0.002	0.00294	0.00436	35
	0.002	0.00283	0.00424	0.00612	50
	0.00247	0.00377	0.00565	0.0086	65
	0.0031	0.00447	0.00671	0.0100	80
308 K	0.001	0.0014	0.0024	0.0036	15
	0.0024	0.0038	0.0054	0.0084	35
	0.004	0.0056	0.008	0.013	50
	0.005	0.0072	0.0106	0.0164	65
	0.0064	0.009	0.0124	0.0194	80
313 K	0.00112	0.00168	0.00252	0.0042	15
	0.00364	0.00504	0.007	0.0106	35
	0.0053	0.00784	0.0104	0.016	50
	0.00756	0.0104	0.0134	0.0204	65
	0.00924	0.0126	0.0168	0.0255	80
318 K	0.002	0.0032	0.0044	0.0072	15
	0.006	0.0084	0.0112	0.0168	35
	0.0088	0.0124	0.0168	0.024	50
	0.0112	0.016	0.0212	0.03	65
	0.014	0.02	0.026	0.0376	80

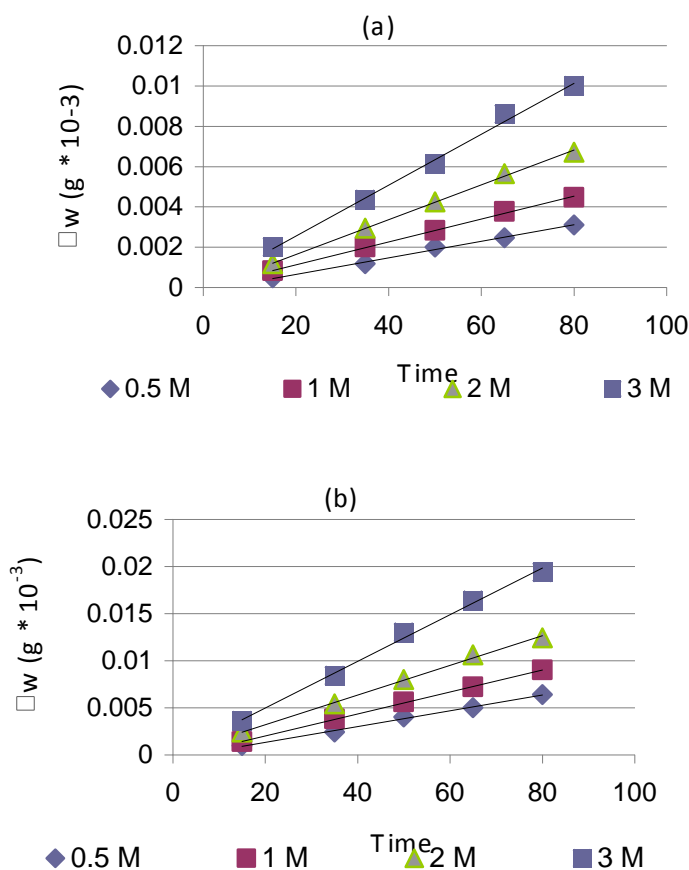
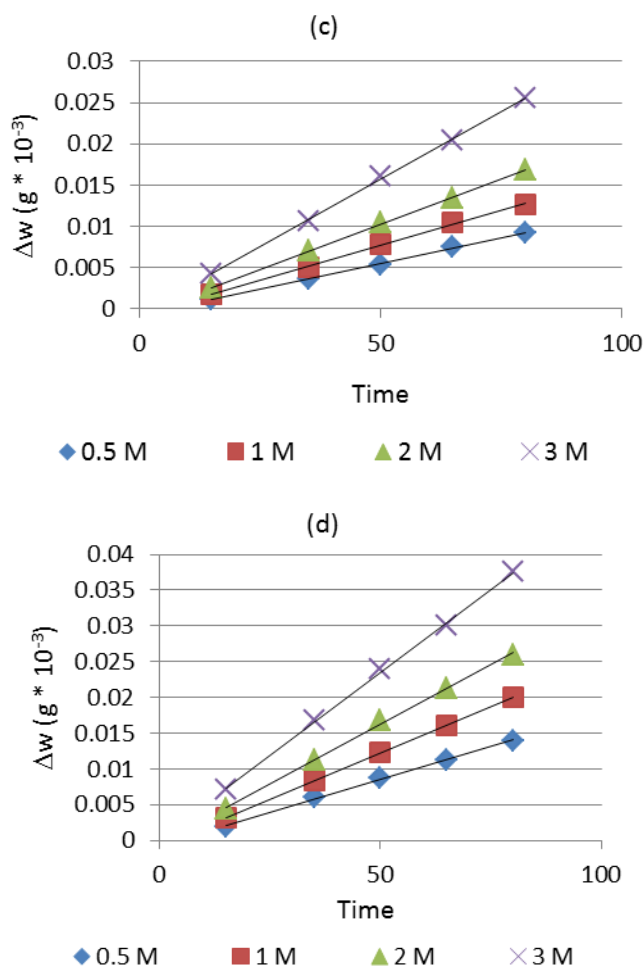


Figure (4): weight loss ($\Delta w/g$) of carbon steel vs. time (hr) in 0.5 M to 3 M HCl at different temperature (a) 300 K, (b) 308 K, (c) 313 K, and (d) 318 K.

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As may be noted from these figures, all the graphs are linear, slopes of such lines were calculated and taken as the rates of reactions and are expressed in $\text{g.cm}^{-2}.\text{hr}^{-1}$.

The calculated values of the rates against concentration are tabulated in table (5).

Table (5): Corrosion rate $\text{g.cm}^{-2}.\text{hr}^{-1}$ ($\times 10^{-4}$) of carbon steel in (0.5 – 3) M *HCl* at four different temperatures.

<i>HCl</i> Conc.	Corrosion rate / $\text{g.cm}^{-2}.\text{hr}^{-1}$			
	300 K	308 K	313K	318 K
0.5 M	4.3	8.5	12.9	20.4
1 M	5.9	11.2	17.1	25.6
2 M	6.2	15.5	22.4	33.1
3 M	13.2	24.1	33.6	48

It was found that corrosion rate of the carbon steel in (0.5 – 3) M *HCl* increased with increasing temperature from 300 K to 318 K at any exposure time.

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Log rate vs. concentration:

Reaction rate data obtained from Figure (4) (a – d) which were presented in table (4) are plotted as log rate vs. molar concentration of acid in Figure (5). It may be noted that all the graphs are straight – line curves establishing a linear function relationship between log rate and concentration.

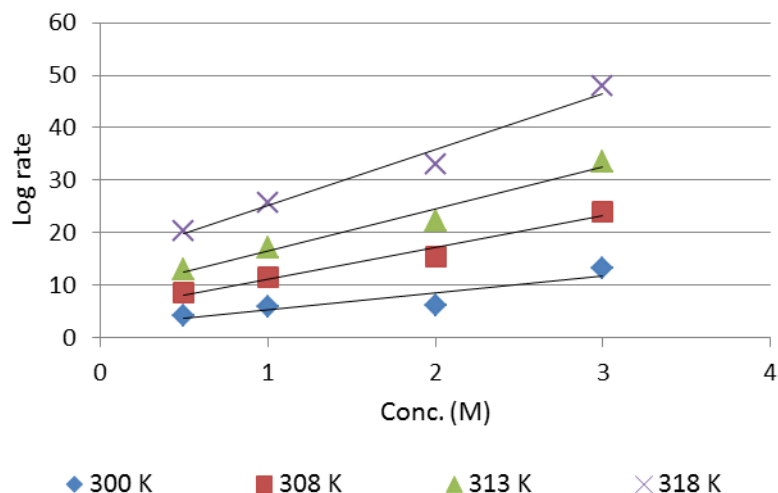


Figure (5): Log rate vs. log concentration (M) at different temperature.

Kinetic Aspects:

The rate of corrosion (r) of carbon steel in hydrochloric acid solution increased with temperature over the range 300 – 318 K and can be replaced by the well known Arrhenius equation:

$$r = A \exp(-E_a/RT) \dots\dots\dots (1)$$

$$\log r = \log A - \frac{E}{2.303RT} \dots\dots\dots (2)$$

Where E the apparent energy of activation for the corrosion is process and A is the pre-exponential factor.

A plot $\log r$ versus reciprocal temperature ($1/T$) in the manner depicted in table (6), Figure (6) and a linear relationship observed.

Table (6): Log rate of corrosion at different temperature.

	0.5 M HCl	1 M HCl	2 M HCl	3 M HCl	1/T
300 K	-3.368	-3.230	-3.086	-2.880	3.33
308 K	-3.071	-2.950	-2.810	-2.618	3.25
313 K	-2.888	-2.768	-2.650	-2.474	3.20
318 K	2.690	-2.592	-2.480	-2.480	3.15

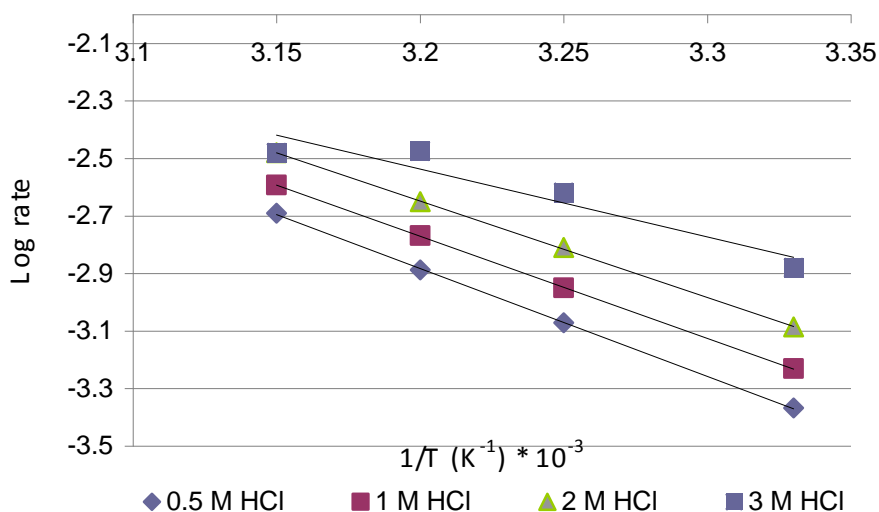


Figure (6): Arrhenius plots for the corrosion of carbon steel in /0.5 – 3) M HCl.

Values of E could thus be derived from the slopes of the plots in Figure (7). Table (7) shows an increase in the apparent energy of activation as the concentration of acid decrease resulting in the consequent decrease of the surface tendency for corrosion.

Table (7): Apparent energy of activation of carbon steel at (0.5 – 3) M HCl.

HCl Conc, (M)	0.5 M	1 M	2 M	3 M
$E_a/KJ.mol^{-1}$	71.23	68.6	63.2	58.6

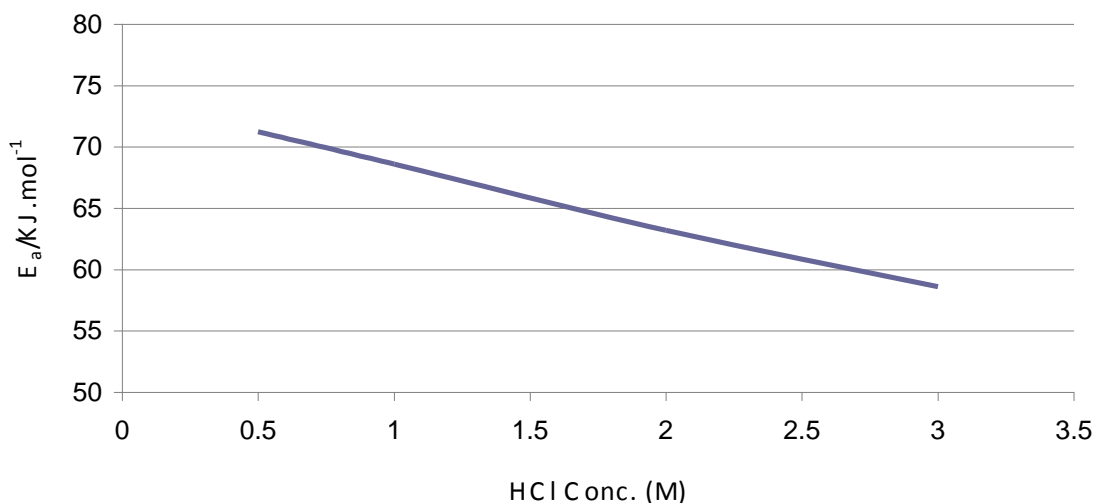


Figure (7): energy of activation of carbon steel at (0.5 – 3) M HCl.

Conclusion:

Carbon steel has been extensively used under different conditions in all industries. An acid wash process is widely used in many industries.

Corrosion attracts the attention of researchers. Researchers all over the world are searching for some methods to avoid corrosion damage, and a method to test corrosion at its early stage.

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The differential pulse polarographic method presented for the quantitative determination of Fe^{3+} allows the accurate determination of corrosion of carbon steel in acidic medium.

The result obtained is very reproducible since with the use of a dropping mercury electrode the electrode surface is always new and the behavior of the electrode is independent of its history. This proposed method is simple, rapid, sensitive, inexpensive, and highly reproducible.

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دراسة بولاروغرافية لتآكل حديد الصلب الكربوني في محاليل حامض الهيدروكلوريك

الخلاصة

يهدف البحث الى امكانية استخدام التحليل البولاروغرافي الكمي لدراسة تآكل حديد الصلب الكربوني في حامض الهيدروكلوريك.

تتضمن الطريقة قياس الموجة البولاروغرافية عند جهد (-0.27v) في محلول 0.1 مولاري حامض الهيدروكلوريك. تم الحصول على منحنى معايرة خطي في مدى من التراكيز تتراوح بين (0.056 – 1.12) ملي غرام / لتر. ولغرض التأكد من نتائج هذه القياسات تم استخدام قياسات فرق الوزن والحصول على نتائج متقاربة في كلا القياسين. وتم ايجاد ثابت سرعة التآكل في مدى من درجات الحرارة من 300 الى 318 كلفن وايجاد طاقة التنشيط الظاهرية لعملية التآكل وذلك من قياسات سرعة التآكل في الدرجات الحرارية المختلفة.