Effect of (1,4) phenylenediamine on the corrosion of lead in 1M hydrochloric acid solution

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Abstract:

The accelerating effect of 1,4- phenylenediamine (PDA) additions in 1M hydrochloric acid solution at temperature rang (20-60) C° has been studied by weight losses measurement during ranging time (1-260) h and by following the pb^{2+} concentration in solution after several times by using Atomic absorption spectroscopy (AAS) . The volume of hydrogen gas involving was followed also in presence and absence of (PDA) in the corrosive solution .Accelerating enhanced by adding (NaCl , NaBr , NaI) was also investigated.

Introduction:

One of the most common application of organic and inorganic additives is their use as pickling additions. During the pickling of metal in acids , which is carried out in order to remove oxide (scale) from its surface , electrochemical dissolution of the metal takes place at those portions from which the scale has been removed , while the oxide is dissolved chemically .In order to reduce the dissolution of metal and there by prevent it from being over pickled (to keep the surface of the articles smooth), and to reduce the weight of metal dissolved as well as the acid consumption various additions are made which retard the attack . These additions are mainly organic compounds , which often form colloidal solutions . The mechanism of their action consists in their being adsorbed at the metal surface , so that the hydrogen over voltages is increased . The fundamental mechanism of such processes was established by the researches of G.V. Akimov and N.D. Tonashov . Evolution of hydrogen gas at the cathode occurs as a result of several consecutive steps :

(1) transfer of hydrated hydrogen ions ($H^+ m H_2O$) to the cathode ;

(2) dehydration of these ions :

(3) discharge of hydrogen ions: $H^+ + e \longrightarrow H_{ads}$;

(4) formation of hydrogen molecules : $H_{ads} + H_{ads} \longrightarrow H_2$;

(5) removal of hydrogen from the cathode by diffusion and by detachment of hydrogen bubbles (1).

It has been found that the over potential of hydrogen evolution depends on the cathode material and on the conditions of its surface . The standard electrode potential of lead : $E_{pb / pb^{+2}} = - 0.126V$, lead has been used ancient times as a metal which is resistant to water, to the atmosphere and to large number of aggressive solutions . The purposes of the present work is to investigate the effect of 1,4- PDA on the acid corrosion of lead and to investigate the effects observed in the presence of sodium halide salt (NaCl , NaBr , NaI) with PPA on the rate of lead dissolution and rate of hydrogen evolution .

Experimental:

Samples of pure grade material 99.9 (obtained from ministry of industry) were used for corrosion rates studies .

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The test pieces (17 x 13.5 x 5)mm were cleaned at 28°c in nitric acid / hydrochloric acid solution , then rinsed with distilled water before being immersed in the corrosive medium (purun grade) which was obtained from Fluka. The solutions prepared from Analar HCl solution using distilled water. The temperature was adjusted electrically to ± 0.1C°. corrosion rate were calculated by using AAS type GBC 933, phus.

For weight losses measurements , the specimens were completely immersed in 50 ml for each specimen of the 1 M HCl solution in conical Flask . They were exposed for different time intervate up to 260 h. and their weight losses was determined, using sensitive (± 10^{-4} g) balance type mettler HL 32 from Switzerland.

Rsults and discussion:

1- Weight loss method :

The corrosion of lead in 1M HCl solution containing various concentrations of 1,4-DPA was studied by weight – loss measurement (1) .

The corrosion rates of lead was calculated at various 1,4-PDA concentrations ranging (1x 10^{-3}–2 x 10^{-1}) M in different exposure times by using the relation:

$$W = \frac{\Delta g}{\Delta t} \quad \text{---------------} \ (1)$$

where : Δg is the mass loss(g).
Δt is the immersion period (h) $^{(2)}$.

The values of weight losses of free lead and with various concentrations of PDA at temperature ranging (293– 323) K and after different time was shown in table 1.

Figure (1) shows the linear variation in corrosion rate [weight loss against time] for various concentrations of PDA ranged (1 x 10^{-3} – 2 x 10^{-1}) M and in the absence of PDA at 289 K° (3).

2- Atomic Absorption spectrophotometer (AAS) measurement:

Atomic Absorption spectrophotometer type GBC 933 plus was used to determined the concentrations of lead ions in the corrosion solution (Free from PDA and with various concentrations of PDA) . The corrosion rates which calculated in different temperatures by using (AAS) measurements and weight losses measurements (Δg) (slops from figure 1) is shown in table (2).

Table 1. Values of weight losses of free lead and with various concentrations of PDA after different time at temperature ranging (293 – 323) K

Temp.(K)	weight losses Δg (g)						
293	Conc.of 1,4 -PDA	After (24 h)	After (60 h)	After (96 h)	After (120 h)	After (156 h)	After (252 h)
	Blank	0.0064	0.012	0.0167	0.0213	0.0266	0.041
	1 * 10^{-3}	0.0080	0.0149	0.0188	0.0225	0.0258	0.0359
	1 * 10^{-2}	0.0043	0.0105	0.0165	0.0212	0.0212	0.047
	5 * 10^{-2}	0.0041	0.011	0.0160	0.0207	0.0260	0.044
	1 * 10^{-1}	0.0075	0.0126	0.16	0.019	0.0251	0.0337
	2 * 10^{-1}	0.0072	0.0128	0.0165	0.2	0.0243	0.0358
	weight losses Δg (g)						
303	Conc.of 1,4 -PDA	After (1 h)	After (2 h)	After(3 h)	After (4 h)	After (4.5 h)	
	Blank	0.0031	0.0053	0.0062	0.0068	0.0072	
	1 * 10^{-3}	0.0025	0.0037	0.0045	0.0052	0.0058	
	1 * 10^{-2}	0.0036	0.0044	0.0051	0.0056	0.0066	
	5 * 10^{-2}	0.0038	0.0055	0.0062	0.0077	0.0083	
	1 * 10^{-1}	0.0041	0.0056	0.0065	0.0072	0.0078	
	2 * 10^{-1}	0.0038	0.0052	0.006	0.0073	0.0082	
	weight losses Δg (g)						
313	Conc.of 1,4 -PDA	after (0.5 h)	After (1.25 h)	After (1.25 h)	After (2.5 h)		
	Blank	0.0024	0.0033	0.0033	0.0041		
	1 * 10^{-3}	0.0024	0.0032	0.0032	0.0041		
	1 * 10^{-2}	0.0029	0.0037	0.0037	0.0049		
	5 * 10^{-2}	0.0029	0.0035	0.0035	0.0044		
	1 * 10^{-1}	0.0023	0.0034	0.0034	0.0045		
	2 * 10^{-1}	0.0018	0.0021	0.0021	0.0035		
	weight losses Δg (g)						
323	Conc.of 1,4 -PDA	After (1 h)	After (2 h)	After (3 h)	After (3.5 h)		
	Blank	0.0018	0.0027	0.0033	0.0044		
	1 * 10^{-3}	0.0016	0.0026	0.0033	0.0038		
	1 * 10^{-2}	0.0023	0.0035	0.0045	0.0051		
	5 * 10^{-2}	0.0023	0.0031	0.0039	0.0044		
	1 * 10^{-1}	0.0020	0.0029	0.0037	0.0044		
	2 * 10^{-1}	0.0020	0.0030	0.0040	0.0045		

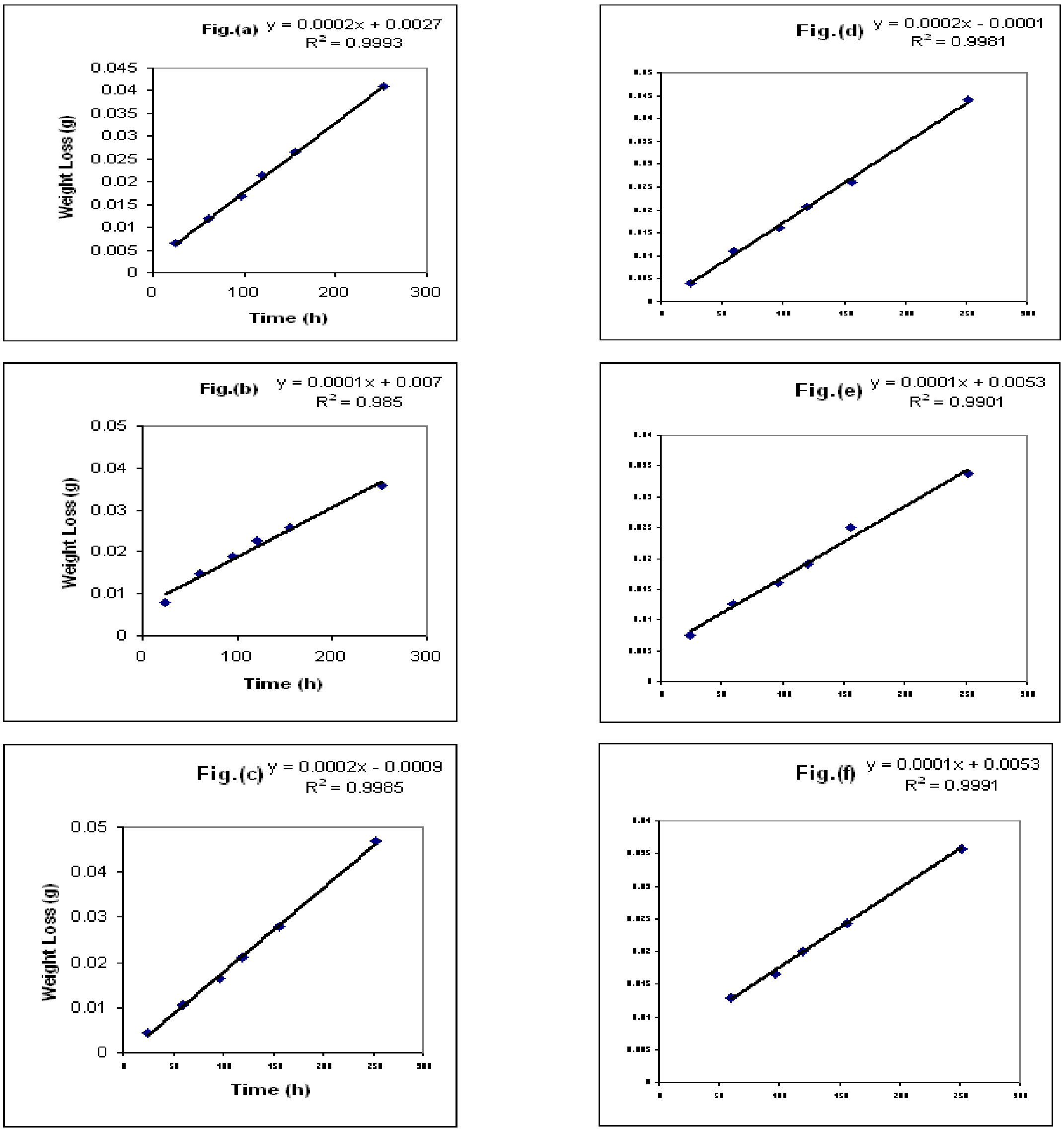


Figure (1) Weight losses of lead in HCl solution against time (a) without PDA (b) with 1 x 10^{-3} M PDA (c) with 1 x 10^{-2} M PDA (d) with 5 x 10-2 M PDA (e) with 1 x 10-1 M PDA (f) with 2 x 10^{-1} M PDA at 293 K from weight losses measurement.

Table 2. Values of weight losses and (AAS), Rate of corrosion calculated from weight losses measurement, and from (AAS) at temperature ranging (289 – 323)K in 1M HCl in absence and present of various concentrations of PDA

Conc.of 1,4 - PDA	289 K				303 K			
	Δg (g)	Rate of Δg (g / h)	AAS (g)	Rate from AAS (g/h)	Δg (g)	Rate from Δg (g / h)	AAS (g)	Rate from AAS (g/h)
Blank	0.0267	$5.7*10^{-5}$	0.0191	$4.07*10^{-5}$	0.0072	$1.57*10^{-3}$	0.0046	$1*10^{-3}$
$1 * 10^{-3}$	0.0252	$2.62*10^{-5}$	50.019	$2.03*10^{-5}$	0.0058	$1.28*10^{-3}$	0.0033	$7.44*10^{-4}$
$1 * 10^{-2}$	0.0299	$6.38*10^{-5}$	0.0197	$4.22*10^{-5}$	0.0066	$1.41*10^{-3}$	0.0030	$6.55*10^{-4}$
$5 * 10^{-2}$	0.039	$8.33*10^{-5}$	0.0022	$4.72*10^{-5}$	0.0083	$1.74*10^{-3}$	0.0034	$7.17*10^{-4}$
$1 * 10^{-1}$	0.0386	$8.24*10^{-5}$	0.0241	$5.15*10^{-5}$	0.0078	$1.61*10^{-3}$	0.0034	$7.11*10^{-4}$
$2 * 10^{-1}$	0.048	$10.25*10^{-5}$	0.0287	$6.13*10^{-5}$	0.0082	$1.66*10^{-3}$	0.0036	$7.41*10^{-4}$
Conc.of 1,4 - PDA	313 K				323 K			
	Δg (g)	Rate of Δg (g / h)	AAS (g)	Rate from AAS (g/h)	Δg (g)	Rate from Δg (g / h)	AAS (g)	Rate from AAS (g/h)
Blank	0.0041	$1.82*10^{-3}$	0.0031	$1.41*10^{-3}$	0.0044	$1.25*10^{-3}$	0.0018	$5.05*10^{-4}$
$1 * 10^{-3}$	0.0041	$1.75*10^{-3}$	0.0022	$9.57*10^{-4}$	0.0038	$1.06*10^{-3}$	0.0017	$4.6*10^{-4}$
$1 * 10^{-2}$	0.0049	$2.02*10^{-3}$	0.0028	$1.19*10^{-3}$	0.0051	$1.39*10^{-3}$	0.0021	$5.76*10^{-4}$
$5 * 10^{-2}$	0.0044	$1.76*10^{-3}$	0.0023	$9.4*10^{-4}$	0.0044	$1.17*10^{-3}$	0.0018	$4.89*10^{-4}$
$1 * 10^{-1}$	0.0045	$1.74*10^{-3}$	0.0021	$8.3*10^{-4}$	0.0044	$1.14*10^{-3}$	0.0018	$4.8*10^{-4}$
$2 * 10^{-1}$	0.0035	$1.31*10^{-3}$	0.0021	$7.91*10^{-4}$	0.0045	$1.14*10^{-3}$	0.0018	$4.64*10^{-4}$

3- Arrhenius Equation:

The activation energyes and Arrhenius constants of free lead in 1 M HCl and with viarious concentrations of PDA which shown in table (3) were calculated by using Arrhenius Equation:

$k = Ae^{-Ea/RT}$ ---------- (2)

$\log k = \log A - Ea / 2.303\ RT$---------- (3)

Where: A = Arrhenius constant, k the rate constant, Ea activation energy,

T = the temperature in Kelvin, R gas constant$^{(4)}$ in two methods. Figures (2) shows Arrhenius relation from the two methods (weight losses and AAS).

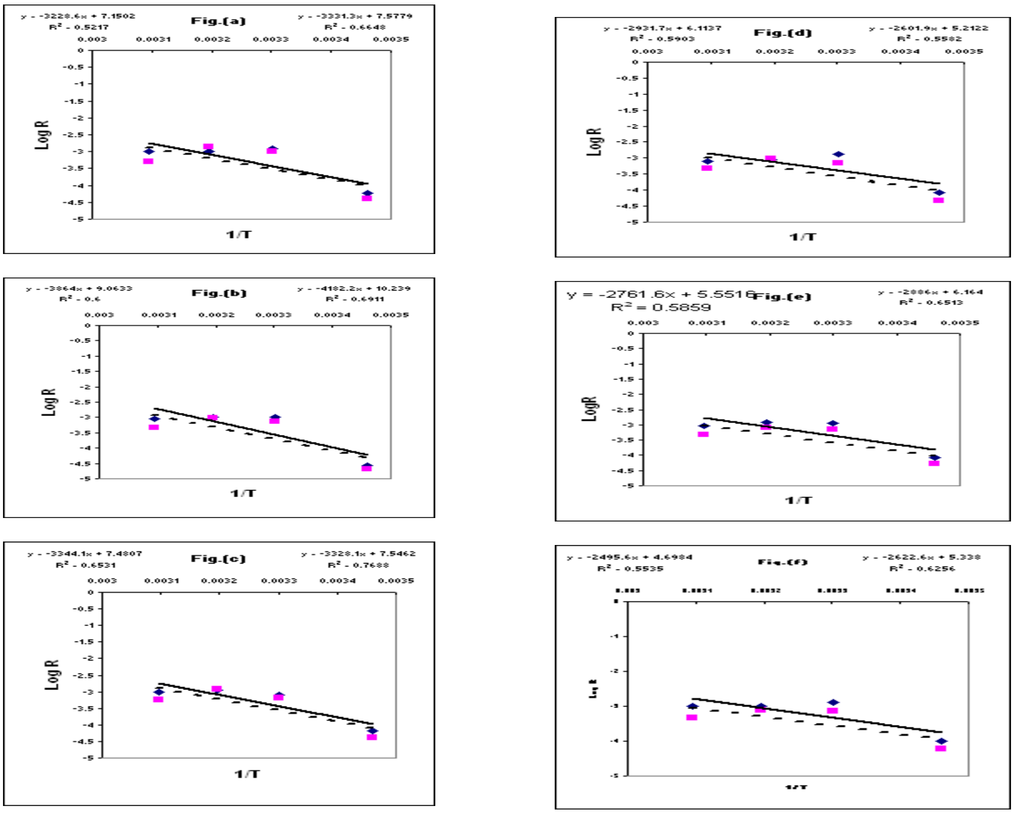


Figure (2) Arrhenius relation [log Rate against 1/T], T(K) (a) without PDA (b) with 1 x 10^{-3} M PDA (c) with 1 x 10^{-2} M PDA (d) with 5 x 10^{-2} M PDA (e) with 1 x 10^{-1} M PDA (f) with 2 x 10^{-1} M PDA , ____ from weight losses measurement, ------- from AAS measurement.

Table 3.Values of activation energy Arrhenius constant calculated from weight losses and (AAS) measurement

Conc. of 1,4 -PDA	Ea Δg (kJ)	Log A	A	Ea AAS (kJ)	Log A	A
Blank	72.4823	7.5749	37575087	62.5235	7.1474	140410631
1 * 10^{-3}	87.4981	10.235	1.7179 x 10^{10}	74.8461	9.0602	1.1487 x 10^{9}
1 * 10^{-2}	73.1605	7.5425	34873858	64.771	7.4775	30026174
5 * 10^{-2}	61.7679	5.2103	162293.08	56.7865	6.1112	1291814
1 * 10^{-1}	61.857	6.1614	1450106.8	53.4928	5.5494	354323.53
2 * 10^{-1}	54.5671	5.3358	216670.6	48.3409	4.6966	49727.886

Figure (3) shows the relationship between Ea and log A in the two methods (weight losses and AAS).

Figure (3) relation (log A against activation energy kJ) (a) from weight losses measurement, (b) from AAS measurement.

4- Entropy of activation:

The entropy of activation (ΔS*) for the corrosion of lead in 1M HCl solution containing various concentrations of PDA was calculated by the equations (3) .

$$A = \frac{kT}{h} \cdot e^{\Delta S^*/R}$$

$$\Delta S^* = (\log A - \log kT/h)\, 2.303R \text{ --- (5)}$$

Where A pre-experimental factor (Arrhenius constant)

k is Boltzman constant
h is blank constant
R is gas constant
T temperature (K)

The entropy of activation calculated in both Methods is shown in table (4).

Table 4. Values of entropy of activation for the corrosion of lead in 1M HCl solution with different concentrations of PDA at temperature ranging (289 – 323)K

Conc.of 1,4 -PDA	293 K		303 K		313 K		323 K	
	ΔS^* (J) Δg	ΔS^* (J) AAS	ΔS^* (J) Δg	ΔS^* (J) AAS	ΔS^* (J) Δg	ΔS^* (J) AAS	ΔS^* (J) Δg	ΔS^* (J) AAS
Blank	-99.58923	-107.8224	-99.98261	-108.1718	-100.2526	-108.4418	-100.5141	-108.7033
$1*10^{-3}$	-48.63368	-71.14813	-49.03026	-71.54151	-49.30025	-71.81150	-49.5617	-72.0730
$1*10^{-2}$	-100.1962	-101.4503	-100.5895	-101.8437	-100.8595	-102.1137	-101.1211	-102.3752
$5*10^{-2}$	-144.8855	-127.9509	-145.2789	-128.0178	-145.5489	-128.2877	-145.8104	-128.5493
$1*10^{-1}$	-126.6613	-138.3870	-127.0547	-138.7803	-127.3246	-139.0503	-127.5862	-139.3119
$2*10^{-1}$	-142.4768	-154.7233	-142.8702	-155.1166	-143.1402	-155.3866	-143.4017	-155.6482

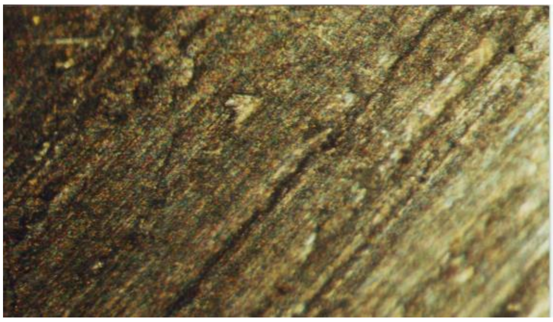
5- Depolarization of H_2 evolution:

The addition of PDA at various concentration case a decrease in the hydrogen evolution which called (Depolarization of H_2). Table (5) shows the percentage decreasing of H_2 evolution for the corrosion of lead in 1 M HCl solution with $5*10^{-2}$ M PDA at 60 C^{o}.

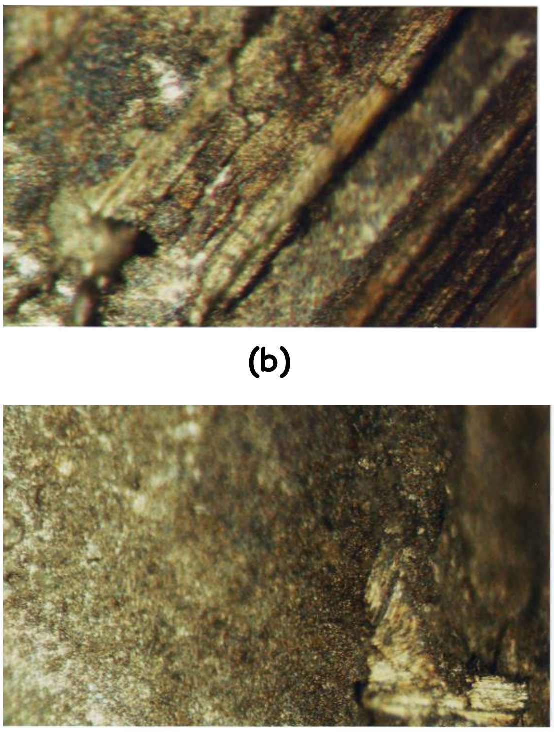
Δg (g) Blank	Δg (g) with $5*10^{-2}$ Conc. of 1,4 -PDA	Time (min)	V (ml) Blank	V (ml) with $5*10^{-2}$ Conc. of 1,4 -PDA	Decreasing % of H_2 evolution
0.0060	0.0035	2	3	2	66.66
		3	4	3	75.00
		5	6	5	83.33
		10	6.8	6	88.23
		15	6.8	6.2	91.17
		20	6.8	6.2	91.17

6- SM analysis:

The surface morphology analysis (SMA) of lead surface was studied by (polarized microscope lights) type (ortho plan). Figure (4a) shows the SMA photograph of lead before corrosion. The SMA taken after corrosion in 1M HCl solution without 1,4-PDA and with 5 x 10^{-2} 1,4-PDA is shown in Figure (4b) and (4c) the surface of lead covered with needle – link deposits, due to the adsorption of PDA, while in the case of absence of PDA (4b) the surface of lead is fragile and brittle due to the penetration of hydrogen, which be like a pit in figure (4b).



(a)



(b)

(c)

Figure 4. SMA micrograph (with magnify x 500) of lead surface taken (a) before corrosion (b) after corrosion in 1 M HCl solution without PDA (c) with 5 x 10^{-2} M PDA.

Conclusion:

The overall reaction during the corrosion of lead in acidic solution is as follows:

$$Pb + 2H^{+} \longrightarrow Pb^{2+} + H_2 \uparrow$$

Which is the sum of the galvanic reaction (5).

Anodic (6) $pb \longrightarrow pb^{+} + e$

$$Pb^{+} \xrightarrow[r.d.s]{} pb^{2+} + e$$

cathodic: (4)

$$H^{+} + e \longrightarrow H_{ads}$$

$$H_{ads} + H_{ads} \xrightarrow[r.d.s]{} H_2 \uparrow$$

(r.d.s = rate determining step)

The anodic and cathodic mechanisms effected with phenylendiamene (PDA) additions , where protonated nitrogen containing compounds the hydrogen evolution by increasing the hydrogen over voltage on the corroding metal. (8,9) The protonated – containing organic compounds act as inhibitors for some metaly like zinc and iron (10-13) , or as accelerator for other metals like lead and copper (14) because this protonated species increase the anodic and cathodic corrosion reaction by changing the (r.d.s) the activation energy of the (v.d.s)

The rate of pickling in Hcl solution increase considerably with temperature increased . however copious evolution of hydrogen gas at the surface of metal were occurred , and the diffusion of the gas into the surface of the metal case to the pentration of hydrogen and the metal becomes fragile and brittle .Hydrogen evolution also leads to formation at metal surface of socalled etch bubbles .

For the prevention of the above characteristic pit falls in chemical pickling it is recommended that certain organic and inorganic compounds , knows as etching additions , should be added to HCl solutions .

Some workers consider that they are present in the pickling solution in a colloidal form and are adsorbed on to the surface of the metal , thus protecting the latter from further attack by the acids ; other authors consider the retarding action of addition agents on the solubility of ametal in acids to be due to their ability to increase the hydrogen over voltage on the metal (15).

The rate of dissolution of metal increase while hydrogen evolution decrease that due to the displacement of protonated species instead of hydrogen ions . In recent years attempts have been made to understand the nature of the interaction between the additives and the metal surface in term of adsorption isotherms(10, 14). The experimental results shows the strong interaction between the metal surface and protonated (PDA) to increase the corrosion rate by decreasing the activation energy Ea and increase Arrhenius constant A , and the different in the (r.d.s) be clear by make comparison between the values of the entropy of activation (ΔS *) which varied from (-48.63 J) to (-155.65 J) when PDA was present (16) at temperature rang (20-60) C°.

The negative ΔS * values due to the increasing of the organization of transition state during corrosion process. In the presence of high concentrations of PDA, values of ΔS * be more negative, that indicate to the more organization of transition state than the case of transition state with absence of PDA.

A similar mechanism has been proposed by Hacker man and Kacsche (17) and by Jalal Mohammed saleh and Khulood Abid Saleh(18). The mechanism of action of few organic compounds containing nitrogen atom was suggested by Shanthamna and others (2) .

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تأثير إضافة 1،4- فنيل ثنائي أمين على سرعة تآكل الرصاص في محلول حامض الهيدروكلوريك 1 مولاري

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الخلاصة:

تمت دراسة تأثير إضافة 1،4- فنيل ثنائي أمين في زيادة سرعة تآكل الرصاص في محلول 1 مولاري حامض الهيدروكلوريك وفي المدى الحراري (20- 60) م° .

وتمت الدراسة بمتابعة فرق الوزن للرصاص بعد أزمان تراوحت (1- 260) ساعة مع متابعة الزيادة في تركيز أيونات الرصاص النازلة الى محلول الحامض بعد أزمان مختلفة باستخدام مطيافية الأمتصاص الذري (AAS) .

كما وتم متابعة حجم الهيدروجين المتحرر كنتيجة لتآكل الرصاص في محلول حامض الهيدروكلوريك 1 مولاري بوجود وبغياب 1،4- فنيل ثنائي أمين.

كما تمت دراسة تأثير وجود بعض ألاملاح (NaI , NaBr NaCl ,) في تعجيل تآكل الرصاص في محلول حامض الهيدروكلوريك.