

The Effect of Temperature on the Corrosion of Mild Steel in H_3PO_4 Containing Halides and Sulfate Ions

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The corrosion behaviour of mild steel in phosphoric acid solution in the presence and absence of pollutants viz. Chloride, Fluoride and Sulfate ions at 302K-333K was studied using mass loss and potentiostatic polarization methods. The addition of chloride and sulfate ions inhibits the mild steel corrosion in phosphoric acid while fluoride ions stimulate it. The effect of temperature on the corrosion behaviour of mild steel indicated that inhibition of chloride and sulfate ions decreased with increasing temperature. The adsorption of these ions (Chloride and sulfate) on the mild steel surface in acid has been found to obey Langmuir adsorption isotherm. The values of activation energy (E_a) and free energy of adsorption (ΔG_{ads}) indicated physical adsorption of these ions (chloride and sulfate) on the mild steel surface. The plot of $\log W_t$ against time (days) at 302K gives a straight line, which suggested that it obeys first order kinetics and also calculate the rate constant k and half-life time $t_{1/2}$.

Keywords : mild steel, phosphoric acid, halides, sulfate, polarization, corrosion inhibition

1. Introduction

Phosphoric acid is a major chemical product, which has many important uses, especially in the production of fertilizers. Most of the acid is produced from phosphate rock by wet process. Generally Nickel-base alloys and stainless steel are frequently used in many parts of the wet process and a considerable quantity of data has been published about the resistance of these materials to corrosion by phosphoric acid solution.¹⁾⁻⁵⁾ Fluorides, chlorides and sulfuric acid are the main impurities present in the manufacturing processes of phosphoric acid.⁶⁾ Many publications address the influence of these impurities on the corrosion resistance of alloy.⁷⁾⁻¹²⁾ The effect of chloride on the dissolution of iron and steel is widely studied.¹³⁾⁻¹⁹⁾ But very few studies have been reported on the effect of other ions.²⁰⁾⁻²²⁾ Hence, attempts have been made in this investigation to study the effect of chloride, sulfate and fluoride in the concentration range of 100 ppm to 500 ppm on the corrosion behaviour of mild steel in 1 N and 5 N phosphoric acid by mass loss and potentiostatic polarization methods at 302K to 333K.

2. Experimental:

2.1 Mass loss measurement:

Mild steel specimens were cut to the size of 5 cm x 1 cm from the mild steel sheets having the following percentage composition Fe = 99.686, Ni = 0.013, Mo = 0.015, Cr = 0.043, S = 0.014, P = 0.009, Si = 0.007, Mn = 0.196, C = 0.017. Mass loss measurements were performed as per ASTM method described previously.²³⁾⁻²⁵⁾ Mass loss measurements were carried out in 1 N and 5 N concentration of phosphoric acid with pollutants like chloride, fluoride and sulfate in the concentration range of 100 ppm to 500 ppm at 302 K to 333 K for an immersion period of 5 hours with and without pollutants. All the solutions were prepared using AR grade chemicals with double distilled water.

2.2 Potentiostatic polarization measurement:

Polarization measurements were carried out in a conventional three-electrode cell assembly. Mild steel strips of same composition coated with lacquer with on exposed area of 1 cm² were used as working electrode. The saturated calomel electrode and the platinum foil were used as reference and counter electrode respectively. The potentiostatic polarization was carried out using BAS-100A

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model instrument and the experiments were carried out at 302K to 333K.

3. Results and discussion:

3.1 Mass loss studies:

The values of corrosion rate, surface coverage (θ) and inhibition efficiency (IE%) obtained from mass loss studies are given in Table 1, 2 and 3. The rate of corrosion

Table 1. Calculated corrosion rate, Inhibition efficiency (IE%) and surface coverage (θ) values for chloride from mass loss data in 1N and 5N H₃PO₄.

Temp. (°K)	Conc. Of chloride (ppm)	1N			5N		
		Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	-	-	26.22	-	-
	100	5.13	0.2444	24.44	20.19	0.2297	22.97
	200	4.66	0.3140	31.40	18.59	0.2911	29.11
	300	4.45	0.3450	34.50	17.83	0.3198	31.98
	400	4.09	0.3989	39.89	16.34	0.3767	37.67
	500	3.41	0.4989	49.89	14.92	0.4311	43.11
313	Blank	11.93	-	-	70.22	-	-
	100	9.28	0.2217	22.17	56.07	0.2014	20.14
	200	8.45	0.2912	29.12	51.17	0.2712	27.12
	300	8.09	0.3212	32.12	50.09	0.2866	28.66
	400	7.41	0.3789	37.89	45.56	0.3512	35.12
	500	6.69	0.4389	43.89	41.48	0.4092	40.92
333	Blank	19.82	-	-	157.39	-	-
	100	16.08	0.1897	18.97	130.98	0.1672	16.72
	200	15.09	0.2398	23.98	122.59	0.2211	22.11
	300	14.36	0.2766	27.66	117.81	0.2515	25.15
	400	13.07	0.3412	34.12	108.74	0.3091	30.91
	500	12.08	0.3912	39.12	100.46	0.3617	36.17

Table 2. Calculated corrosion rate, Inhibition efficiency (IE%) and surface coverage (θ) values for sulfate from mass loss data in 1N and 5N H₃PO₄.

Temp. (°K)	Conc. Of Sulfate (ppm)	1N			5N		
		Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)	Corrosion Rate (mmpy)	Surface coverage (θ)	Inhibition efficiency (IE%)
302	Blank	6.80	-	-	26.22	-	-
	100	5.23	0.2310	23.10	20.72	0.2097	20.97
	200	4.76	0.3000	30.00	19.14	0.2699	26.99
	300	4.59	0.3248	32.48	18.35	0.3001	30.01
	400	4.28	0.3699	36.99	16.75	0.3610	36.10
	500	3.90	0.4276	42.76	15.47	0.4097	40.97
313	Blank	11.93	-	-	70.22	-	-
	100	9.44	0.2087	20.87	56.90	0.1897	18.97
	200	8.69	0.2711	27.11	52.19	0.2567	25.67
	300	8.32	0.2019	20.19	51.87	0.2612	26.12
	400	7.74	0.3511	35.11	46.97	0.3311	33.11
	500	6.96	0.4167	41.67	43.43	0.3815	38.15
333	Blank	19.80	-	-	157.39	-	-
	100	16.40	0.1697	16.97	133.81	0.1498	14.98
	200	15.47	0.2188	21.88	124.81	0.2070	20.70
	300	14.71	0.2572	25.72	120.07	0.2371	23.71
	400	13.43	0.3215	32.15	111.95	0.2887	28.87
	500	12.34	0.3766	37.66	102.67	0.3477	34.77

Table 3. Calculated corrosion rate values for fluoride from mass loss data in 1N and 5N H₃PO₄.

Conc. Of chloride (ppm)	1N			5N		
	Rate of corrosion (mmpy)					
	302K	313K	333K	302K	313K	333K
Blank	6.80	111.93	19.82	26.49	70.22	157.39
100	7.91	14.01	23.58	31.13	83.39	189.04
200	8.85	15.75	26.75	35.01	94.17	214.32
300	9.93	17.67	29.88	39.15	104.60	237.94
400	10.63	18.98	32.33	42.15	113.66	257.76
500	11.29	20.15	33.88	44.70	119.86	272.44

Table 4. Calculated values of activation energy Ea (KJ/mole), free energy of adsorption (ΔG_{ads}), rate constant k (Time⁻¹) and half-life t_{1/2} (time) for mild steel corrosion in 1N and 5N phosphoric acid with chloride and sulfate.

Pollutants	Conc. of pollutants (ppm)	Ea from Eqn.1 (KJ/mole)	Ea from Arrhenius plot (KJ/mole)	- ΔG_{ads} (KJ/mole)			Rate constant k X 10 ⁻⁶ (Sec ⁻¹)	Half -life t _{1/2} (Sec)
				302K	313K	333K		
Chloride + 1N H ₃ PO ₄	Blank	28.90	28.72	-	-	-	5.73	120934
	100	30.90	30.64	20.74	21.16	21.97	5.33	129997
	200	31.70	31.59	19.87	20.31	20.88	5.14	134706
	300	31.60	31.20	19.20	19.62	20.29	4.98	139018
	400	31.40	31.40	19.06	19.53	20.32	4.77	145255
	500	34.30	34.46	19.52	19.60	20.31	4.56	152047
Sulphate + 1N H ₃ PO ₄	Blank	28.83	28.72	-	-	-	5.73	120934
	100	30.86	30.64	23.33	23.84	24.65	5.30	130645
	200	31.79	30.63	22.48	22.93	23.61	5.06	136823
	300	31.41	30.55	21.75	22.66	23.07	4.87	142084
	400	30.85	30.39	21.53	22.10	23.14	4.66	157213
	500	31.11	30.60	21.57	22.24	23.20	4.48	154759
Chloride + 5N H ₃ PO ₄	Blank	48.40	47.87	-	-	-	22.82	30369
	100	50.50	49.21	20.53	20.84	21.54	21.19	32702
	200	50.90	50.93	19.60	20.05	20.58	20.10	34482
	300	51.00	51.12	18.92	19.20	19.92	19.45	35614
	400	51.20	51.31	18.82	19.22	19.92	19.08	36314
	500	51.50	51.50	18.83	19.28	19.96	18.13	38232
Sulphate + 5N H ₃ PO ₄	Blank	48.35	48.74	-	-	-	22.82	30369
	100	50.33	50.38	23.01	23.53	24.24	21.06	32910
	200	50.59	50.19	22.11	22.73	23.41	19.99	34664
	300	50.68	50.14	21.46	21.74	22.77	19.24	35804
	400	51.25	51.06	21.43	21.87	22.72	18.92	36616
	500	51.62	51.44	21.39	21.86	22.85	17.99	38517

increased with the increase in acid concentration and temperature from 302 K to 333 K. The addition of chloride and sulfate ions inhibits the mild steel corrosion in phosphoric acid while fluoride ions stimulate it.^{26,33} It is shown in the table 1, 2 and 3. It clearly indicates that addition chloride and sulfate to the acid has reduced the corrosion rate. The inhibition efficiency for chloride and sulfate increases with the increase in concentration and

decreases with the increase in temperature from 302 K to 333 K^{27,29,30} and in acid concentration from 1 N to 5 N.

Table 4 shows the calculated values of activation energy Ea (KJ/mole), free energy of adsorption ΔG_{ads} (KJ/mole), rate constant k (Sec⁻¹) and half-life t_{1/2} (Sec) for mild steel corrosion in 1 N and 5 N phosphoric acid with chloride, sulfate and fluoride. Energy of activation Ea has been calculated from the slopes of plot log corrosion rate (CR)

versus 1/T in Fig. 1 and 2 for chloride (Similar plots were also obtained for sulfate) and also with the help of the Arrhenius equation.^{27),29),31)}

$$\log \frac{p_2}{p_1} = \frac{Ea}{2.303R} \left[\frac{1}{T_1} - \frac{1}{T_2} \right] \quad (1)$$

Where p₁ and p₂ are the corrosion rate at temperature T₁ and T₂ respectively. Ea values given in Table 4 show that the Ea values for the corrosion of mild steel in 1N and 5N phosphoric acid are 28.86 KJ/mole and 48.34 KJ/mole respectively. The Ea values are found to be higher than that of the uninhibited system. The values of Ea calculated from the slopes of Arrhenius plot and using equation (1) are approximately almost similar.

The values of free energy of adsorption ΔG_{ads} were calculated with the help of the following equation³²⁾

$$\Delta G_{ads} = -RT \ln(55.5K) \quad (3)$$

and k is given by

$$K = \theta / C(1 - \theta) \quad (4)$$

Where θ is surface coverage, C is the concentration of pollutants in (mole/l) and K is the equilibrium constant.

The values of ΔG_{ads} obtained indicate that the spontaneous adsorption of the inhibitor and are usually chara-

acteristics of strong interaction with the metal surface. It is found that the ΔG_{ads} values are less than (less - ve values) -40 KJ/mole indicating that inhibitors are physically adsorbed on the metal surface.^{27),32)}

The values of rate constant k were evaluated from the plots of logW_f versus time (days) in Fig. 3 and 4 for chloride (similar plots were also obtained for sulfate). Linear plots were obtained which revealed first order kinetics. The values of half-life t_{1/2}(sec) were calculated using the equation below

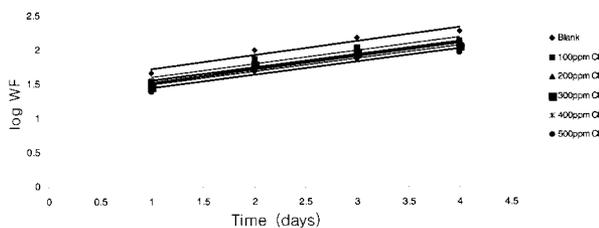


Fig. 3. Plot of log WF Versus time(days) for 1N H₃PO₄ with chloride

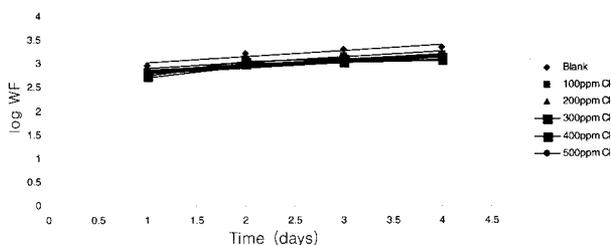


Fig. 4. Plot of log WF Versus time(days) for 5N H₃PO₄ with chloride

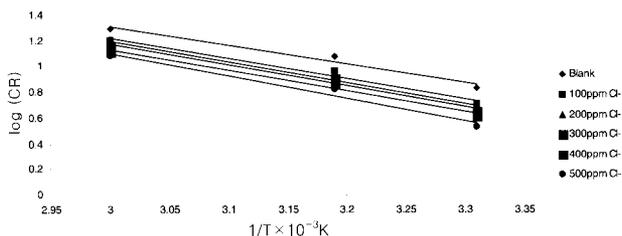


Fig. 1. Arrhenius plot for 1N H₃PO₄ with chloride

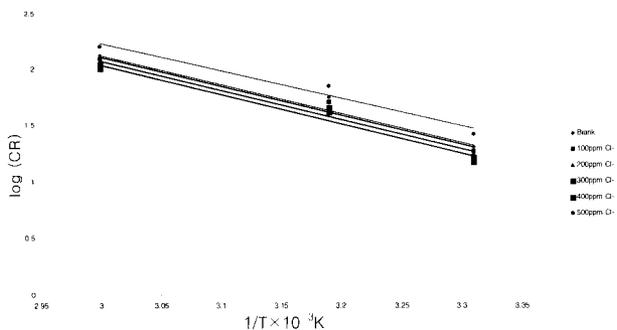


Fig. 2. Arrhenius plot for 5N H₃PO₄ with chloride

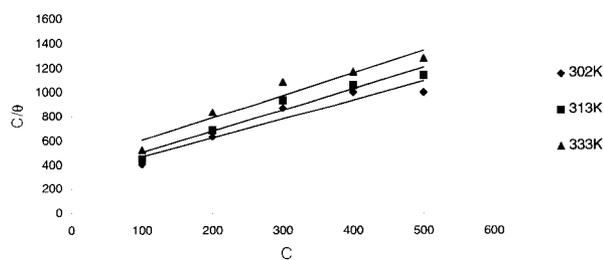


Fig. 5. Langmuir adsorption isotherm plot for 1N H₃PO₄ with chloride

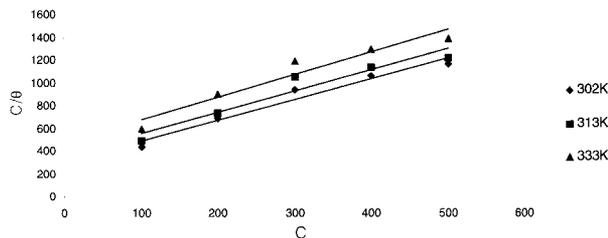


Fig. 6. Langmuir adsorption isotherm plot for 5N H₃PO₄ with chloride

Table 5. Electrochemical polarization parameters for the corrosion of mild steel in 1N and 5N phosphoric acid in absence and presence of halides and sulfate ions at 302K-333K.

Conc. Of pollutants (ppm)	1N					5N				
	E _{corr} V _s SCE(mV)	I _{corr} μ A/cm ²	Tafel Constants (mV/decade)		IE%	E _{corr} V _s SCE(mV)	I _{corr} μ A/cm ²	Tafel Constants (mV/decade)		IE%
			ba	-bc				ba	-bc	
302K										
Blank	-543	210	50	130	-	-510	700	50	150	-
100 Cl ⁻	-540	180	50	125	14.29	-505	625	50	145	10.71
200 Cl ⁻	-537	150	40	110	28.57	-505	570	35	150	18.57
300 Cl ⁻	-533	137	35	105	34.76	-498	510	35	140	25.71
400 Cl ⁻	-542	130	45	95	38.09	-497	480	30	130	31.43
500 Cl ⁻	-538	210	35	90	42.86	-503	450	35	125	35.71
Blank	-543	210	50	130	-	-510	700	50	150	-
100 SO ₄ ²⁻	-562	185	50	127	11.90	-556	627	55	147	10.42
200 SO ₄ ²⁻	-555	154	45	117	26.66	-551	586	39	142	16.28
300 SO ₄ ²⁻	-550	144	40	110	31.43	-547	544	37	140	22.28
400 SO ₄ ²⁻	-548	136	40	100	35.23	-544	496	35	135	29.14
500 SO ₄ ²⁻	-545	127	37	95	29.52	-541	475	36	132	32.14
Blank	-543	210	50	130	-	-510	700	50	150	-
100 F ⁻	-510	215	55	130	-	-549	712	52	150	-
200 F ⁻	-505	217	55	135	-	-545	717	55	151	-
300 F ⁻	-507	220	60	137	-	-543	720	60	154	-
400 F ⁻	-498	223	64	140	-	-538	725	60	157	-
500 F ⁻	-490	226	68	144	-	-536	727	62	160	-
313K										
Blank	-535	680	100	150	-	-505	1000	30	175	-
100 Cl ⁻	-530	597	95	148	12.20	-500	908	35	170	9.20
200 Cl ⁻	-527	507	94	144	25.44	-497	831	33	168	16.90
300 Cl ⁻	-525	468	95	140	31.18	-495	769	35	165	23.10
400 Cl ⁻	-522	441	90	138	35.15	-490	696	39	160	30.40
500 Cl ⁻	-520	414	85	134	29.12	-488	668	40	156	33.20
Blank	-535	680	100	150	-	-505	1000	30	175	-
100 SO ₄ ²⁻	-555	617	97	149	9.26	-544	913	35	172	8.70
200 SO ₄ ²⁻	-550	517	95	147	23.97	-540	853	30	169	14.70
300 SO ₄ ²⁻	-547	481	94	144	29.26	-537	798	32	166	20.20
400 SO ₄ ²⁻	-544	455	92	140	33.08	-535	729	34	163	27.10
500 SO ₄ ²⁻	-542	429	90	137	36.91	-530	696	35	160	30.40
Blank	-535	680	100	150	-	-505	1000	30	175	-
100 F ⁻	-502	682	99	154	-	-545	1007	30	177	-
200 F ⁻	-400	685	100	156	-	-535	1016	30	178	-
300 F ⁻	-498	687	100	157	-	-532	1022	29	180	-
400 F ⁻	-495	689	98	160	-	-530	1025	30	182	-
500 F ⁻	-492	691	101	165	-	-544	1030	30	184	-
333K										
Blank	-523	1400	150	150	-	-483	3000	75	190	-
100 Cl ⁻	-520	1271	148	145	9.21	-480	2813	70	188	6.23
200 Cl ⁻	-520	1116	140	142	20.29	-474	2597	70	186	13.43
300 Cl ⁻	-518	1026	135	140	26.71	-470	2388	68	183	20.40
400 Cl ⁻	-516	963	132	137	31.21	-465	2186	65	180	27.13
500 Cl ⁻	-514	944	130	135	35.42	-463	2096	64	176	30.13
Blank	-523	1400	150	150	-	-483	3000	75	190	-
100 SO ₄ ²⁻	-546	1313	145	148	6.20	-540	2837	70	189	5.43
200 SO ₄ ²⁻	-542	1131	143	145	19.21	-533	2666	73	187	11.13
300 SO ₄ ²⁻	-539	1048	140	144	25.14	-530	2490	72	188	17.00
400 SO ₄ ²⁻	-534	980	138	142	30.00	-526	2276	70	185	24.13
500 SO ₄ ²⁻	-530	946	135	140	32.42	-524	2191	69	180	26.97
Blank	-523	1400	150	150	-	-482	3000	75	190	-
100 F ⁻	-497	1407	150	152	-	-538	3004	75	190	-
200 F ⁻	-494	1412	149	155	-	-534	3010	76	192	-
300 F ⁻	-492	1417	150	157	-	-530	3013	75	195	-
400 F ⁻	-490	1422	151	158	-	-529	3017	76	197	-
500 F ⁻	-483	1429	150	160	-	-525	3020	76	198	-

$$t_{1/2} = 0.693/k \quad (5)$$

The rate constant k decreases with increase in concentration of pollutants (chloride and sulfate) where as the half-life increases with concentration of pollutants (chloride and sulfate).²⁷⁾

3.2 Application of adsorption isotherm:

The values of C/θ in the plot in Fig. 5 and 6 evaluated directly from equation for chloride (similar plot was also obtained for sulfate). It was found that the experimental data obtained within the temperature range 302K-333K fits Langmuir adsorption isotherm, which is given by

$$C/\theta = 1/b + c \quad (6)$$

Where C is the inhibitor concentration and θ is the surface coverage.

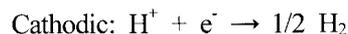
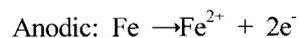
3.3 Potentiostatic polarization studies:

From potentiostatic polarization studies, the corrosion parameters deduced from Tafel curves such as corrosion current i_{corr} , corrosion potential E_{orr} , Tafel slopes ba and $-bc$ and inhibition efficiency are given in Table 5 for mild steel in 1N and 5N phosphoric acid with and without chloride and sulfate ions at 302K-333K. It is observed that in the presence of chloride and sulphate decreases the i_{corr} values. But in the presence of fluoride increases the i_{corr} value.

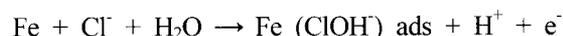
3.4 Mechanism of inhibition:

Stabilization of adsorbed pollutant ions (chloride and sulfate) on the metal surface gives the inhibition efficiency. Pollutants are good ligands (chloride and sulphate) because they exhibit low electro negativity (less than 3.5) except fluoride ion (Electronegativity of F^- is 4.0)^{34,35)} while atomic radius of fluoride ion is very small and also electron affinity less than that of chloride and sulfate. The small size of fluoride ions with its high electron density makes the addition of electrons energetically less favorable than chloride and sulfate. In spite of the fact that fluoride ion has lower electron affinity³⁷⁾ than chloride and sulfate is a better oxidizing agent than chloride and sulfate. So the pollutants chloride and sulfate ions inhibit the mild steel corrosion in phosphoric acid while fluoride ions stimulate it. The inhibiting effect of pollutants (chloride and sulfate) can be explained as due to adsorption of pollutants according to mechanism given below.

The corrosion of steel in acidic solution is the sum of the following reactions.



However, each of the reactions proceeds with many consecutive steps depending on the pH and the type of anion present in the solution. There are two main theories based on the works of Heusler¹⁴⁾ and Bockris.¹⁵⁾ Both theories indicate the participation of $(\text{OH})^-$ ions directly. Anodic dissolution of iron in acidic solution could be written as



Adsorption of pollutant ions (chloride and sulphate) on the electrode surface affects the kinetic dissolution of mild steel.^{17),18),19)} Hackerman et. al²¹⁾ suggested that the pollutant ions (chloride and sulfate) interaction with the metal surface possibly through chemisorption's. Anion adsorption is found to be chloride and sulfate. Moreover the lower corrosion rate for mild steel in phosphoric acid containing pollutants (chloride and sulfate) might be due to the formation of $\text{Fe}(\text{OH})_{\text{ads}}$ species where as in phosphoric acid free from pollutants, only hydroxide ions are involved and so the formation of $[\text{Fe}(\text{OH})]_{\text{ads}}$.²¹⁾

4. Conclusion:

On the basis of the studies the following conclusions can be drawn.

1. The corrosion rate of mild steel is more in phosphoric acid free from pollutants (chloride and sulfate)
2. The pollutants chloride and sulfate ions inhibit the mild steel corrosion in phosphoric acid while fluoride ions stimulate it.
3. The effect of temperature on the corrosion behaviour of mild steel indicated that inhibition of pollutants decreased with increasing temperature.
4. The inhibition efficiency decreased with increasing concentration of phosphoric acid.
5. From the values of activation energy E_a , the inhibition was probably due to the adsorption of pollutants (chloride and sulfate) on the metal surface.
6. The ΔG_{ads} values were negative which suggest that they were strongly adsorbed on the metal surface. The values of ΔG_{ads} indicated the spontaneous adsorption of pollutants (chloride and sulfate) and were usually characteristic of strong adsorption with metal surface.
7. Pollutants (chloride and sulfate) were found to obey

Langmuir at all the concentrations.

8. In the kinetics studies, linear plots were obtained which revealed first order kinetics.

Acknowledgement

We thank Dr. K. Srinivasan, Head of the Department, Govt. College of Engineering, Salem-11 for his kind encouragement in pursuing this work.

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