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Effect Of Different Phenols On Aluminum Corrosion In Alkaline Medium

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ABSTRACT

Inhibition of aluminum corrosion in NaOH solution by phenol, o-cresol, p-cresol, p-aminophenol and p-chlorophenol has been studied using weight-loss and hydrogen evolution methods. It is found that the inhibition efficiency depends on the type of phenols as well as its concentration. The order of increasing inhibition is as follows p-aminophenol>p-chlorophenol>O-cresol>P-cresol>phenol thermodynamic parameters were calculated.

KEYWORDS

Pulsincap;
Colon target;
Pulsatile drug delivery;
Arthritis;
Micro sponge;
Indomethacin.

INTRODUCTION

Aluminum is an important and commonly used metal for construction in the industry, especially in its anodized form. It is reactive and is susceptible to corrosion very easily, although it develops an oxide coatings or film that protects it from corrosion in various environments[1-2]. This film is stable in neutral and acidic solution but is attacked by alkali. It has been observed[3-9] that several organic compounds including surface active agents possess corrosion property for different metals in acidic medium. The study of the corrosion of aluminum in different aggressive environments has continued to attract considerable attention[10-17] because of the many important applications of the metal. Aluminum is known to exhibit passive behaviour in aqueous solutions. The corrosion of the metal has been reported to depend on processes associated with the passivating surface oxide film such as metal ion transfer to the metal/oxide interface, metal ion and oxygen ion transfer to the oxide/solution interface, ion migration in the oxide film, and electron transfer from the metal to acceptor species in solution[18]. Variety of organic compounds[9-21] have been investigated as inhibitors of metallic corrosion in different aqueous media in efforts to obtain more efficient inhibitors and to further elucidate the mechanisms of the inhibition process[19-21]. The inhibition abilities of such compounds have attributed to the presence of pi-electron systems as well as polar N, S or O atoms as active centers for the adsorption of the organic molecules to the metal surface[22-24].

Corrosion of metals in different media and environments is one of the serious problems facing industry. Different methods such as paining-plating and alloying have been used to prevent corrosion. However, technological and financial consideration sometimes favor the addition of some chemical substances called inhibitors to the medium in order to reduce the rate of corrosion. The use of organic inhibitors in either acid or alkaline solution is common particularly in case of high corrosion rate.

The inhibition of corrosion and its alloys in different corrosion media has been subject of numerous investigations[25-26]. The decrease in the corrosion rate is attributed to physical and chemical adsorption[27-29], but the mechanism of action of inhibitor is controversial and might involve interference with the anodic and/or cathodic partial reaction[30,31].

Corrosion of aluminum in acid or alkaline solution can be inhibited by the addition of certain inhibitors[32] to adsorption of the inhibitor molecules on the metal surface forming a protective layer. The extent of the adsorption of an inhibitor depends on many factors[33]. The nature of metal, the mode of adsorption and the surface condition of metal.

The aim of this work is to study the effect of phenol derivatives on corrosion behavior of Al in basic media at 25^0C using weight loss method and gasometric techniques.

EXPERIMENTAL

The dissolution rates of aluminum were determined by weight loss and geometry techniques[34]. The specimen used is aluminum rod of cross section $30.7cm^3$ with the chemical composition given in TABLE 1.

Before using the specimen, it was mechanically polished then etched in alkaline solution (15g Na_2CO_3+15g of Na_3PO_4). Etching was conducted at 353.3k for 30 sec. The specimen was then rinsed with distilled water then dried up. Analar BDH grade of phenol, O-cresol, P-cresol, p-aminophenol and p-chlorophenol were used.

TABLE 1 : Chemical composition of Al

Element	Al	Fe	Si
Amount %	99.6	0.16	0.22

Gasometric method

Al specimen(rods of cross section $30.7cm^2$ and surface area $4.7cm^2$) were mechanically polished with emery paper. Polished electrodes were degreased in CCl_4 and finally rinsed in doubly distilled water. This electrode was in a gasometric vessel[34] containing the solution under investigation and the volume of hydrogen gas evolved was measured as a function of time. The % inhibition was calculated using equation (1):

$$\% \text{ inhibition} = 100(1-R/R_0) \qquad (1)$$

Where R and R_0 are the corrosion rates in presence and absence of the inhibitor respectively.

Weight loss method

100ml of the inhibitor solution was taken in the reaction vessel(a graduated glass vessel with 6cm inner diameter and a total volume of 250ml). Aluminum specimen of 20×20×2 mm was cleaned as described in the gasometric method. The specimen was then dried, weighed and suspended in the solution 1 cm below the surface of the solution. After specified time, the piece was taken out, rinsed with distilled water, dried and weighed. Each experiment was repeated three times with fresh sample and solution. The average weight loss was recorded.

Weight loss of the aluminum sample(in mg per cm^2 of surface area) was determined in an open system at various time intervals in absence and in presence of the inhibitors. The percentage inhibition of aluminum was calculated in each case using equation (2):

$$\%\text{Inhibition} = \frac{W_0 - W}{W_0} \times 100 \qquad (2)$$

Where W_0=weight loss in inhibitor-free solution and W=weight loss in solution containing the inhibitor.

RESULTS AND DISCUSSION

Figure 1 is a typical plot showing the variation of the volume of hydrogen evolved as a function of time when the specimen was immersed in 1M NaOH solution containing different concentrations of inhibitor at 25^0C. Weight loss vs time curves figure 2

TABLE 2 : Effect of concentration on the percentage inhibition at 25^{0}C

(2a) O-Cresol

Conc. M×10^5	% inhibition (wt loss method)	% inhibition (gasometric method)
5.25	11.4	10.2
10.53	26.3	26.5
15.8	37.1	36.8
21.04	44.2	43.2
28.40	59.6	56.7
33.70	64.2	63.2
38.95	75.1	75.3
46.3	80.1	79

(2b) O-Cresol.

Conc. M×10^5	% inhibition (wt loss method)	% inhibition (gasometric method)
5.25	22	23.0
10.53	28.3	29.1
15.8	37.0	38.1
21.04	45	44.3
28.40	52.1	51.0
33.70	60.8	60.1
38.95	65.4	65.2
46.3	68.1	69.1

(2c) Phenol

Conc. M×10^5	% inhibition (wt loss method)	% inhibition (gasometric method)
5.25	26.1	24.3
10.53	31.1	30.5
15.8	34.1	36.1
21.04	43.1	42.2
28.40	49.0	47.6
33.70	52.1	52.3
38.95	55.2	54.3
46.3	61.0	62.0

(2d) P-aminoPhenol

Conc. M×10^5	% inhibition (wt loss method)	% inhibition (gasometric method)
5.25	24.3	23.8
10.53	30.3	29.2
15.8	38.6	37.00
21.04	46.00	44.00
28.40	54.2	52.1
33.70	64	62.1
38.95	71.2	70.1
46.3	80.2	78.3

(2d) P-ChloroPhenol

Conc. M×10^5	% inhibition (wt loss method)	% inhibition (gasometric method)
5.25	16	15.5
10.53	30	27.3
15.8	40	38
21.04	45	43
28.40	65.7	60
33.70	70	68
38.95	80	77
46.3	85	81

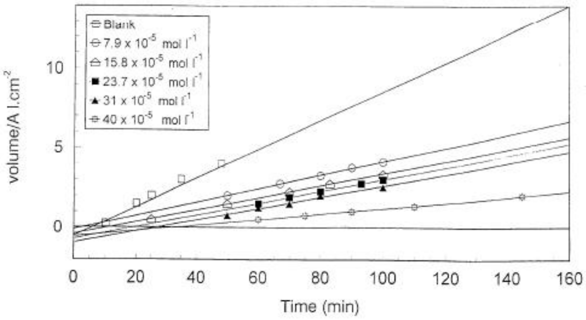

Figure 1 : Volume-time curve for P-cresol at 25^0

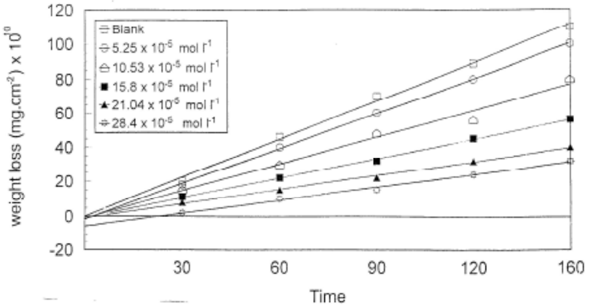

Figure 2 : Weight loss-time curve for P-cresol at 25^0

showed that the solutions containing inhibitors fall below that of free NaOH. This indicated that phenol derivatives inhibited corrosion of steel.

The protection efficiency p, of inhibitor was calculated by applying the equation

$$P = 100\,(1-R/R_0) \qquad (3)$$

Where R_0 and R are the corrosion rates in absence and presence of inhibitor respectively using gasometric technique.

TABLE 2 shows the relation between the percentage inhibition of alkaline corrosion by phenols and their concentration using gasometric technique.

Figure 3 and TABLE 2 show also that, the efficiency of the inhibitors increases in the order

p-aminophenol>p-chlorophenol>O-cresol>P-cresol>phenol

The mass loss technique was also used in order to investigate the effect of phenols on the rate of corrosion of Al in 1M-NaOH solution. Figure 3 shows the relation between the mass loss of Al and concentration of inhibitors as example. It is clear that the mass loss of Al decreases with increasing

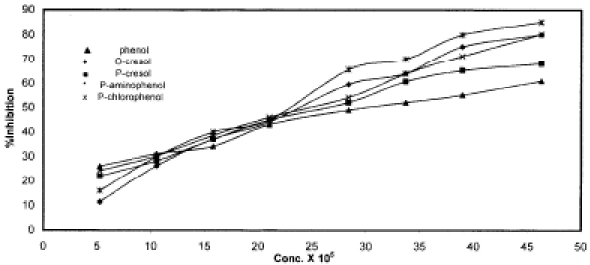

Figure 3(a) : The relation between% inhibition and concentration of phenol using weight loss method

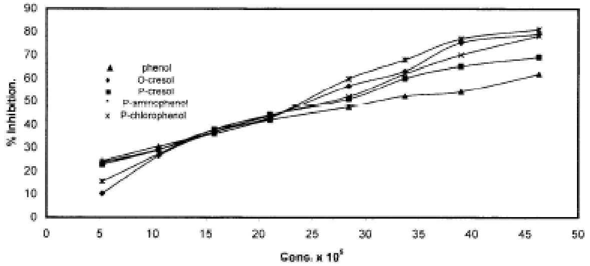

Figure 3(b) : The relation between% inhibition and concentration of phenol using Gasmetric method

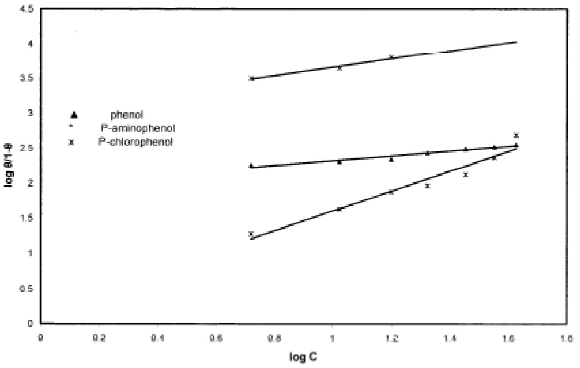

Figure 4 : The relation between log1/1-θ and log C for some derivatives at 25⁰c

the inhibitors concentration. TABLE 2 and figure 3 show that, there is a good agreement between the results obtained from both techniques (mass loss and gasometry). Figure 1, 2, 3 and TABLE 3 show that the efficiency increases in order p-aminophenol>p-chlorophenol>O-cresol>P-cresol>phenol

Figure 4 reveals that the order of inhibition efficiency in alkali solution, over most of the concentration ranges, is p-aminophenol, p-chlorophenol, O-cresol, P-cresol and phenol. The surface coverage θ was evaluated by the following equation

$$\theta = \frac{R_0 - R}{R_0} \tag{4}$$

Where R_0 and R are the corrosion rates in absence and in presence of inhibitor, respectively.

TABLE 3 : Adsorption relation for phenol derivatives at 25⁰C

(3a)o-Cresol

Conc. M×10^5	θ	1-θ	θ/1-θ	Log=θ/1-θ	Log C
5.25	0.114	0.886	0.1286	-1.1092	0.72
10.53	0.263	0.737	0.3565	-1.553	1.02
15.8	0.371	0.629	0.503	-1.702	1.20
21.04	0.442	0.558	0.792	-1.898	1.32
28.40	0.596	0.404	1.475	0.169	1.45
35.60	0.642	0.358	1.7952	0.2536	1.55
42.3	0.751	0.249	3.012	0.478	1.63

(3b) p-Cresol

Conc. M×10^5	θ	1-θ	θ/1-θ	Log=θ/1-θ	Log C
5.25	0.22	0.78	0.282	-1.45	0.72
10.53	0.283	0.717	0.395	-1.596	1.02
15.8	0.37	0.63	0.587	-1.768	1.20
21.04	0.45	0.55	0.818	-1.912	1.32
28.40	0.521	0.479	1.0899	0.0374	1.45
35.60	0.608	0.392	1.551	0.191	1.55
42.3	0.654	0.346	1.89	0.276	1.63

(3c) Phenol

Conc. M×10^5	θ	1-θ	θ/1-θ	Log=θ/1-θ	Log C
5.25	0.261	0.729	0.358	0.261	0.72
10.53	0.311	0.689	0.451	0.311	1.02
15.8	0.341	0.651	0.523	0.341	1.20
21.04	0.431	0.569	0.757	0.431	1.32
28.40	0.49	0.510	0.960	0.49	1.45
35.60	0.52	0.480	1.083	0.52	1.55
42.3	0.552	0.448	1.232	0.552	1.63

(3d) pϖ-aminoPhenol

Conc. M×10^5	θ	1-θ	θ/1-θ	Log=θ/1-θ	Log C
5.25	0.24	0.76	3.167	1.5005	0.72
10.53	0.303	0.697	0.4353	1.638	1.02
15.8	0.385	0.615	0.626	1.797	1.20
21.04	0.46	0.56	0.8518	-1.93	1.32
28.40	0.64	0.36	1.777	0.2498	1.45
35.60	0.71	0.29	2.448	0.388	1.55
42.3	0.8	0.2	4.00	0.602	1.63

(3e) p-ChloroPhenol

Conc. M×10^5	θ	1-θ	θ/1-θ	Log=θ/1-θ	Log C
5.25	0.16	0.84	0.19	-0.72	0.72
10.53	0.30	0.7	0.423	-0.37	1.02
15.8	0.4	0.57	0.7544	-0.122	1.20
21.04	0.484	0.52	0.923	-0.034	1.32
28.40	0.57	0.43	1.326	0.1224	1.45
35.60	0.7	0.3	2.333	0.3679	1.55
42.3	0.83	0.17	4.882	0.688	1.63

Adsorption isotherm

The electrochemical processes on the metal surface are likely to be closely related to adsorption of the inhibitor[35], and adsorption is known to depend on the chemical structure of inhibitors[36-38]. Adsorption of the inhibitor molecules from aqueous solutions was regarded as quasi-substitution process[36] between the organic compound in aqueous phase, $org_{(aq)}$ and water molecules at the electrode surface, $H_2O_{(s)}$.

Adsorption isothrerms are very important in determining the mechanism of organo-electrochemical reactions. The most frequently used isotherms are those Langmuir, Frumkin, Parsons, Temkin, Florry-Huggins and Bockris-Swinkels[29-92]. All these isotherms are of the general form:

$$f(\theta,x)\exp(-\alpha\,\theta) = KC \qquad (5)$$

Where f (θ,x) is the configurational factor that depends essentially on the physical model and assumptions underlying the derivation of the isotherm[43].

The mechanism of inhibition of corrosion was generally believed to be due to the formation and maintenance of a protective film on the metal surface.

Inhibitor adsorption characteristics were estimated by using the Langmuir isotherm[19]:

$$KC = (\theta/1-\theta) \qquad (6)$$

Assuming that the adsorbed molecules, have decreased the metal surface area available for corrosion. The degree of surface coverage(θ) at constant temperature was determined [20] from equation (7):

$$\theta=1-W/W_0 \qquad (7)$$

plot of log θ/θ-1 versus log C gave good straight line. Deviation of the slope from unity suggested that there were some interactions in the adsorbed layer. The Frumkin isotherm was tested to fit the experimental data on the inhibitory action of halides:

$$KC=(\theta/1-\theta)\exp[-(2f\theta)] \qquad (8)$$

Where C is the inhibitory concentration, f represents the variation of adsorption potential with coverage and depends upon molecular interactions in the adsorption layer, and k is the equilibrium constant for adsorption, related to the free energy of adsorption [9].

The plot of θ versus log C is shown in figure 4 the curves has an S-shape characteristic of the Langmiur adsorption isotherm[44,45]. This suggested occurrence of multilayer adsorption on the aluminum surface [14].

Structural effects

Corrosion rate of aluminum decreases with concentration of inhibitors (TABLE2). The efficiency of inhibitors increases by concentration. The order of decreased inhibition of inhibitor decreased p-aminophenol>p-chlorophenol>O-cresol>P-cresol>phenol

Some authors[45] have studied O-substituted phenol as corrosion inhibitors for aluminum-copper alloys in NaOH. They described that phenol(63.3%) inhibit less than cresol (83.9%). They explained the inhibitor efficiency increased with concentration.

It has been found that the presence of electron releasing groups in the benzene nucleus pushes electron to the ring. This increases the electron density on the oxygen atom, intensifies the negative charge and thus destabilizes the phenoxide ion. The release of proton will be less probable.

Hence, the presence of electron releasing groups decreases the acid strength of phenol. Therefore, OC gives more inhibition than PC and phenol. Alcohol protonizes in acid environment to from $R\text{-}OH^+$ type species owing to the existence of negative zero charge potential of iron in hydrochloric acid, the adsorption of protonized phenols molecule on the metal surface takes place resulting in corrosion inhibition[46]. All the inhibitors contain delocalized Π-electron which may adsorb on the metal surface. Pati et al. [46] and Quaraishi et al.[47] have explained that the inhibitors inhibit corrosion of steel in hydrochloric acid by getting adsorbed on the metal surface through their Π-electron. P-chloro and P-aminophenol are strong inhibitors than other because Cl is electron attracting group led to ionization of phenol to $C_6H_5O^-$ which adsorbed on the metal surface than other.

It is found that, the higher inhibition of P-amino is attributed to either their coordination type of bonding to the metal surface or to their electron releasing effect leading to increase the electron density at the functional group site[48] i.e. strong coordination type bond with aluminum.

TABLE 4 : Thermodynamic parameters for all acid used

Derivative	Parameter	
Blank	E	20.190±1.943
	ΔH	17.711± 1.943
	-ΔS	-229.6101±6.3612
	ΔG	86.170 ±3.840
Phenol	E	14.729±0.667
	ΔH	12.250±0.667
	-ΔS	-248.4229 ±2.185
	ΔG	86.317±1.319
O-Cresol.	E	21.212±1.852
	ΔH	18.734 ±1.852
	-ΔS	-230.030±6.0628
	ΔG	87.317±3.659.
P-Cresol	E	24.248±3.524.
	ΔH	21.770±3.524.73344
	-ΔS	-219.0247±11.538
	ΔG	87.072 ±6.964
P-ChloroPhenol	E	29.638±6.815
	ΔH	27.159±6.815
	-ΔS	-202.2834±22.3070
	ΔG	87.470±13.4656
P-aminoPhenol	E	25.705±1.955
	ΔH	23.22±1.954
	-ΔS	-214.9435±6.3987
	ΔG	87.311±3.862

Thermodynamic treatment of the reaction

From the integrated form of Arrhenius equation

$$\mathrm{In}k = \frac{-E}{RT} + \mathrm{In}A \qquad (9)$$

Where R is the gas constant, E is the activation energy and A is the frequency factor. The values of E are given in TABLE 4. The values of E show that reaction is diffusion controlled.

The values for enthalpy of activation, ΔH*, entropy of activation ΔS*, and free energy of activation ΔG*, can be obtained by using the following equations:

$$\Delta H^* = E - RT \qquad (10)$$

$$\frac{\Delta S^*}{R} = \mathrm{In}A - \mathrm{In}\left(\frac{\alpha Te}{h}\right) \qquad (11)$$

$$\Delta G^* = \Delta H^* - T\Delta S^* \qquad (12)$$

Where α is the Boltzman constant, e is 2.7183 and h is Plank's constant.

Although the change in the free energy of activation, ΔG*, with the acids concentration for all used acids is only small, TABLE 4, and variations occur in the enthalpy of activation ΔH* and the entropy of activation ΔS*, with phenols concentration where in all these cases ΔH* and ΔS* compensate each other to produce little changes in ΔG*.

It is noticed that all values of ΔS* are highly negative values, indicating a more ordered system and non-random distribution of the phenols on the electrode. These values are found to be independent of the type of phenols and the position of the substituents of the phenols compound where these phenol compounds affect the corrosion process by dissolution of aluminum metal.

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