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RESEARCH ARTICLE

The Synergistic Effects of Halide Ions and Cations on the Corrosion Inhibition of Mild Steel in H_2SO_4 Using Amodiaquine

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Abstract: The synergistic effect of amodiaquine (AMQ) and some selected metal cations (Na^+, Mg^{2+}) and halides (Cl^-, Br^-, I^-) on the corrosion of mild steel in 0.5 M H_2SO_4 was studied by weight loss methods, electrochemical impedance spectroscopy and potentiodynamic polarization measurements. Efforts were taken to enhance the inhibition efficiency at different concentration of amodiaquine with fixed concentration of cations and halides. As the concentration of amodiaquine increased the inhibition efficiency (IE) increases. Addition of fixed concentration of halides on different concentration of amodiaquine inferred the increase in inhibition efficiency with concentration of amodiaquine. Maximum inhibition efficiency was observed with 10^{-2} M amodiaquine and 10^{-2} M I^- ion. The synergistic action was also noted when 10^{-2} M Na^+, Mg^{2+} with 10^{-4} M amodiaquine. Synergistic parameter for amodiaquine with cations and halides confirmed the synergistic effect of halides and cations and corrosion of mild steel in the presence of 0.5 M H_2SO_4. Potentiodynamic polarization and electrochemical impedance spectroscopy for mild steel in the synergistic addition of halide and cations confirmed the mixed mode of inhibition.

Keywords: Synergistic effect, Corrosion inhibition, Mild steel, Amodiaquine, Halides, Cations

Introduction

Corrosion problems are receiving more and more attention due to their attack on materials. Corrosion scientists all over the world are doing their best to avoid assaulting by all kinds of corrosion. An effective method for corrosion scientists to control the corrosion of metal can be achieved by using inhibitors[1]. Most organic compounds that act for corrosion prevention are mixed inhibitors. In the presence of two or more adsorbed species, lateral interaction between the inhibitor molecules can significantly affect the inhibitor performance. Synergism is a combined action of compounds greater in total effect than the sum of the individual effects. Synergism of corrosion inhibitors is either due to the interaction between components of the inhibitor composition or due to interaction between the inhibitor and one of the ions present in the aqueous solution[2]. Synergistic inhibition is an effective means to improve the inhibitive force of an inhibitor, to decrease the amount of usage, to diversify the application of inhibitors in acidic media. It is necessary for corrosion scientists to discover, explore and use synergism in the complicated corrosive media. Actually, many investigations concerning synergistic inhibition have been carried out and are being carried out. Feng *et al.*[3] have studied the synergistic inhibition between propargyl alcohol and iodide ion for steel corrosion in sulfuric acid. Zhang *et al.*[4] have investigated synergistic effect of 2-mercapto benzimidazole and KI on copper corrosion inhibition in sulfuric acid. Tang *et al.*[5] have reported there is a synergism between chloride ion and neutral red during the corrosion inhibition of steel in hydrochloric acid. And the synergism between them played an important role in the process of adsorption. Synergistic effects between organic inhibitors and halide ion on metal corrosion in sulfuric acid medium have been carried out by many authors[3,6-7]. Based on this, an organic medicinal compound Amodiaquine was selected for the corrosion of mild steel in 0.5 M H_2SO_4. The objective of the present investigation is to study the corrosion inhibition of mild steel in sulphuric acid medium using amodiaquine, amodiaquine halide mixture, amodiaquine cation mixture, combination of halides and cations with amodiaquine.

Experimental

The mild steel (MS) samples were obtained from a locally available industrial Fe-C steel with very low percentage of carbon. A large sheet of cold rolled mild steel coupons with a chemical composition of carbon 0.13%, manganese 0.23%, silicon 0.03%, phosphorus 0.03%, sulphur 0.016%, chromium 0.022%, nickel 0.012% and iron 99.95% was utilized for the present study. The mild steel samples, with an active surface of 1 cm x 5 cm were used for Mass loss measurements and 1 cm x 1 cm specimen for electrochemical measurements. The mild steel samples were mechanically polished, degreased, washed in double distilled water and dried in warm air. Mass loss experiments and electrochemical measurements were done according to ASTM G1-03[8].

Preparation of stock solutions

0.1 M solution of AMQ, sodium sulphate, magnesium sulphate, potassium chloride, potassium bromide, and potassium iodide were prepared. Various concentrations were made from these stock solutions.

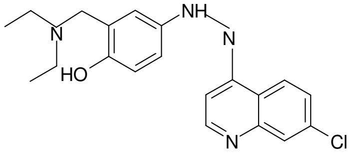

Figure 1. Structure of amodiaquine

Weight loss measurements

The MS coupons were weighed in Denvar balance. Weighed samples in triplicate were immersed in 100 mL of acid solution (with and without inhibitor) for a fixed duration. The specimens were removed and washed with saturated sodium bi carbonate solution and water, dried and reweighed. The average weight loss of the coupons was recorded. Influence of various parameters on the dissolution of mild steel studied by these methods is,

Inhibitor concentration : 10^{-2} M to 10^{-4} M of AMQ
Cationic concentration : 10^{-2} M of Na^+ and Mg^{2+}
Anionic concentration : 10^{-2} M of Cl^-, $Br^-$and I^-

Acid **:** 0.5 M H_2SO_4
Immersion time **:** 3 h

- At fixed concentration of the cations (10^{-2} M) varying the concentrations of AMQ (10^{-2} M to 10^{-4} M).
- At fixed concentration of the halide ions (10^{-2} M) varying the concentrations of AMQ (10^{-2} M to 10^{-4} M).
- At fixed concentration of the AMQ (10^{-4} M) with combination of cations and anions (10^{-2} M).

The percentage inhibition efficiency was calculated from,

$$IE\ (\%) = W^o - W\ \ / W^o \times 100$$

Where W^o and W are mass loss of mild steel in uninhibited and inhibited solutions.

Electrochemical measurements

Electrochemical measurements were performed using Solatron 1208B potentiostat, supported with corrware and z plot softwares. Experiments were carried out in a conventional three electrode cell with a platinum counter electrode, saturated calomel electrode (SCE) as reference electrode and mild steel specimens having an exposed area of 1 cm^2 as working electrode. The anodic and cathodic polarization curves were recorded at a constant sweep rate of 2 mV/s. Impedance spectra were obtained in the frequency ranges of 20 kHz to 0.1 Hz with an alternating current of 10 mV amplitude (10 points/decades) at the corrosion potential. Electrochemical parameters such as I_{corr}, $E_{corr,}$ $R_{p,}$ R_{ct} and C_{dl} were evaluated for MS/0.5 M H_2SO_4 in the presence of amodiaquine, Na^+, Mg^{2+} and halide ions.

Results and Discussion

Weight loss measurements

Effect of cations and halides on MS/0.5 M H_2SO_4/AMQ

Data recorded in Table 1 represent the effect of AMQ concentration with 10^{-2} M concentration of cations (Mg^+, Na^+) and concentration of halide ions (Cl^-, Br^-, I^-) at 3 h of immersion. It is noted that as the concentration of AMQ increases, the IE also increases in 0.5 M H_2SO_4.

Table 1. Synergistic effect of cations and halides on the inhibiting effect of AMQ

S .No.	Conc.of AMQ	IE, %	Concentration of cations & halides, 10^{-2} M				
			Mg^{2+}	Na^+	Cl-	Br-	I^-
			Inhibition efficiency, %				
1	10^{-5}	6	11.5	21.4	54.2	48.5	97.3
2	10^{-4}	13	20.1	33.5	62.7	52.4	97.6
3	10^{-3}	49	34.2	53.9	67.6	61.3	99.2
4	10^{-2}	70	75.4	86.3	83.4	81.6	99.3

The inhibition efficiency enhances from 70% for 10^{-2} M AMQ to 75% and 86% in the case of cation addition and 83%, 81% and 99% in the case of halide addition. This might be due to the synergistic influence of cations and halides on AMQ. This behavior could be attributed to the increased surface coverage due to the increase of the number of adsorbed molecules at the metal surface.

The high efficiency of AMQ in the presence of iodide can be explained as due to its larger ionic size, stronger adsorption due to easy polarizability of its electron shells & possible formation of surface layer on the metal with the inhibitor[9-10].

Effect of the synergistic mixture on MS corrosion

Synergistic effects of cations, halide ions and AMQ mixture are presented in the Table 2. Analysis of the table reveals that IE of AMQ increases with the addition of cations to some extent and increases periodically with mixture of AMQ, halides and cations. The highest inhibition efficiency was observed for iodide combined mixture.

Table 2. Synergistic effect of mixture of anions and cations with AMQ

S.No	Concentration of synergistic mixture	Inhibition efficiency, %
1	10^{-4} AMQ	13
2	10^{-4} AMQ+ 10^{-2} M Mg^{2+}	20
3	10^{-4} AMQ +10^{-2} M Na^{+}	33
4	10^{-4} AMQ+10^{-2} M Cl^{-}+ 10^{-2} M Na^{+}+10^{-2} M Mg^{2+}	43
5	10^{-4} AMQ+10^{-2} M Br^{-}+ 10^{-2} M Na^{+}+10^{-2} M Mg^{2+}	54
6	10^{-4} AMQ+10^{-2} M I^{-}+ 10^{-2} M Na^{+}+10^{-2} M Mg^{2+}	98

This may due to adsorption of amodiaquine combined cations and anions on the MS surface through non bonding electron pairs of sulfur and oxygen atoms as well as π electrons of aromatic rings. The inhibition efficiency of the AMQ (10^{-4}) enhances from 13% to 98% in the presence of halides, cations and AMQ mixture. This enhancement is mainly due to joint adsorption of AMQ with halides and cations.

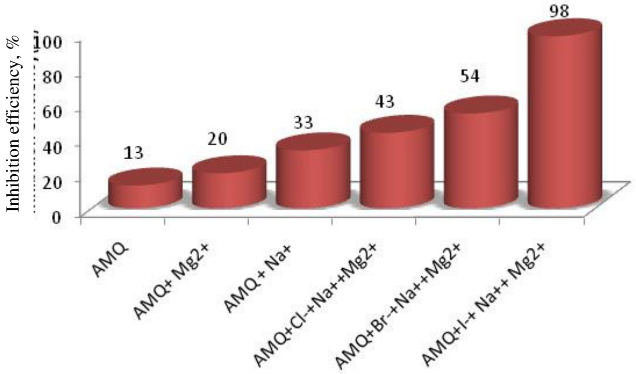

Figure 2. Comparison of inhibition efficiency of mixture of anions and cations with AMQ

Electrochemical measurements

Potentiodynamic polarization studies

Figure 3a shows the potentiodynamic polarization plots of mild steel for various concentrations of mixture of amodiaquine, halides and cations. The corrosion kinetic parameters determined from these curves are given in Table 3. It can be seen from Table 3 that AMQ/halide & cation mixture inhibits the corrosion of mild steel more effectively compared to cation combined AMQ mixture. The highest inhibition efficiency observed from corrosion current density calculation is 94.7%. The strong chemisorption of iodide ions on the metal surface is responsible for the synergistic effect of iodide ions, in attraction with AMQ. The AMQ is then adsorbed by coulombic attraction at the steel surface, where iodide ions are already adsorbed by chemisorption. Stabilization of adsorbed iodide ions by means of electrostatic interaction with AMQ leads to greater surface coverage and thereby, greater inhibition[11]. The strong synergistic inhibition of AMQ with halide and cation mixture makes the corrosion potential (E_{corr}) shift to anodic direction. Both cathodic Tafel slopes (b_c) and anodic Tafel slopes (b_a) change remarkably and the corrosion current (Icorr) decreases remarkably, which means that both anodic and cathodic reactions are drastically inhibited and has a satisfactory IE[12].The values of Tafel slopes and E_{corr} confirm that the inhibitor (AMQ) in the presence of anions and cations behave like mixed type.

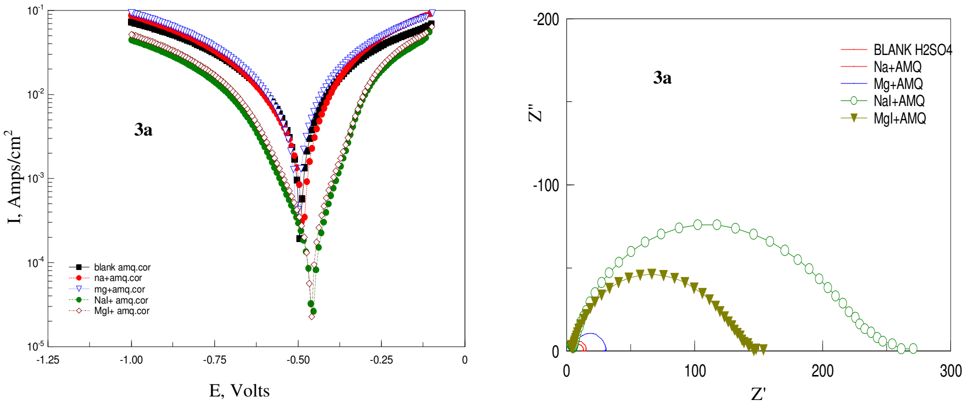

Figure 3a & 3b. Potentiodynamic polarization curves and Nyquist plots for MS/0.5M H_2SO_4 in the presence of AMQ with cations and halides

Table 3. Electrochemical parameters for MS in 0.5 M H_2SO_4 in the presence of 10^{-3} M AMQ cations (10^{-2} M) and anions (10^{-2} M)

S.No	Concentration of AMQ with cations and anions	b_a mV/dec	b_c mV/ dec	I_{corr} , Amp/ cm^2	E_{corr} mV/ sec	IE, %	Rp Ohm/ cm^2	IE, %	R_{ct}, ohms	IE, %	C_{dl} X 10^{-5} , µ farads	θ
1	Blank	172	116	0.001811	-478	-	12.7	-	10.768	-	4.123	-
2.	10^{-3} AMQ	87	83	0.005070	-513	21.8	6.1	30.8	153.21	71.10	1.443	0.65
3.	10^{-3} AMQ+ 10^{-2} Na^+	60	54	0.000523	-484	71.1	30.7	54.3	36.86	70.78	3.010	0.27
4.	10^{-3} AMQ+ 10^{-2} Mg^{2+}	140	113	0.001410	-485	22.14	14.3	11.3	26.86	59.91	2.927	0.29
5.	10^{-3} AMQ+ 10^{-2} Na^++I^-	112	75	0.000114	-451	93.6	132.1	90.3	217.01	95.03	0.498	0.88
6.	10^{-3} AMQ+ 10^{-2} $Mg^{2+}+ I^-$	117	86	0.000184	-457	89.8	96.8	86.3	140.98	92.36	0.577	0.86
7.	10^{-3} AMQ + 10^{-2} Cl^-	132	91	0.000559	-472	69.11	35.3	64.1	36.66	70.78	3.496	0.63
8.	10^{-3} AMQ+ 10^{-2} Br^-	147	107	0.001086	-473	40.05	20.6	38.2	12.537	59.91	4.259	0.55
9.	10^{-3} AMQ+ 10^{-2} I^-	98	71	0.000058	-452	94.7	126.1	89.9	322.25	95.03	1.323	0.86

Electrochemical impedance spectroscopy

The effect of inhibitor concentration on the impedance behavior of mild steel in 0.5 M H_2SO_4 solution at room temperature is presented in Figure 3b. The curves show a similar type of

Nyquist plots for mild steel in the presence of various concentrations of AMQ with cation and anion mixture. The deviation from the perfect semicircle shape (depression) is often referred to the frequency dispersion of interfacial impedance. This anomalous behaviour is generally attributed to the inhomogeneity of the metal surface arising from surface roughness or interfacial phenomena[13-16].

The values of R_{ct} increase with the increase in concentration of AMQ and in the presence of synergistic cations and anions. Values of R_{ct} are enhanced to a maximum in the presence of synergistic cations and anions. From the Table 3 it was noted that maximum IE of 10^{-3} M AMQ was found to be 71% and enhancement in inhibition efficiency in the presence of cations and Iodide was found to be 95%. This tremendous enhancement in IE of AMQ in the presence of synergistic cations and anions can be attributed to the joint adsorption of AMQ, cations and anions mixture on MS surface.

Synergism parameter

The synergism parameter 'S' was evaluated using the relationship given by Aramaki and Hackermann[17].

$$\text{Synergistic parameter } [S] = 1-[I_A+I_B] / 1-I_{AB},$$

Where I_A = Inhibition efficiency of the amodiaquine, I_B = Inhibition efficiency of the halides and cations, I_{AB} = Inhibition efficiency of the amodiaquine with halides and cations S approaches 1 when no interaction between the inhibitor compounds exists, while S > 1, points to a synergistic effect. In the case of S < 1, the antagonistic interaction prevails, which may be attributed to the competitive adsorption. The calculated values are presented in the Table.4. The values of S are greater than unity in the presence of halides with AMQ which suggest that the enhanced IE caused by the addition of halide ions to AMQ (which is in the order of Cl^-<, Br^-< I^-) may be only due to synergistic effect. This can be explained on the basis that halides have a greater tendency to be absorbed on the surface. It can also be concluded that the iodide ion is strongly adsorbable and facilitates the adsorption of organic cations, thereby leading to an inhibition synergism. The order indicates that the radii and electronegativity of the halides play an important role in the adsorption process.

Table 4. Calculation of synergistic parameter for AMQ with cations and halides

S.No	Cation/Halide	Concentration of AMQ	I_A	I_B	I_{AB}	S
1	Cl^-	10^{-4}	13	45.6	62.7	0.9335
		10^{-3}	49	45.6	67.6	1.4050
		10^{-2}	75	45.6	83.4	1.4510
2	Br^-	10^{-4}	13	46.9	52	1.1540
		10^{-3}	49	46.9	61.3	1.5730
		10^{-2}	75	46.9	81.6	1.5000
3	I^-	10^{-4}	13	99.3	97.6	1.1520
		10^{-3}	49	99.3	99.2	1.5000
		10^{-2}	75	99.3	99.3	1.7640
4	Mg^{2+}	10^{-4}	13	30	20	2.2100
		10^{-3}	49	30	34.7	2.3140
		10^{-2}	75	30	75	1.4050
5	Na^+	10^{-4}	13	46.7	33	1.5000
		10^{-3}	49	46.7	53.6	1.8343
		10^{-2}	75	46.7	86	1.8003

The inhibition efficiency for the corrosion of mild steel in 0.5 M in H_2SO_4 in the presence of amodiaquine increases with increase in concentration. The adsorbed intermediate formed at the metal surface by the interaction with amodiaquine is probably a complex. At lower concentration of amodiaquine, the adsorption intermediate formed may be a soluble complex, leading to low values of inhibition efficiency. At higher concentration, the complex formed is insoluble and the higher values of inhibition efficiency due to complex arise from the blocking of most of the activities on the metal surface due to increased coverage[18].

From Table 4, it can be seen that the values of S, are greater than unity which clearly shows that the corrosion inhibition brought about by amodiaquine and combination of halides is synergistic in nature. It may therefore also be concluded that halide ions and cations are initially chemisorbed on the metal surface. Amodiaquine is then adsorbed by coulombic attraction on the metal surface, where the anion is already chemisorbed and thus suppresses the self corrosion rate by the stabilization of the adsorbed anion and cation by the increase in surface coverage[7].

Conclusion

i. AMQ with halides and cations are highly favourable as an inhibitor for the mild steel corrosion in 0.5 M H_2SO_4.This fact can be explained by the formation of an insoluble complex by joint adsorption.
ii. Inhibition efficiency increases with increasing inhibitor concentration for mixture of cations and halides with AMQ.
iii. Addition of iodide ions enhances the inhibition efficiencies.
iv. Electrochemical measurements reveal that mixed nature of the inhibitor.
v. The synergism parameter values *S* show that the corrosion inhibition produced by AMQ and anion and cation mixture is synergistic in nature.
vi. The electrochemical measurements are in good agreement with weight loss measurements. This improves the validity of the results obtained.

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