Enhancement of the Inhibitor Efficiency of Atropine Methochloride in Corrosion Control of Mild Steel in Sulphuric Acid

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Abstract: The inhibition efficiency and synergistic behaviour of 10^{-4} M Atropine methochloride was carried out using mass loss and polarisation methods in the presence of (i) metal ions, Ni^{2+} and Cu^{2+} between 10^{-2} M to 10^{-6} M concentrations, (ii) different concentrations of metal ions and 10^{-3} M I^- , 10^{-3} M Cl^- and 10^{-3} M Br^- solutions and (iii) different metal ions, 10^{-3} M I^- and at three different temperatures. The analysis reveals that the inhibition efficiency of Atropine methochloride was maximum at 10^{-2} M in 5 hours of immersion period. Halides decreased the corrosion rate of mild steel in Sulphuric acid. The decrease is maximum with 10^{-3} M I^- . As the temperature increased from 298K to 308K, the inhibition efficiency gradually decreased. The inhibitor was found to be effective up to 303K

Keywords: Atropine Methochloride (AMCI); Metal ions; Halides; Temperature resistant.

Introduction

Mild steel has been extensively used under different conditions in chemical and allied industries in handling alkalis, acids and salt solution. Mild steel undergoes corrosion during acid cleaning, pickling, decaling, mining and oxidizing of oil wells. Corrosion rate of mild steel is affected by pH (4 to 10) of a solution, temperature and also in the presence of dissolved oxygen. The use of various Organic inhibitors to decrease the rate of corrosion processes has been studied. The industrial importance of corrosion inhibitors is wide spread ranging from pickling to application in water-cooling systems. The selection of an inhibitor for a given system depends on the corrosion medium, the nature of the metal, the magnitude of the charges at the metal solution interface and the cathodic reaction. The inhibition of iron corrosion in acidic solutions by organic inhibitor has been well studied¹ The most efficient inhibitors used in industry are heterocyclic organic compounds having higher electron density on the hetero atoms like "Sulphur", "Oxygen", "Nitrogen" and the molecules with

multiple bonds through which they are adsorbed on the metal surface, thus help in inhibition of corrosion. Especially inhibitors containing nitrogen atom like long chain nitrogenous organic materials including amines, imines, amides and its derivatives are effective in acid corrosion for industrial applications. Synergistic effects describe the increase in effectiveness of a corrosion inhibitor in the presence of other substances in the corrosive medium²⁻⁴

Atropine methochloride

AMCl is a heterocyclic compound, it contains oxygen and nitrogen. The molecular formula ($C_{18}H_{26}ClNO_3$) has been tried for its potential in the retardation of corrosion of mild steel. Earlier studies carried out using AMCl as an inhibitor revealed that it is effective at 10^{-2} M concentrations and the inhibition efficiency was found to be only 40% with 10^{-4} M. To increase the inhibitive effect of AMCl at the lower concentrations, a set of metal ions and halides are being selected. AMCl can act as potential inhibitor in synergism with metal ions and halides. In the present investigation, efforts have been taken to study the inhibiting efficiency of AMCl and the effect of metal ions and halides on mild steel corrosion in 1M sulphuric acids by weight loss and polarization methods^{5,6}

Experimental

Mild steel was selected as sample material for this study because of it is most versatile, least expensive and wide industrial importance (fabrication of reaction vessels, pipes, tanks, cooling water system)⁷. Sulphuric acid is the choice of test media, due to tremendous increase in industrial activities, like acid cleaning/pickling and descaling. Inhibitors are generally used in industrial processes to control both dissociation and acid consumption. A large sheet of cold rolled mild steel was press cut into rectangular coupons of area $1 \times 5 \text{ cm}^2$. They were mechanically polished degreased and washed with distilled water and dried thoroughly for all investigation. The percentage elemental composition was analyzed and found to be as given in the Table 1,

Table 1. The percentage elemental composition

S. No.	Element	% Composition of mild steel
1	Carbon	0.048
2	Manganese	0.335
3	Silicon	0.029
4	Phosphorus	0.041
5	Sulphur	0.025
6	Chromium	0.050
7	Molybdenum	0.016
8	Nickel	0.019
9	Iron	99.437

Instrumentation

The technical methods adapted and the instruments used in the present studies are Denvar balance, Thermostat Solartron (UK) (1284 Z). Techniques; weight loss method and polarisation method⁸

Reagents and solutions

Sulphuric acid of commercial grade and deionised water are used for the preparation of 1 M acid solutions. 0.1 M solutions of AMCl, nickel sulphate, copper sulphate, potassium iodide, sodium bromide and sodium chloride were prepared. Various concentrations were made from these bulk solutions⁹.

Triplicate pre-weighed coupons were suspended with the help of glass hook into 100 mL of acid containing different concentrations of inhibitor for a fixed duration and then removed, washed, dried and reweighed¹⁰. The average weight losses of the coupons were recorded. The same is done with varying concentrations of AMCl (from 10^{-2} M to 10^{-6} M); At fixed concentration of AMCl (10^{-4} M) and with different concentrations of cations (from 10^{-2} M to 10^{-6} M of Ni^{2+} & Cu^{2+}); At fixed concentration of AMCl (10^{-4} M) and with different concentrations of anions (from 10^{-3} M to 10^{-6} M of I^- , Br^- and Cl^-); At fixed concentration of AMCl (10^{-4} M) and a fixed concentration of any one of the anions (10^{-3} M of I^- , Br^- and Cl^-) with varying concentrations of cations (10^{-3} M to 10^{-6} M of Ni^{2+} & Cu^{2+}). To study the stability of the inhibitor in the presence of various metal ions, 10^{-3} M I^- and at various temperatures, temperature study was performed at 298K, 303K and 308K. The time of immersion of temperature study was fixed as half an hour.

Calculation of corrosion rate

The corrosion rate for both room temperature and high temperature studies with various concentrations of inhibitor and various concentrations of cations and various concentrations of anions was obtained from the following formula¹¹,

$$\text{Corrosion rate (mpy)} = \frac{436.095 \times 1000 \times W}{A \times T}$$

Where, W = Weight loss in g

A = Area of specimen in cm^2

T = Exposure time in hours.

The unit of the corrosion rate is in mils penetration per year (mpy).

Percentage inhibition efficiency was calculated from the formula,

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

Where, W_0 = Weight loss of mild steel in the absence of inhibitor

W = Weight of mild steel in the presence of inhibitor.

Activation energy of corrosion reaction was calculated from Arrhenius equation,

$$\log K = \frac{-E_a + C}{2.303RT}$$

Where K = Corrosion rate

R = gas constant

T = temperature

E_a = energy of activation.

Results and Discussion

The inhibitor effect of AMCl in 1M sulphuric acids at various concentrations for 5 hours period of immersion is carried out by weight loss method. As the concentration of the inhibition increased, the inhibitor efficiency also increased. Maximum inhibitor effect was at 10^{-2} M at 5 hours period of immersion was found to be 89.5% (Table 2).

It may be due to the increase in the surface area of the inhibitor molecules on the metal surface. Inhibitor efficiency of AMCl was enhanced by the addition of increasing concentrations of metal ions, and the enhancement of inhibition efficiency of AMCl is observed from 40% to 50.28% and 55.25% in the presence Ni^{2+} and Cu^{2+} respectively (Table 3).

Table 2. Dependence of concentration of AMCl on the corrosion inhibition of MS in 1M H₂SO₄(5 hours study).

S. No.	Molar Concentration	CR mpy	IE, %
1	Blank	1224.99	--
2	10 ⁻⁶	1190.89	3.00
3	10 ⁻⁵	935.87	24.00
4	10 ⁻⁴	731.52	41.75
5	10 ⁻³	333.79	75.50
6	10 ⁻²	142.19	89.50*

Table 3. Effect of metal ions (Ni²⁺ & Cu²⁺) on the IE of AMCl (10⁻³M) in the corrosion of MS in 1M H₂SO₄ (5 h study)

S. No	Concentration of		Ni ²⁺		Cu ²⁺	
	AMCl, M	Metal ions M	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	1578.98	--	1449.87	--
2	10 ⁻⁴	10 ⁻⁶	949.85	40.89	754.52	48.56
3	10 ⁻⁴	10 ⁻⁵	867.70	48.36	755.30	50.10
4	10 ⁻⁴	10 ⁻⁴	831.77	49.14	733.65	51.42
5	10 ⁻⁴	10 ⁻³	816.06	50.28	693.52	52.06*

CR-corrosion rate; AMCl:Atropiune methochloride; IE: Inhibition efficiency; mpy: mils penetration per year MS –Mild steel

This might be due to the synergistic influence of metal cations on AMCl. It may therefore be assumed that the rate of corrosion goes on decreasing with increasing concentration of the metal. Increase in concentration of halide ions with 10⁻⁴M AMCl increased the inhibition efficiency from 37.43 to 75.06%, 36.20-52.65% and 38.64 to 50.43% for iodide, bromide and chloride ions respectively (Table 4)

Table 4. Effect of various halides on the corrosion inhibition of MS in the presence of AMCl (10⁻⁴M) in 1M H₂SO₄ (5 h study)

S.No	Concentration of		I ⁻		Br ⁻		Cl ⁻	
	AMCl, M	Halides, M	CR, mpy	IE,%	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	1577.73	--	1577.73	--	1577.73	--
2	10 ⁻⁴	10 ⁻⁶	1003.56	37.43	1022.93	36.20	984.41	38.64
3	10 ⁻⁴	10 ⁻⁵	930.62	42.05	833.96	48.18	908.82	43.43
4	10 ⁻⁴	10 ⁻⁴	769.99	52.24	808.68	49.79	825.96	48.69
5	10 ⁻⁴	10 ⁻³	410.22	75.06*	763.45	52.65	798.58	50.43

Iodide was found to be more effective than chloride and bromide. The enhanced inhibition efficiency is due to joint adsorption of halide ions and inhibitor cations or molecules¹². The high efficiency of iodide can be explained as due to its larger ionic size, stronger adsorption due to easy polarizability of its electron shells and possible formation of surface layer on the metal with the inhibitor. Analysis of Table 5, 6 & 7 reveals that there is enhancement in the inhibition efficiency from 40% (10⁻⁴M AMCl) to 98.90% and 99.54%

due to the presence of 10^{-3} M Ni^{2+} and 10^{-3} M Cu^{2+} in the presence of 10^{-3} M I^- . The enhancement in the inhibition efficiency from 40% (10^{-4} M AMCl) to 69.08% and 68.13% by the addition of 10^{-3} M Ni^{2+} and 10^{-3} M Cu^{2+} in the presence of 10^{-3} M Br^- . The inhibition efficiency increase from 40% (10^{-4} M AMCl) to 64.99% and 59.87% in the case addition of 10^{-3} M Ni^{2+} and 10^{-3} M Cu^{2+} in 10^{-3} M Cl^- respectively. This is due synergistic effect of metal ions and halides^{13,14}.

Table 5. Role of metal ions(Ni^{2+} & Cu^{2+}) and iodide (10^{-3} M) on the corrosion inhibition of MS in the presence of 10^{-4} M AMCl in 1M H_2SO_4

S. No.	Concentration of			Ni^{2+}		Cu^{2+}	
	AMCl, M	I- M	Metal ions, M	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	Blank	1135.59	-	1135.59	-
2	10^{-4}	10^{-3}	10^{-6}	27.91	98.64	28.12	98.62
3	10^{-4}	10^{-3}	10^{-5}	24.100	98.90	31.54	98.32
4	10^{-4}	10^{-3}	10^{-4}	33.72	98.13	26.20	98.79
5	10^{-4}	10^{-3}	10^{-3}	40.99	97.49	18.94	99.54*

Table 6. Tabulation of Cr and IE for the various concentrations of different metal ions(Ni^{2+} & Cu^{2+}) with 10^{-4} M AMCl and 10^{-3} M bromide in 1M H_2SO_4 (5 h study)

S. No	Concentration of			Ni^{2+}		Cu^{2+}	
	AMCl, M	Br- M	Metal ions, M	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	Blank	913.90	-	913.90	-
2	10^{-4}	10^{-3}	10^{-6}	370.96	60.48	471.27	60.40
3	10^{-4}	10^{-3}	10^{-5}	295.13	68.79	366.61	60.96
4	10^{-4}	10^{-3}	10^{-4}	295.13	68.79	366.61	60.96
5	10^{-4}	10^{-3}	10^{-3}	292.47	69.08	301.19	68.13

Table 7. Variation of IE in the presence of various concentrations of different metal ions(Ni^{2+} & Cu^{2+}) with 10^{-4} M AMCl and 10^{-3} M chloride in 1M H_2SO_4 (5 h study)

S. No	Concentration of			Ni^{2+}		Cu^{2+}	
	AMCl, M	Cl- M	Metal ions, M	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	Blank	892.10	-	892.10	-
2	10^{-4}	10^{-3}	10^{-6}	514.15	51.36	542.50	48.62
3	10^{-4}	10^{-3}	10^{-5}	435.65	58.96	517.78	51.01
4	10^{-4}	10^{-3}	10^{-4}	410.58	61.387	448.25	57.74
5	10^{-4}	10^{-3}	10^{-3}	373.14	64.99	426.20	59.87

To study the stability of the inhibitor in the presence of various cations and 10^{-3} M I^- . Temperature study has been performed at 298K, 303K and 308K. The time of immersion of temperature study was fixed as half an hour. Results are tabulated in Table 8. On increasing the concentration of Ni^{2+} , the enhancement of inhibition efficiency of 10^{-4} M

AMCl with 10^{-3} M I in 1M H_2SO_4 also increased from 91% to 94%. As the temperature increased from 298K to 308K, the inhibition efficiency gradually decreased. At 298K, the efficiency was found to be 94%, 86% at 303K and 79.10% at 308K and the inhibitor was effective up to 303K. The standard electrode potential Ni^{2+}/Ni (-0.250V) and of Fe^{2+}/Fe (-0.4402V). The differentiation is small, so metal Nickel hardly form a protection film on the steel surface. Therefore, the effect of Ni^{2+} for steel was not obvious.

Table 8. Variation of IE with different concentration of Ni^{2+} in the presence of 10^{-4} M AMCl and 10^{-3} M iodide in 1M H_2SO_4 at different temperatures (1 h study)

S. No	Concentration of			298K		303K		308K	
	AMCl, M	I, M	Ni^{2+}	CR, mpy	IE, %	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	Blank	3886.62	-	9749.92	-	21869.72	-
2	10^{-4}	10^{-3}	10^{-6}	371.69	91.36	3463.67	65.38	5648.33	56.32
3	10^{-4}	10^{-3}	10^{-5}	306.32	93.66	2996.44	70.33	4988.23	61.84
4	10^{-4}	10^{-3}	10^{-4}	275.34	93.83	2704.33	73.18	4767.52	63.22
5	10^{-4}	10^{-3}	10^{-3}	271.18	94.08	1407.23	86.33	2799.89	79.10

From the Table 9, it is observed that there is increase in enhancement of inhibition efficiency of 10^{-4} M AMCl with 10^{-3} M I in 1M H_2SO_4 as the concentration of Cu^{2+} increased. The inhibition efficiency increased from 89.89% to 95.84%. There is a decrease in inhibition efficiency the temperature from 298K to 308K. The inhibition efficiency was found to be 95.84% at 298K, 94.68% at 303K and 78.05% at 308K. Adsorption of Cu^{2+} on the steel at lower concentration may have been an important reason for the inhibition also the oxidizing reaction¹⁵

Table 9. Variation of IE with different concentrations of Cu^{2+} in the presence of 10^{-4} M AMCl and 10^{-3} M iodide in 1M H_2SO_4 at different temperatures (1 h study)

S.No	Concentration of			298K		303K		308K	
	AMCl, M	I, M	Cu^{2+}	CR, mpy	IE, %	CR, mpy	IE, %	CR, mpy	IE, %
1	Blank	Blank	Blank	3886.71	----	9749.71	-----	12774.13	-----
2	10^{-4}	10^{-3}	10^{-6}	431.74	89.89	2337.47	76.02	5922.17	53.64
3	10^{-4}	10^{-3}	10^{-5}	200.60	95.84	518.95	94.68	2804.09	78.05
4	10^{-4}	10^{-3}	10^{-4}	126.47	97.75	466.62	95.21	1077.16	91.57
5	10^{-4}	10^{-3}	10^{-3}	100.30	98.42	283.47	97.09	889.63	93.04

The kinetic parameter of the systems under consideration was evaluated using the data obtained from weight loss method for various concentrations of different metal ions, 10^{-4} M AMCl and 10^{-3} M I at higher temperatures. The activation energy values presented in the Table 10 and 11 were found to be greater in the presence of synergistic metal ions and halides and it may be interpreted¹⁶. This indicated the physical adsorption of inhibitor molecule on the metal surface. Higher activation energy for the corrosion process in the presence of synergistic ions lead to the conclusion that the inhibitor might have been bounded to the surface by specific adsorption process and as a result of which a surface filling of reaction product may be formed on the metal surface resulting in the inhibition. With the help of the temperature studies results, thermodynamic parameters such as ΔG , ΔH and ΔS were

calculated. The values of thermodynamic parameters are represented in the Tables 10 and 11 for various concentrations of cations in the presence of 10^{-3}M I and 10^{-4}M AMCl. The negative values of ΔG and ΔS values are characteristic of strong interaction between the inhibitor and the metal surface¹⁷. The free energy values for the investigated inhibitor decreases with increases in concentration of the investigated metal ions and with increase in temperature.

Table 10. Kinetic parameters of corrosion and thermodynamic parameters of adsorption of AMCl, I⁻ and Ni²⁺ ions for MS in H₂SO₄

Concentration Ni ²⁺ , M	Activation energy, J/mol	Free energy of adsorption (-ΔG), KJ/mol			Entropy change ΔS, KJ/mol	Heat of adsorption ΔH, KJ/mol
		298K	303K	308K		
Blank	-45379.727	--	--	--	--	--
10 ⁻⁶	-95526.091	54.0763	51.2368	51.6163	-0.098689	84.56784
10 ⁻⁵	-97172.746	48.5484	45.5469	45.8678	-0.103790	80.34579
10 ⁻⁴	-99087.460	42.7621	39.6622	40.4578	-0.124192	82.54679
10 ⁻³	-91734.967	36.7178	35.6240	36.7782	-0.126415	78.31579

Table 11. Kinetic parameters of corrosion and thermodynamic parameters of adsorption of AMCl, I⁻ and Cu²⁺ ions for MS in 1M H₂SO₄

Concentration Cu ²⁺ , M	Activation energy, J/mol	Free energy of adsorption (-ΔG), KJ/mol			Entropy change ΔS, KJ/mol	Heat of adsorption ΔH, KJ/mol
		298K	303K	308K		
Blank	-45341.432	--	--	--	--	--
10 ⁻⁶	-95526.091	53.6260	52.5003	51.5001	-0.104208	86.81445
10 ⁻⁵	-115879.503	49.7346	51.1256	48.1786	-0.160002	101.9087
10 ⁻⁴	-117162.362	44.9876	45.2008	44.5612	-0.166654	99.11122
10 ⁻³	-108278.088	39.2345	40.3333	38.9632	-0.120253	78.71132

Conclusions

The investigations of the study of “Synergistic effect of metal ions and halides on corrosion inhibition of mild steel in the presence of atropine methochloride in acidic medium” reveal that;

- As the concentration of AMCl increased, the inhibition efficiency also increased.
- Halide ions decreased the corrosion rate of mild steel in sulphuric acid. A steady decrease in corrosion rate is observed by increasing the concentration of iodide, chloride and bromide ions. The decrease is maximum with iodide ions. Enhancement of inhibition efficiency of 10^{-4}M AMCl in the presence of different cations with 10^{-3}M iodide ion and at higher temperature was found to be maximum.
- Activation energy in the presence of synergistic metal ions and halides was found to be higher than the blank values. This indicated that the physical adsorption of inhibitor molecule on the metal surface.
- The negative values of the free energy of adsorption indicate that there was a strong interaction between the inhibitor molecules and metal surface values of ΔH and ΔS were found to be inter related with ΔG . The values of ΔG could confirm the adsorption process is physical adsorption.

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