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Synergistic Effect of Halide Ions on the Corrosion Inhibition of Mild Steel in Sulphuric Acid Using Alkyl Substituted piperidi-4-one Thiosemicarbazones

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Abstract: The inhibition effect of alkyl substituted piperdin-4-one with thiosemicarbazones on mild steel corrosion in 1N sulphuric acid solution was studied by weight loss method and electrochemical techniques. The influence of halides viz., KCl, KBr and KI on the corrosion inhibition of thiosemicarbazones were also investigated. Results show that alkyl substituted piperidin-4-one with thiosemicarbazones alone provided satisfactory inhibition on the corrosion of mild steel and it was also found that the inhibition efficiency increased synergistically in the presence of halide ions. The synergistic effect of halide ions was found to follow the order: KI > KBr > KCl. The inhibitor reduced the corrosion rate through adsorption.

Key Words: Corrosion, mild steel, inhibitors, Halide ions, inhibition efficiency, Electrochemical measurements, synergistic effect.

I. Introduction

The corrosion behavior of mild steel has been widely investigated in several environments. Corrosion of metals such as mild steel is an electrochemical reaction which can cause the degradation and damage of the physical and chemical properties of the attacked metal. Besides the natural factors such as air humidity and wetness time, the usage of acid is found to be major factor that drives to the corrosion problem. Strong acids like hydrochloric acid and sulphuric acid are widely used in industries for many purpose especially for acid pickling, industrial acid cleaning, acid descaling and oil well acidizing. In order to reduce the undesirable acid metal dissolution, the use of inhibitors is one of the most practical methods for the surface protection against the corrosive media especially in acidic environments. There are various organic inhibitors which tend to decrease the corrosion rate of steel and iron in acidic solutions[1-5]. Most of the effective organic inhibitors used contain heteroatom such as O,N,S and multiple bonds in their molecules through which they are adsorbed on the metal surface[6-10]. Piperidiones have been found to inhibit acid corrosion of mild steel in different aspects [11-15].

Most acid inhibitors are known for their specificity of action. However, the addition of other substances and the combination of inhibitors has provided multiple effects of effective corrosion inhibition. Interestingly, the addition of halide ions into the acidic medium in the presence of organic inhibitors has been found to enhance the efficiency of inhibitive effects [16-19]. It is generally seen that the addition of halide ions to the corrosive media has increased the ability of adsorption of the organic cations by forming the interconnecting bridge between negatively charge metal surface and inhibitor cations. The introduction of the halide ions synergistically enhanced the inhibition efficiency of the organic inhibitors [20-27].

Although the synergistic effect of various halide ions with alkyl substituted piperidin-4-ones[28] are well known, the mechanism for their beneficial action is little known and there exist a limited number of attempts to explain the nature of mechanism. Halide ions are known both to stimulate and inhibit the corrosion of metal. The aim of the present work is undertaken

- To estimate the inhibition efficiency of alkyl substituted piperidin-4-ones with thiosemicarbazone in controlling the corrosion of mild steel in 1 N H_2SO_4.
- To study the effect of alkyl substituted piperidin-4-ones with thiosemicarbazone and halide ions concentration on its inhibition efficiency.
- To study the corrosion inhibition using the polarization techniques and AC impedance spectra.

II. Materials and Methods

Preparation of the specimen

Tests were performed on mild steel specimens of the following composition have been used throughout the present work. Carbon 0.07, Sulphur Nil, Phosphorous 0.008, Silicon Nil and Manganese 0.34. The mild steel specimen of 5×2.5 cm^2 was polished mirror finish and degreased with trichloroethylene, and used for the weight loss method.

Inhibitors

The inhibitors were synthesized according to the procedure that of Balasubramanian and Padma

01 TS-Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-methyl piperidin-4-one
02 TS-Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-ethyl-N-methyl piperidin-4-one
03 TS-Thiosemicarbazone of γ-2,c-6-diphenyl-t-3-ethyl piperidin-4-one

Weight loss method

Mild steel specimens in triplicate were immersed in 250 ml of the solution containing the inhibitor (alkyl substituted piperidin-4-ones with Thiosemicarbazone) in the presence and absence of halide ions for one hour. The weight of the specimen before and after immersion was measured. The corrosion inhibition was then calculated by using the following equation

Corrosion rate (mmpy) = $87.6 \times W / (D \times A \times T)$

Where W = Weight loss in mg
D = Density in g/cc
A = Area of exposure in cm^2 and
T = Time in hours.

Inhibitor efficiency has been calculated by using the following equation

Inhibitor efficiency (%) = $W_0 - W_e / W_0$

Where
W_0 is the weight loss without inhibitor and
W_e is the weight loss with inhibitor.

Potentiostatic polarization studies

This study was carried out using an electrochemical impedance analyzer with a three electrode cell assembly was used. Mild steel rod was used as working electrode, platinum electrode was used as the counter electrode, and saturated calomel electrode (SCE) was used as the reference electrode. Corrosion potential, corrosion current and tafel slopes were calculated [29-30].

Ac impedance measurements

Ac impedance measurements were taken out at the open circuit potential using electrochemical interface and a frequency response analyzer from 10 KHZ to 1 MHZ by applying 5m V A.C voltage. Nyquist plots were plotted from these experiments and R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were obtained from the Nyquist plots [31].

III. Results and Discussion

Weight Loss Method

Table 1 gives the values of the inhibition efficiency of alkyl substituted piperidin-4-ones of thiosemicarbazone [32] in 1N H_2SO_4 in presence of 1M KCl, KBr, KI and 0.2mM inhibitors by weight loss method.

Table 1

Corrosion parameters of Alkyl substituted piperidin-4-ones with thiosemicarbazone and Halide ions on mild steel in 1 N H_2SO_4 from weight loss measurements

SL NO.	Name of the inhibitor		Weight Loss (gm)	Corrosion Rate (mmpy)	Inhibition efficiency (%)	Surface Coverage (θ)
1	Blank		0.089	79.96		
2	01TS	KCl	0.0071	6.379	92.02	0.9202
		KBr	0.0065	5.84	92.70	0.9270
		KI	0.0059	5.30	93.37	0.9337
3	02TS	KCl	0.0163	14.64	81.69	0.8169
		KBr	0.0148	13.30	83.37	0.8337
		KI	0.0084	7.55	90.56	0.9056
4	03TS	KCl	0.0161	14.47	81.91	0.8191
		KBr	0.0153	13.75	82.93	0.8293
		KI	0.0092	7.55	89.66	0.8966

01- Methyl Substitution
02- Ethyl-N-Methyl substitution
03- Ethyl substitution

Weight loss of the mild steel was reduced while inhibition efficiency increased. The weight loss measurement indicates the synergistic effect caused by halide ions. Addition of 1 M halide ion increases the inhibition efficiency of 0.2 mM inhibitor, when compared with blank. The order of synergism of halide ions was found to be in the order of KI>KBr>KCl.

Potentiostatic polarisation studies

Figure 1 to 3 gives the potentiodynamic polarization plots of mild steel for alkyl substituted piperidin-4-ones of Thiosemicarbazone with halide ions. It is clear that corrosion current density decreases with adding inhibitors. The corrosion kinetic parameters derived from these curves are given in Table 2.

Figure – 1
Potentiodynamic polarization curves for mild steel in 1N H_2SO_4 in the absence and presence of Halide ions with (01TS)

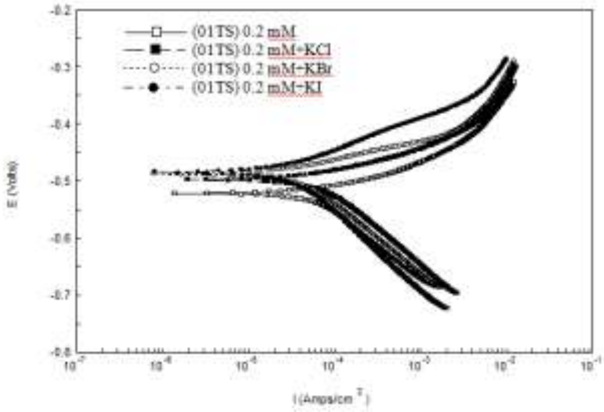

Figure – 2
Potentiodynamic polarization curves for mild steel in 1N H_2SO_4 in the absence and presence of Halide ions with (02TS)

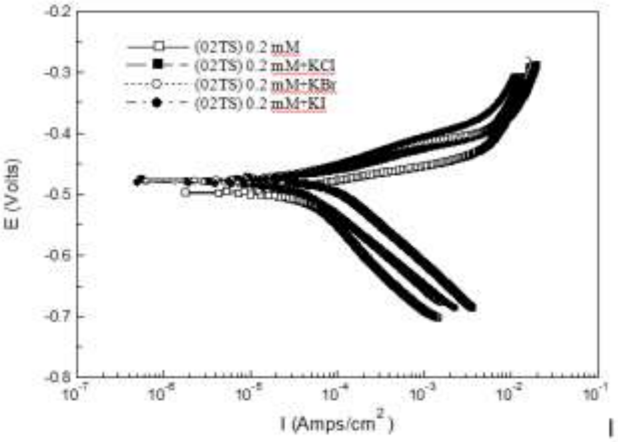

Figure – 3
Potentiodynamic polarization curves for mild steel in 1N H_2SO_4 in the absence and presence of Halide ions with (03TS)

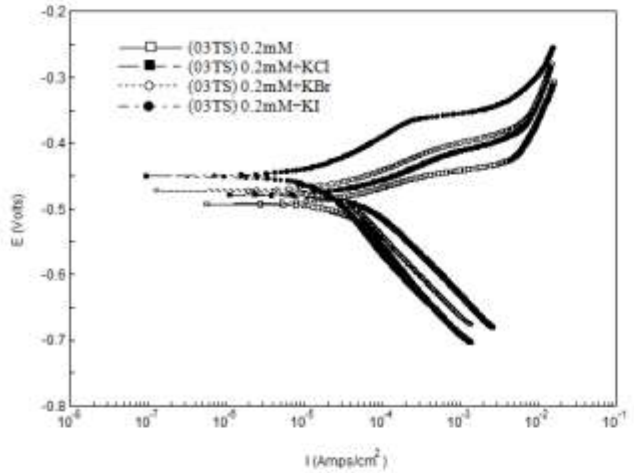

Table 2
Potentiodynamic polarization parameters for the corrosion of mild steel in 1 N H_2SO_4 with and without Alkyl substituted piperidin-4-ones with thiosemicarbazone and Halide ions

SL NO.	Inhibition concentration		Icorr (mA/cm2) x10^{-2})	Ecorr (mV vs SCE)	ba (mV/dec)	bc (mV/dec)	Corrosion Rate (mmpty)	Inhibition Efficiency (%)
1	Blank		4.57	-524	120	-137	104.71	
2	01TS	KCl	0.77	-480	42	-124	17.64	83.15
		KBr	0.30	-470	51	-120	6.87	93.44
		KI	0.25	-482	45	-119	5.73	94.53
3	02TS	KCl	0.83	-499	52	-127	19.02	81.84
		KBr	0.51	-491	53	-125	11.69	88.84
		KI	0.29	-485	56	-119	6.64	93.65
4	03TS	KCl	0.90	-473	44	-125	20.62	80.30
		KBr	0.54	-484	47	-124	12.37	88.18
		KI	0.33	-476	50	-117	7.56	92.78

From this it is seen that the corrosion current density decreases when the addition of inhibitors, so the studied inhibitor cause a decrease in corrosion rate of mild steel in acid media influencing both the acidic and cathodic reactions. The potentiodynamic polarization data of the inhibitors shows its mixed type character but the addition of halide ions still enhance the shift of Ecorr towards less negative side making the nature of inhibitor cathodic. The low corrosion rate in potentiodynamic polarization studies by halide ions shows that it is perfectly acting on the metal surface

A.C impedance measurements

Nyquist plots for mild steel in 1N H_2SO_4 for alkyl substituted piperidin-4-ones of thiosemicarbazone with halide ions are shown in the figure 4 to 6. Table 3 gives the value charge transfer resistance (R_t), double layer capacitance (C_{dl}) and inhibition efficiency obtained from the above plots

Figure 4
Nyquist plots for mild steel in 1 N H_2SO_4 in the absence and presence of Halide ions with (01TS)

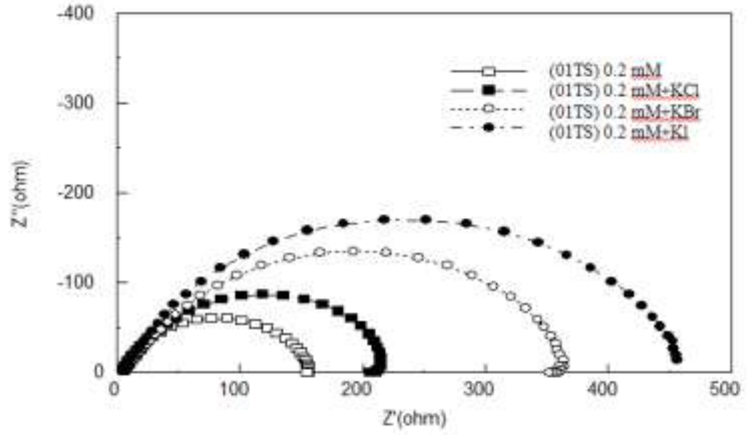

Figure 5
Nyquist plots for mild steel in 1 N H_2SO_4 in the absence and presence of Halide ions with (02TS)

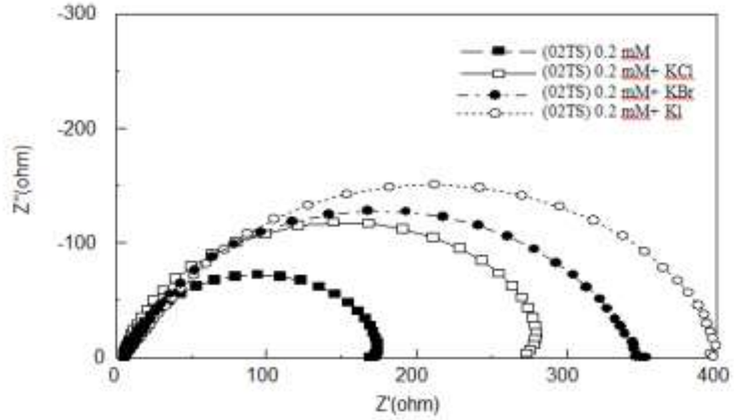

Figure 6
Nyquist plots for mild steel in 1 N H_2SO_4 in the absence and presence of Halide ions with (03TS)

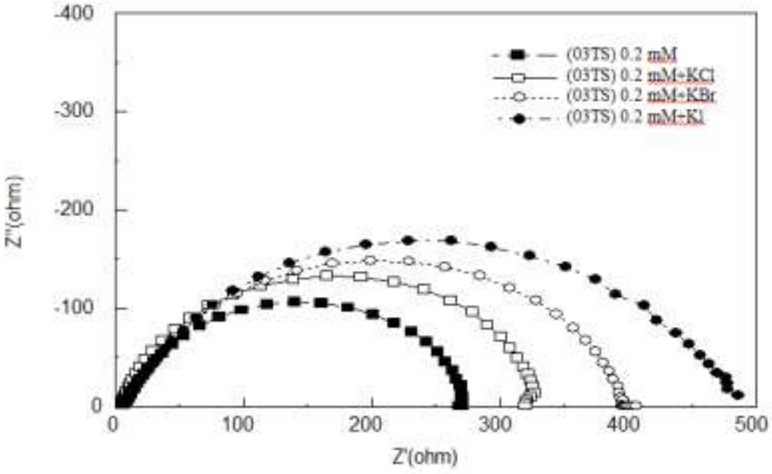

Table 3
Impedance parameters for the corrosion of mild steel in 1 N H_2SO_4 with and without of piperidin-4-ones with thiosemicarbazone and Halide ions

SL NO.	Name of the inhibitor		R_t (ohms)	C_{dl} (μ farads)	Inhibition efficiency (%)
1	Blank		32.13	0.14	
2	01TS	KCl	270.04	0.37	88.10
		KBr	392.07	0.28	91.81
		KI	477.33	0.21	93.27
3	02TS	KCl	201.36	0.29	84.04
		KBr	351.45	0.26	90.86
		KI	441.89	0.24	92.73
4	03TS	KCl	156.92	0.35	79.52
		KBr	329.78	0.28	90.25
		KI	384.33	0.22	91.64

From the table (3) the decrease in the double layer capacitance Cdl values may be attributed to decrease in local dielectrical constant or an increase in the thickness of the electrical double layer [32]. The double layer capacitance Cdl decreases with increasing by adding halide ions when compared with blank. The additions of halide ions increases the R_t values. The decreases in C_{dl} values in presence of inhibitors indicate the fact that these additives inhibit corrosion by adsorption on the metal surface.

Synergism of alkyl substituted piperidin-4-ones thiosemicarbazone with halide ions

All the experimental results have revealed that the addition of halide ions to the inhibited solution enhances the inhibition efficiency and the surface coverage θ. This behavior to the synergistic effect between added halide ions and alkyl substituted piperidi-4-ones.

To determine the existence of the synergism phenomenon between piperidin-4-ones and halide ions, synergism parameter was evaluated using the equation initially proposed by the Aramaki and Hackermann in 1964 and reported elsewhere [33-35]

$S_I = (1- I_{1+2}) / (1-I'_{1+2})$
$S_\theta = (1-\theta_{1+2}) / (1-\theta'_{1+2})$
Where
$I_{1+2} = (I_1+I_2)- I_1I_2$
I_1 = inhibition efficiency of the anion
I_2 = inhibition efficiency of the cation
I'_{1+2} = measured inhibition efficiency for the cation in combination with anion.
$\theta_{1+2} = (\theta_1+\theta_2)- \theta_1\theta_2$
θ_1 = surface coverage by anion.
θ_2 = surface coverage by cation.
θ'_{1+2} = measured surface coverage by both anion and cation.

This parameter was calculated from the values of inhibition efficiency and degree of surface coverage (θ) i.e., S_I and S_θ and their values are given in the Table 4.

Table 4
Synergistic parameters

Sl. No	Halide ion concentration (1 M)	(01TS)		(02TS)		(03TS)	
		S_I	S_θ	S_I	S_θ	S_I	S_θ
1	KCl	0.84	1.01	0.85	1	0.84	1
2	KBr	0.11	1.22	0.11	1	0.11	1.09
3	KI	0.13	1.31	0.12	1.74	0.12	1.65

The S_1 values given in the Table 4 are more than unity and this suggests that the enhanced inhibition efficiency caused by halide ions to the inhibitors is only due to a synergistic effect.

The synergistic effect brought by the combination of inhibitor and halide ions for corrosion of mild steel in 1N H_2SO_4 can be explained as follows. The strong chemisorptions of halide ions on the metal surface is responsible for the synergistic effect. The halide ions in combination with inhibitor cation. The positively charged inhibitor ions (protonated thiosemicarbazone group) are then absorbed by coulometric attraction at the metal surface, where halide ions already absorbed by chemisorptions. Stabilization of absorbed halide ions by means of electrostatic interaction with positively charged inhibitor leads to greater surface coverage and there by greater inhibition.

The order of synergism observed in halide ions is KI > KBr > KCl.

IV. CONCLUSION

1) Thiosemicarbazones of alkyl substituted 2,6-diphenyl piperidin-4-one exhibits maximum efficiency towards inhibition of corrosion of mild steel in 1N H_2SO_4 media. This is probably caused by the formation of an complex at lower concentrations due to adsorption.
2) Addition of halide ions enhances the inhibition efficiency.
3) Thiosemicarbazone of alkyl substituted piperidin-4-ones and halide ions in combination inhibits the corrosion of mild steel in 1N H_2SO_4 by affecting both cathodic and anodic reactions.
4) Values of the synergism parameters (S_I and S_θ) shows that corrosion inhibition produced by alkyl substituted piperidi-4-ones and halide ions combination is synergistic in nature.

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