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CORROSION INHIBITION PROPERTIES OF THIOSEMICARBAZONE AND SEMICARBAZONE DERIVATIVES IN CONCENTRATED ACID ENVIRONMENT

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ABSTRACT

The corrosion inhibition properties of thiosemicarbazone and semicarbazone derivatives in 5 M H_2SO_4 have been evaluated using hydrogen evolution via the gasometric assembly at 30° and 40°C. 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), 2-acetylpyridine thiosemicarbazone (2APTSC), 2-acetylpyridine-(4-phenyl) semicarbazone (2AP4PSC) and 2-acetylpyridine semicarbazone (2APSC) were tested for their inhibition abilities on the corrosion of mild steel in 5 M H_2SO_4 solutions. ixtures of 0.05 M KI and different concentrations of the organic compounds were also tested. The thiosemicarbazones were found to inhibit mild steel corrosion in H_2SO_4 at the higher concentrations range tested (5×10^{-4} M - 1×10^{-3} M) but accelerated the corrosion rate at lower concentrations (1×10^{-5} M - 1×10^{-4} M). The semicarbazones behaved as corrosion accelerators of mild steel corrosion at all the concentrations tested. The inhibition efficiencies of the compounds follow the trend: 2AP4PTSC > 2AP4MTSC > 2APTSC > 2AP4PSC > 2APSC. Physical adsorption of the compounds on the metal surface is proposed as the mechanism of inhibition. Inhibition synergism and antagonism with KI were observed at high concentrations (5×10^{-4} M - 1×10^{-3}) and low concentrations (1×10^{-5} M - 1×10^{-4} M) respectively for the thiosemicarbazones, while antagonism was observed at all concentrations for the semicarbazones.

KEYWORDS: Corrosion inhibition, mild steel, thiosemicarbazone, semicarbazone, synergism, antagonism.

INTRODUCTION

Semicarbazones and thiosemicarbazones as well as their derivatives have emerged recently as a new and potential class of corrosion inhibitors (Babaqi *et al.*, 1989; Ebenso *et al.*, 1999; 2001; Ekpe *et al.*, 1995; 2001; Ita and Offiong, 1997; 2001; Okafor *et al.*, 2004). A detailed and systematic investigation of their corrosion inhibiting characteristics under widely varying conditions has been the interest in our laboratories in recent times. This is to enable better insight on the factors that are most likely to affect their performance, assess the nature of their dependence on such factors and determine the most appropriate choice of environmental conditions for optimum performance. Results obtained so far reveal a strong dependence of inhibition efficiencies and even inhibition mechanisms on the inhibitor structure and composition, temperature as well as nature and concentration of the aggressive environment, but these are still to be further explored. In continuation of our investigations, we present here a study of the inhibitive effect of some semicarbazone and thiosemicarbazone derivatives namely; 2-acetyl-pyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), 2-acetylpyridine thiosemicarbazone (2APTSC), 2-acetylpyridine-(4-phenyl) semicarbazone (2AP4PSC) and 2-acetylpyridine semicarbazone (2APSC) on the corrosion of mild steel in 5 M H_2SO_4. The corrosion inhibiting efficacies of some of these compounds in dilute aqueous acid solutions have been established in earlier reports (Ebenso *et al.*, 1999; 2001; Ekpe *et al.*, 1995; 2001; Okafor *et al.*, 2004). The effects of temperature and addition of KI on the inhibition efficiency are also reported.

Experimental/Materials preparations

The chemical composition of mild steel specimen used in this study was: C=0.19%, Mn=0.64%, Si=0.26%, S=0.05%, P=0.06%, Ni=0.09%, Cr=0.08%, Md=0.02%, Cu=0.27% and the balance Fe. The sheets were mechanically press-cut into coupons of dimension 2cm×5cm×0.08cm. The coupons were polished using emery papers up to 600 grits, degreased with absolute ethanol and dried using acetone.

The aggressive solution employed was 5 M H_2SO_4 solution, prepared from AR grade sulphuric acid. The test inhibitors, 2AP4PTSC, 2AP4MTSC, 2APTSC, 2AP4PSC and 2APSC were synthesized in our laboratory as described elsewhere (Offiong, 1990; Offiong and Martelli, 1993). concentrations of 1×10^{-5} M, 5×10^{-5} M, 1×10^{-5} M, 5×10^{-4} M and 1×10^{-3}M were prepared in 5 M H_2SO_4 solution as solvent. The effect of the iodide ion was studied by introducing 0.05 M KI into the inhibited solutions containing the respective organic compounds.

Gasometric experiments

The gasometric assembly and procedure for the measurement of hydrogen gas evolution were similar to that described previously (Onuchukwu, 1988; Ekpe *et al.*, 1997; Ita and Offiong, 2001). The experiments were conducted at temperatures of 30°C and 40°C. The volume of hydrogen gas evolved was monitored as a function of time and the rate was determined from equation:

$$Rate\ (cm^3/\min) = \frac{dv}{dt} \qquad (1)$$

where dv and dt are changes in volume and time respectively.

RESULTS AND DISCUSSION

The spontaneous corrosion of mild steel in acidic solutions can be represented by the anodic dissolution reaction:

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$$Fe \rightarrow Fe^{2+} + 2e \quad (2)$$

Accompanied by the corresponding cathodic reaction:

$$2H^{+} + 2e \rightarrow H_2 \quad (3)$$

The corrosion rate of mild steel in 5 M H_2SO_4 in the absence and presence of the organic compounds was thus assessed by careful volumetric measurement of the evolved hydrogen gas at fixed time intervals at 30 and 40°C. This technique apart from its experimental rapidity ensures a more sensitive monitoring, in situ, of any perturbation by an inhibiting additive vis-à-vis gas evolution at the metal-corrodent interphase (Ebenso *et al.*, 2005). Results obtained by the gasometric method are corroborated by other well established methods including weight loss and thermometric (El-Etre, 2003), potentiostatic polarization (Abdallah, 2004) and impedance spectroscopy (Aytac *et al.*, 2005). The results obtained are shown in Figure 1 and 2. The plots reveal higher rates of hydrogen gas evolution in the presence of the additives, at all concentrations of the semicarbazones (2AP4PSC, 2APSC) compared to the blank acid. Similar trend is observed at low concentrations of the thiosemicarbazones (2AP4PTSC, 2AP4MTSC, 2APTSC), which completely reverses at higher concentrations, where the corrosion rates were lower than in the blank. Higher corrosion rates in inhibited solutions imply that the compounds lose their reported corrosion inhibiting abilities in the concentrated acid environment, and rather accelerate the corrosion reaction to different extents depending on their chemical structure and concentration. Corrosion rates generally decreased with increasing additive concentration but increased with rise in temperature.

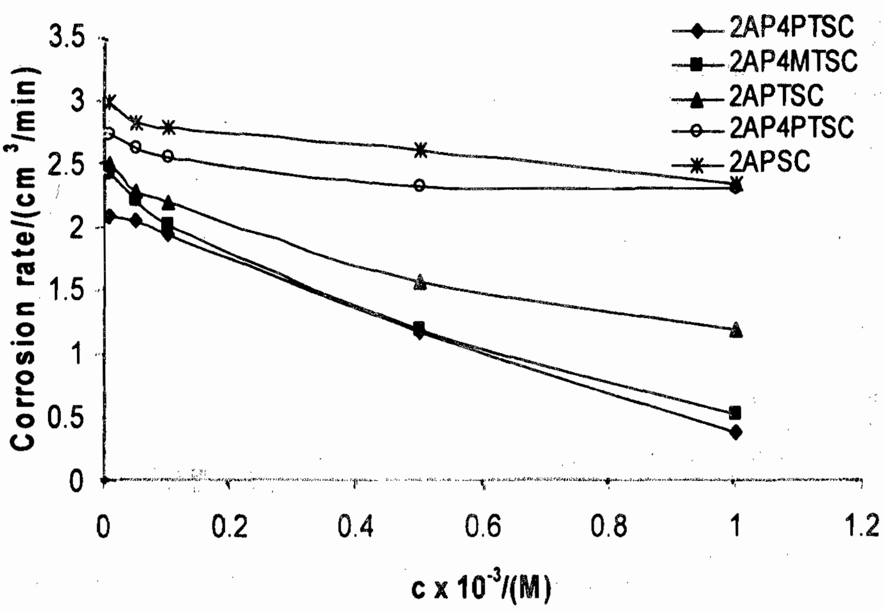

Figure 1: Variation of corrosion rate (cm^3/min) with concentration of the organic compounds at 30°C.

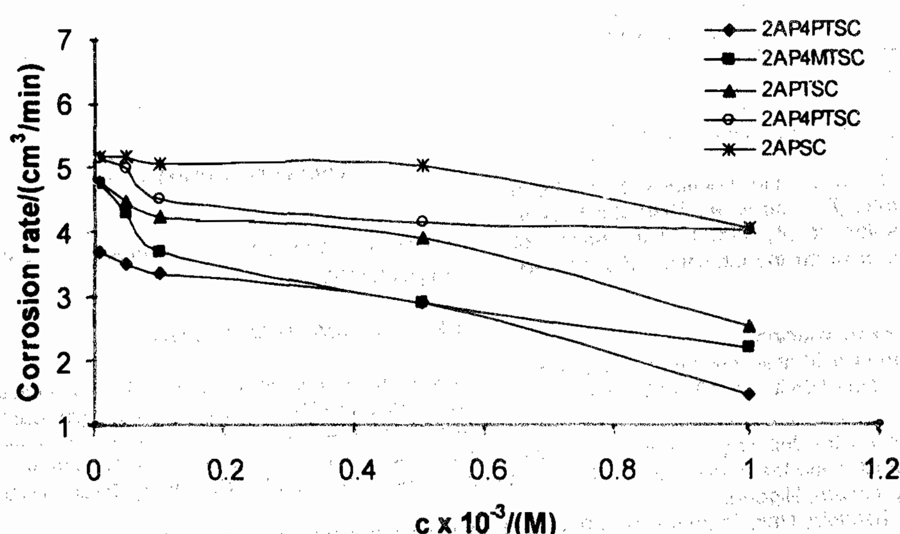

Figure 2: Variation of corrosion rate (cm^3/min) with concentration of the organic compounds at 40°C.

A comparison of the corrosion rates of the mild steel coupons in absence and presence of different concentrations of the additives was undertaken to assess the existence or lack of an inhibiting effect as follows:

$$I\% = \left(1 - \frac{R_i}{R_0}\right) \times 100 \qquad (4)$$

where R_i and R_0 are the corrosion rates of the mild steel coupon in the inhibited and uninhibited corrodent respectively. A positive value of the calculated parameter indicates an inhibiting effect of the additive, which corresponds to the inhibition efficiency (I %), whereas a negative value signifies a catalytic effect that accelerates the metal corrosion. The results obtained at different temperatures are shown in Table 1 as well as Figures. 3 and 4.

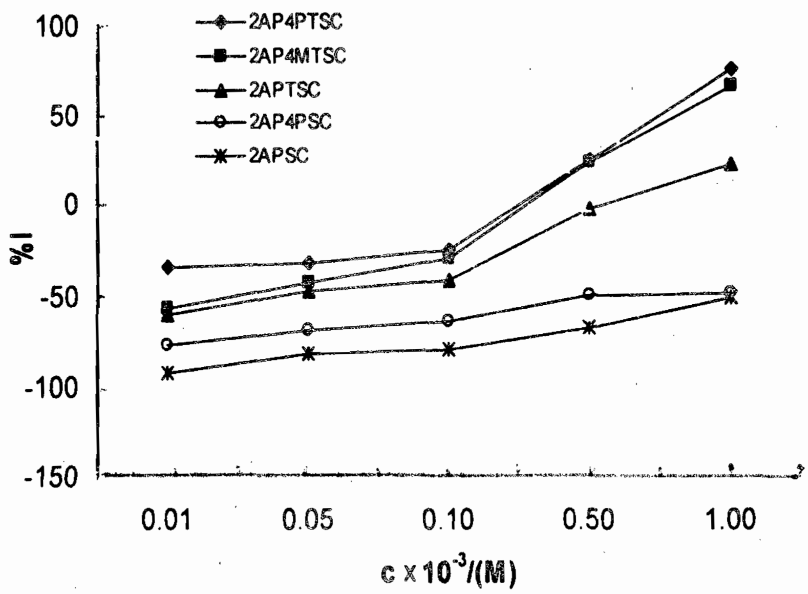

Figure 3: Variation of inhibition efficiency with concentration of the organic compounds at 30°C.

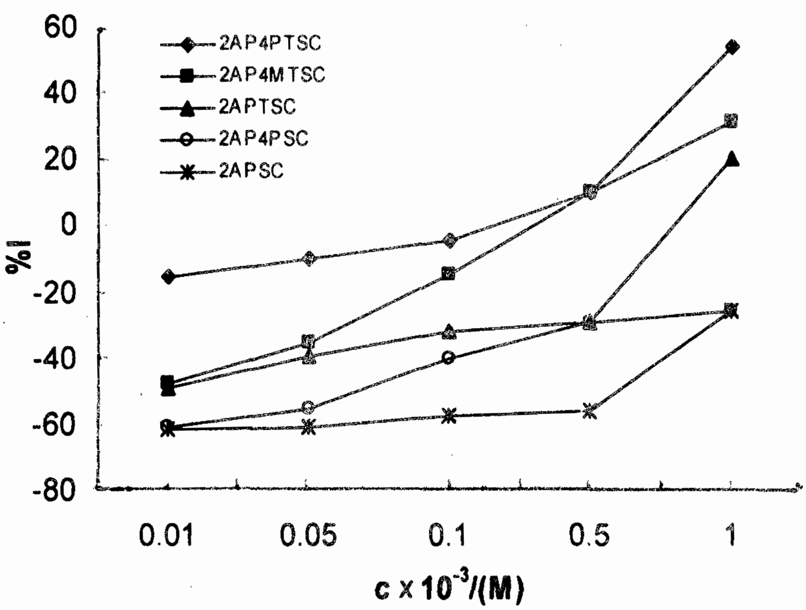

Figure 4: Variation of inhibition efficiency with concentration of the organic compounds at 40°C.

The results indicate negative values of the inhibition efficiency at all concentrations of 2AP4PSC and 2APSC, and at lower concentrations of 2AP4PTSC (1×10^{-5} - 1×10^{-4}M) and 2AP4MTSC, (1×10^{-5} - 5×10^{-4}M). The effect of each additive is however observed to become more positive with increasing in concentration. Inhibiting effects were however observed at higher concentrations of 2AP4PTSC, 2AP4MTSC and 2APTSC, with a maximum efficiency of 76.2 % for 2AP4PTSC. This implies that the thiosemicarbazones retain their corrosion inhibiting efficacy even in the concentrated acid environment.

Table 1 : Calculated values of corrosion rate (cm^3/min), surface coverage (θ), inhibition efficiency (%) and activation energies (KJ/mol) for mild steel in 5M H_2SO_4 containing the organic compounds.

System	Corrosion rate/(cm^3/min)		Surface coverage, θ		Inhibition efficiency/%		Activation energy/ (KJ/mol)
	30°C	40°C	30°C	40°C	30°C	40°C	
5 M H_2SO_4 (blank)	1.553	3.215	-	-	-	-	57.4
1 x 10^{-5} M 2AP4PTSC	2.081	3.708	-0.340	-0.153	-34.0	-15.3	45.6
5 x 10^{-5} M 2AP4PTSC	2.039	3.530	-0.313	-0.098	-31.2	-09.8	43.3
1 x 10^{-4} M 2AP4PTSC	1.937	3.369	-0.247	-0.048	-24.7	-04.8	43.7
5 x 10^{-4} M 2AP4PTSC	1.159	2.900	0.254	0.098	25.4	09.8	72.3
1 x 10^{-3} M 2AP4PTSC	0.369	1.494	0.762	0.536	76.2	53.6	110.3
1 x 10^{-5} M 2AP4MTSC	2.425	4.750	-0.561	-0.477	-56.1	-47.7	53.0
5 x 10^{-5} M 2AP4MTSC	2.211	4.300	-0.423	-0.337	-42.3	-35.7	52.5
1 x 10^{-4} M 2AP4MTSC	2.008	3.700	-0.293	-0.151	-29.3	-15.1	48.2
5 x 10^{-4} M 2AP4MTSC	1.186	2.907	0.237	0.096	23.7	09.6	70.7
1 x 10^{-3} M 2AP4MTSC	0.522	2.220	0.664	0.309	66.4	31.0	114.2
1 x 10^{-5} M 2APTSC	2.488	4.788	-0.602	-0.489	-60.2	-48.9	51.7
5 x 10^{-5} M 2APTSC	2.280	4.487	-0.468	-0.396	-46.8	-39.6	53.4
1 x 10^{-4} M 2APTSC	2.183	4.233	-0.405	-0.317	-40.5	-31.7	52.2
5 x 10^{-4} M 2APTSC	1.570	3.900	-0.018	-0.213	-1.8	-29.3	72.3
1 x 10^{-3} M 2APTSC	1.189	2.560	0.234	0.204	23.4	20.4	60.5
1 x 10^{-5} M 2AP4PSC	2.733	5.166	-0.760	-0.607	-76.0	-60.7	50.2
5 x 10^{-5} M 2AP4PSC	2.620	4.988	-0.687	-0.551	-68.8	-55.1	50.8
1 x 10^{-4} M 2AP4PSC	2.540	4.514	-0.635	-0.404	-63.5	-40.4	45.4
5 x 10^{-4} M 2AP4PSC	2.312	4.155	-0.488	-0.292	-48.8	-29.2	46.2
1 x 10^{-3} M 2AP4PSC	2.306	4.040	-0.485	-0.257	-48.5	-25.7	44.2
1 x 10^{-5} M 2APSC	2.981	5.185	-0.919	-0.613	-91.9	-61.3	43.7
5 x 10^{-5} M 2APSC	2.825	5.180	-0.819	-0.611	-81.9	-61.1	47.8
1 x 10^{-4} M 2APSC	2.785	5.063	-0.793	-0.575	-79.3	-57.5	47.1
5 x 10^{-4} M 2APSC	2.600	5.025	-0.674	-0.563	-67.4	-56.3	52.0
1 x 10^{-3} M 2APSC	2.329	4.055	-0.499	-0.261	-50.0	-26.1	43.7

Several factors could contribute to the disappearance of the inhibiting efficacy of some of the studied compounds under the present circumstances. According to the mechanism for the anodic dissolution of Fe in acidic sulphate solutions proposed initially by Bockris *et al.* (1961), Fe electro-dissolution in acidic sulphate solutions depends primarily on the adsorbed intermediate $FeOH_{ads}$ as follows:

$$Fe + OH^- \Leftrightarrow FeOH_{ads} + H^+ + e \quad (5a)$$

$$FeOH_{ads} \xrightarrow{rds} FeOH^+ + e \quad (5b)$$

$$FeOH^+ + H^+ \Leftrightarrow Fe^{2+} + H_2O \quad (5c)$$

Another mechanism, involving two adsorbed intermediates has been used to account for the retardation of Fe anodic dissolution in the presence of an inhibitor (Ashassi- Sorkhabi and Nabavi- Amri, 2000).

$$Fe + H_2O \Leftrightarrow Fe.H_2O_{ads} \quad (6a)$$

$$Fe.H_2O_{ads} + Y \Leftrightarrow FeOH^-_{ads} + H^+ + Y \quad (6b)$$

$$Fe.H_2O_{ads} + Y \Leftrightarrow FeY_{ads} + H_2O \quad (6c)$$

$$FeOH^-_{ads} \xrightarrow{rds} FeOH_{ads} + e \quad (6d)$$

$$FeY_{ads} \Leftrightarrow FeY^+_{ads} + e \quad (6e)$$

$$FeOH_{ads} + FeY^+_{ads} \Leftrightarrow FeY_{ads} + FeOH^+ \quad (6f)$$

$$FeOH^+ + H^+ \Leftrightarrow Fe^{2+} + H_2O \quad (6g)$$

where Y represents the inhibitor species.

According to the detailed mechanism above, displacement of some adsorbed water molecules on the metal surface by inhibitor species to yield the adsorbed intermediate FeY_{ads} (Eq.6c) reduces the amount of the species $FeOH^-_{ads}$ available for the rate determining step. Such adsorbed intermediate could, depending on its relative solubility, either inhibit or catalyse further metal dissolution. Hence the integrity and effectiveness of the metal-inhibitor complex depends on the environmental capacity to dilute it. From the foregoing, it seems the complexes formed by the studied compounds were readily soluble in the 5 M H_2SO_4 corrodent, thus accelerating the corrosion reaction. With increasing additive concentration, more inhibitor molecules become available for complex formation, which subsequently diminishes the solubility of the surface layer, leading to a reduction in the catalytic effect, and in the case of 2AP4PTSC and 2AP4MTSC, resulted in an inhibiting effect. Another consideration may be that the excess positive charge on the mild steel surface in 5 M H_2SO_4 restrained adsorption of the compounds, which predominantly exist as protonated species in acid solution, due to electrostatic repulsion. Which ever way we consider the present circumstances; either from the point of view of the high solubility of the adsorbed metal-inhibitor complex or the repulsion of inhibitor cations from the positively charged metal surface, the fact remains that the studied semicarbazone derivatives do not exert an inhibiting effect on steel corrosion in 5 M H_2SO_4 solution.

The observed differences in the behaviour of the additives may be rationalized by considering their molecular structures. The better inhibiting abilities of the thiosemicarbazones could be attributed to the effect of the electron density of the adsorbed species (anchoring atoms) on the surface of the metal. Thiosemicarbazones contain sulphur which has greater electron density available for adsorption than oxygen present in semicarbazones, and as such demonstrate a better inhibiting effect. Comparing the inhibition efficiencies of the thiosemicarbazones, the phenyl derivative exhibits better inhibiting ability than the methyl derivative. This is in agreement with previous reports (Ekpe *et al.*, 1995; Ebenso *et al.*, 1999). The phenyl group possesses a greater electron releasing ability than the methyl group and as such exerts a greater stabilizing effect on the anchoring S atom. In addition, the larger size of the phenyl derivatives forms a more functional blanket, thereby preventing the metal from coming into contact with the active species in the corrosive medium. Similar explanation also holds for the observed sequence of the semicarbazones where the adsorbed intermediate formed by 2AP4PSC is less soluble than that of 2APSC.

The existence therein of catalytic or inhibitive effects was further confirmed by evaluating the apparent activation energies (E_a) for mild steel corrosion in 5 M H_2SO_4 solution in the presence and absence of the additives as follows:

$$Log\frac{R_2}{R_1}=\frac{E_a}{2.303R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right) \quad (7)$$

where R_1 and R_2 are the corrosion rates at temperatures T_1 and T_2 respectively. The calculated values are given in Table 1. At additive concentrations where corrosion acceleration was observed, E_a values were correspondingly lesser than that obtained in the blank acid. Such tendency to lower the activation energy of the corrosion reaction is indicative of a catalytic effect. On the other hand, in systems where adsorption of the additives resulted in an inhibiting effect, E_a values were above that of the blank corrodent, indicating that the adsorbed intermediates retard the rate of the corrosion reaction. This corresponds to an inhibiting effect.

Effect of KI

Addition of halide salts to sulphuric acid solution containing any organic compound has been reported to result in a cooperative effect which inhibits Fe dissolution (Gomma, 1993; 1998; Ebenso, 2003; 2004; Oguzie, 2004; Oguzie *et al.*, 2004; Oguzie *et al.*, 2006). It is thought that the anions are able to improve adsorption of the organic cations in acidic solution by forming intermediate between the positively charged metal surface and the positive end of the organic inhibitor. Corrosion inhibition synergism results from increased surface coverage arising from ion-pair interactions between the organic inhibitor and the halide ions. Controversy however exists on the actual role of the anions as regards the improved adsorption of the organic inhibitors. In a previous report (Oguzie, 2004), it was suggested that the halide ion is first specifically adsorbed on the metal surface and the inhibitor is then drawn into the double layer by the adsorbed halide ion such that the ion-pair formation occurs directly on the metal surface. Hence, a recharging of the metal surface electrical double layer by specifically adsorbed halide ions is responsible for the increased adsorption of organic cations

$$X_s \rightarrow X_{ads} \quad (8a)$$

$$Y_s + X_{ads} \rightarrow (YX)_{ads} \quad (8b)$$

Y_s, X_s and $(YX)_s$ represent the inhibitor, halide ion and ion-pair respectively in the bulk of the solution while Y_{ads}, X_{ads} and $(YX)_{ads}$ refer to the same species in the adsorbed state

The effect of KI additives on the inhibition efficiencies of the studied organic compounds is illustrated in Table 2. KI on its own is observed to exhibit very high inhibition efficiency due essentially to its strong electrostatic interaction with the positively charged steel surface. In order to characterise the co-operative effects of KI and the organic compounds, the synergism parameter S_I was calculated as follows;

$$S_1=\frac{1-I_{1+2}}{1-I'_{1+2}} \quad (9)$$

where $I_{1+2}=(I_1+I_2)$; I_1 is the inhibition efficiency of the KI, I_2 is the inhibition efficiency of the organic compounds and I'_{1+2} is the inhibition efficiency of the organic compounds in combination with KI. The values calculated are less than unity at lower concentrations of (1×10^{-5} - 1×10^{-4}) M 2AP4PTSC, (1×10^{-5} - 1×10^{-4}) M 2AP4MTSC (1×10^{-5} - 5×10^{-4}) M 2APTSC, and at all concentrations of the semicarbazones indicating antagonistic effects, and higher than unity at higher concentrations of the thiosemicarbazones [(5×10^{-4} - 1×10^{-3}) M 2AP4PTSC and 2AP4MTSC, and 1×10^{-3} M 2APTSC] ing synergistic effects. These results imply that the ability of KI to synergistically improve the adsorption of the organic compounds was greatly impeded by the high concentration of the acid corrodent. The reason for this is not quite clear, but it seems the high positive surface charge on the steel samples effectively neutralizes the negative charge of the iodide ion, thereby precluding any possibility of ion pair interactions with the inhibitor cations. Moreover, if such interactions do occur, the attractive force will be relatively weak and the resulting surface complex would be readily dissolved as observed with the organic compounds alone. Presently, we are studying to see if positive results will be obtained by first immersing the steel sample in KI solution before introduction into the inhibitor solution.

Table 2: Calculated values of corrosion rate (cm^3/min), surface coverage (θ), inhibition efficiency (%) and synergism parameter (S_1) at different temperatures for mild steel in 5M H_2SO_4 containing KI – organic compounds mixtures.

System	Corrosion rate/(cm^3/min)		Surface coverage, θ		Inhibition efficiency/%		Synergism parameter, S_1	
	30°C	40°C	30°C	40°C	30°C	40°C	30°C	40°C
5 M H_2SO_4 (blank)	1.553	3.215	-	-	-	-	-	-
0.05 M KI	0.081	0.100	0.948	0.969	94.8	96.9	-	-
1 x 10^{-5} M 2AP4PTSC	0.074	0.182	0.952	0.943	95.2	94.3	0.634	0.863
5 x 10^{-5} M 2AP4PTSC	0.077	0.180	0.951	0.944	95.0	94.4	0.665	0.922
1 x 10^{-4} M 2AP4PTSC	0.087	0.175	0.944	0.946	94.4	94.6	0.739	0.974
5 x 10^{-4} M 2AP4PTSC	0.100	0.154	0.936	0.952	93.6	95.2	1.287	1.122
1 x 10^{-3} M 2AP4PTSC	0.097	0.116	0.937	0.964	93.7	96.4	1.834	1.567

1 x 10^{-5} M 2AP4MTSC	0.077	0.085	0.946	0.974	94.6	97.4	0.403	0.499
5 x 10^{-5} M 2AP4MTSC	0.069	0.087	0.944	0.973	94.4	97.3	0.551	0.625
1 x 10^{-4} M 2AP4MTSC	0.054	0.112	0.928	0.965	92.8	96.5	0.702	0.846
5 x 10^{-4} M 2AP4MTSC	0.080	0.082	0.947	0.975	94.7	97.5	1.253	1.094
1 x 10^{-3} M 2AP4MTSC	0.072	0.113	0.927	0.965	92.7	96.5	1.746	1.328
1 x 10^{-5} M 2APTSC	0.069	0.096	0.938	0.970	93.8	97.0	0.361	0.489
5 x 10^{-5} M 2APTSC	0.067	0.086	0.945	0.973	94.5	97.3	0.503	0.585
1 x 10^{-4} M 2APTSC	0.069	0.108	0.930	0.966	93.0	96.6	0.579	0.672
5 x 10^{-4} M 2APTSC	0.073	0.102	0.934	0.968	93.4	96.8	0.996	0.695
1 x 10^{-3} M 2APTSC	0.063	0.112	0.928	0.965	92.8	96.5	1.277	1.217
1 x 10^{-5} M 2AP4PSC	0.056	0.143	0.908	0.956	90.8	95.6	0.199	0.373
5 x 10^{-5} M 2AP4PSC	0.038	0.105	0.932	0.967	93.2	96.7	0.272	0.426
1 x 10^{-4} M 2AP4PSC	0.036	0.066	0.958	0.980	95.8	98.0	0.319	0.572
5 x 10^{-4} M 2AP4PSC	0.044	0.117	0.925	0.964	92.5	96.4	0.491	0.699
1 x 10^{-3} M 2AP4PSC	0.041	0.123	0.921	0.962	92.1	96.2	0.498	0.738
1 x 10^{-5} M 2APSC	0.044	0.149	0.904	0.954	90.4	95.4	0.021	0.367
5 x 10^{-5} M 2APSC	0.082	0.167	0.893	0.948	89.3	94.8	0.135	0.371
1 x 10^{-4} M 2APSC	0.054	0.195	0.875	0.939	87.5	93.9	0.167	0.414
5 x 10^{-4} M 2APSC	0.087	0.100	0.936	0.969	93.6	96.9	0.285	0.413
1 x 10^{-3} M 2APSC	0.072	0.082	0.947	0.975	94.7	97.5	0.468	0.723

CONCLUSIONS

The inhibiting effect of 2-acetylpyridine-(4-phenyl) thiosemicarbazone (2AP4PTSC), 2-acetylpyridine-(4-methyl) thiosemicarbazone (2AP4MTSC), 2-acetylpyridine thiosemicarbazone (2APTSC), 2-acetylpyridine-(4-phenyl) semicarbazone (2AP4PSC) and 2-acetylpyridine semicarbazone (2APSC) on mild steel corrosion in 5 M H_2SO_4 was studied using the gasometric technique. The steel corrosion reaction was accelerated by 2AP4PSC and 2APSC at all studied concentrations whereas 2AP4PTSC, 2AP4MTSC, 2APTSC accelerated corrosion only at low concentrations and exhibited appreciable corrosion inhibiting effect at higher concentrations due essentially to the presence of the S atom in their molecular structures. Inhibition efficiency was scantly improved in the presence of KI. The observed behaviour is attributed to the high solubility of the metal-inhibitor complex in the concentrated acid environment.

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