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Use of 1-phenylamino-3-(4-phenylthiosemicarbazone)-butane-1,3-dione derivatives as corrosion inhibitors for C-steel in acidic chloride solutions

A.K. Mohamed, H.A. Mostafa, G.Y. El-Ewady and A.S. Fouda
Department of Chemistry, Faculty of Science, El-Mansoura University,
El-Mansoura, Egypt.

Abstract

The corrosion inhibition of nitrogen, oxygen and sulphur containing compounds in acidic chloride solutions was studied by chemical and electrochemical techniques. The percentage inhibition efficiency was calculated from both methods is in good agreement. The corrosion rate was found to be a function of the nature, concentration and temperature of the medium. The increase in temperature was found to increase the corrosion rate. The inhibitors are adsorbed on the C-steel surface according to the Langmuir isotherm. Some themrodynamic functions were computed and discussed. Quantum data were calculated and the results of HOMO and LUMO showed that the increase in energy of HOMO corresponds to an increase in the inhibition efficiency.

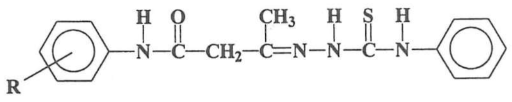
Key words: Corrosion, C-steel, acid chloride solution, butane-1,3- dione derivatives.

Introduction

As known that the economic power of a country is determined by its output of steel, since progress in the principal economic branches be it mining, transport, manufacturing engineering or agriculture is unthinkable without steel. So, studies of steel properties in general and electrochemical, especially, have been received a great attention. In such respect, the corrosion and corrosion inhibition of steel in the different media become very interesting and important, owing to its wide applicability in industry and domestic life. Numerous studies on iron and steel were done including the corrosion nature and its mechanism in different media. Corrosion inhibition using different inhibitors and the various factors affecting on it were studied by many authors [1-17]. The object of this work is undertaken to investigate the role played by some 1-phenylamino-3-(4-phenylthiosemicarbazone)-butan-1,3-dione derivatives in retarding the dissolution of C-steel in 2M HCl and throw some light on their mechanism of inhibition.

Experimental

The selected organic inhibitors used in this investigation were new compounds and prepared [18] by the condensation of equimolar amounts of 4-phenylthiosemicarbazide and the appropriate acetoacetanilide (2-methoxyl, 2-methyl, 4-methoxyl, 4-methyl and 4-nitroacetoacetanilide) in ethanolic solution in presence of few drops of dilute HCl, reflux for four hours, cool and recrystallized several times. The purity was checked by elemental analysis and IR spectra. These organic inhibitors used are:



where R = H(I), o-OCH_3(II) and o-CH_3(III) for first group compounds and p-CH_3(VI), p-OCH_3(V) and p-NO_2(VI) for second group compounds.

All the chemicals used were of A.R grade quality. The composition of C-steel specimens (weight %) used was: C = 0.2, Mn = 0.35, P = 0.024, Si = 0.003 and Fe = rest. C-steel test pieces measuring 20x20x2 mm^3 were used for weight loss measurements. A cylindrical rod with a diameter of 0.646 mm was used as working electrode in galvanostatic polarization measurements. The specimens were abraded mechanically with different grades of emery paper (2/0 and 3/0), degreased with acetone [19], washed with double distilled water, and finally dried between filter papers.

Apparatus and working procedure

The percentage inhibition efficiency, %I, was calculated from weight loss method using the following equation:

$$\%I = (1 - \frac{w_2}{w_1})x100 \qquad (1)$$

where w_1 and w_2 are weight losses in uninhibited and inhibited solutions, respectively.

For galvanostatic polarization measurements a saturated calomel reference electrode and a platinum wire counter electrode were used. The procedure adopted for the potential measurements was the same as described before [20]. The corrosion current densities were determined by the intersection of the extrapolating anodic and cathodic Tafel lines to free corrosion potential values. The percentage inhibition efficiency was calculated from corrosion current density values using the equation:

$$\%I = (1 - \frac{i_2}{i_1})x100 \qquad (2)$$

where i_1 and i_2 are the corrosion current densities ($\mu A\ cm^{-2}$) without and with inhibitor respectively and the degree of surface coverage (θ) was calculated from equation (3).

$$\theta = 1 - \frac{i_2}{i_1} \qquad (3)$$

Method of calculation

The extended Hückel method [21,22] was applied to calculate the electronic structure and reactivity indices of the molecules. The structural parameters of molecules utilized in the calculation are obtained form the work by Dewar et al. [23].

Results and Discussion

Weight loss measurements

The loss in the weight of C-steel pieces in presence and in absence of the additives was determined. The weight loss is plotted (Fig. 1) as function of time for compound I. Curves having the same shape were obtained for the other additives. The corrosion rate of C-steel decreased appreciably even in the presence of traces of these compounds. The extent of decrease in the corrosion rate depends on the nature and concentration of the additives. The percentage inhibition of these additives after 5 hours are recorded in Table 1. As shown from this Table, the sequence of decreasing inhibition efficiency for first group compounds at most concentrations is: III > II > I where as it is: V > IV > VI for those of the second.

Table 1. Variation of the percentage inhibition efficiency of first and second group compounds with their molar concentrations from weight loss method.

Concentration (M)	% Inhibition (%I)					
	First group			Second group		
	I	II	III	IV	V	VI
$1x10^{-6}$	5.84	7.00	10.90	2.66	3.86	2.16
$5x10^{-6}$	17.15	15.54	26.43	19.48	21.19	4.10
$1x10^{-5}$	32.59	25.08	30.90	33.90	35.10	5.02
$5x10^{-5}$	49.40	63.95	64.92	50.70	53.13	33.38
$1x10^{-4}$	82.57	84.54	85.91	82.78	85.58	48.72

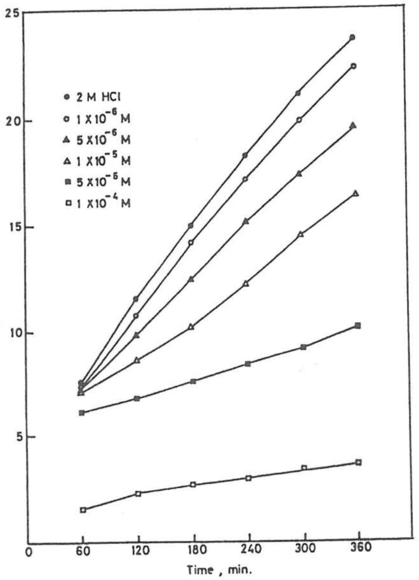


Fig. 1. Weight loss-time curves for C-steel in 2M HCl in presence and in absence of different concentrations of compound (I)

Polarization measurements

Figure 2 shows the galvanostatic polarization curves of C-steel in 2M HCl alone and containing different concentrations of compound I at 25°C. Cathodic and anodic polarization curves obtained exhibited Tafel-type behaviour. The results obtained for other inhibitors were quite similar. It is clear that, the increase of the concentration of the inhibitors cause the following: a) decrease of the rate of corrosion (i_{corr}) and b) An increase in both cathodic and anodic over voltages with parallel displacement to more negative and positive values, respectively. The values of the variation of free corrosion potential ($E_{corr.}$), corrosion current ($i_{corr.}$), Tafel slopes (β_a and β_c), degree of surface coverage (θ) and percentage inhibition (%I) with the concentrations of compound I can be shown in Table 2. Because of the parallel Tafel lines (constant β_a and β_c) one can use equation (3) in calculating θ (There is no change in mechanism in absence and in presence of inhibitors).

A correlation between C/θ vs. C (Fig. 3) for compound I gave a straight line with nearly unit slope suggesting that the adsorption of compound I on C-steel surface obeys the equation of Langmuir's adsorption isotherm (equation 4).

Table 2. Electrochemical parameters of C-steel in the presence of different concentrations of compound I at 25C°.

Concentration (M)	$-E_{corr.}$ mV	$i_{corr.}$ $\mu A\ cm^{-2}$	β_c mV decade^{-1}	β_a	θ	%I
0.0	485	223.87	97.5	75.0	-	-
$1x10^{-7}$	485	188.36	97.5	72.5	0.1586	15.9
$5x10^{-7}$	483	177.83	97.5	72.5	0.2057	20.6
$1x10^{-6}$	478	141.25	105.0	77.5	0.3691	36.9
$5x10^{-6}$	468	84.14	110.0	77.5	0.6242	62.4
$1x10^{-5}$	460	83.40	105.0	77.5	0.6274	62.7
$5x10^{-5}$	430	61.40	117.5	80.0	0.7257	72.6
$1X10^{-4}$	430	45.62	120.0	85.0	0.7962	79.6

$$\frac{C}{\theta} = C + \frac{1}{K} \qquad (4)$$

where K is the adsorption equilibrium constant, θ is the surface coverage and C the inhibitor concentration in mole L^{-1}.

The order of decreasing inhibition efficiency (Table 3) of the additives is: III > II > I for first group compounds and V > IV > VI for second group compounds.

The two different techniques gave the same order of inhibition efficiency of the tested materials but yielded different absolute values, probably due to the different experimental conditions.

Table 3. Variation of the percentage inhibition efficiency of first and second group compounds with their concentrations from polarization method.

Concentration (M)	% Inhibition					
	First group			Second group		
	I	II	III	IV	V	VI
$1x10^{-7}$	15.9	29.2	36.9	20.6	32.2	20.6
$5x10^{-7}$	20.6	40.4	45.4	29.2	42.9	25.0
$1x10^{-6}$	36.9	49.9	52.7	36.9	46.2	33.2
$5x10^{-6}$	62.4	64.5	66.5	43.8	52.0	40.4
$1x10^{-5}$	62.7	70.2	71.8	62.4	66.5	43.8
$5x10^{-5}$	72.6	83.2	84.2	71.8	73.4	70.2
$1x10^{-4}$	79.6	85.0	86.7	81.2	87.5	78.8

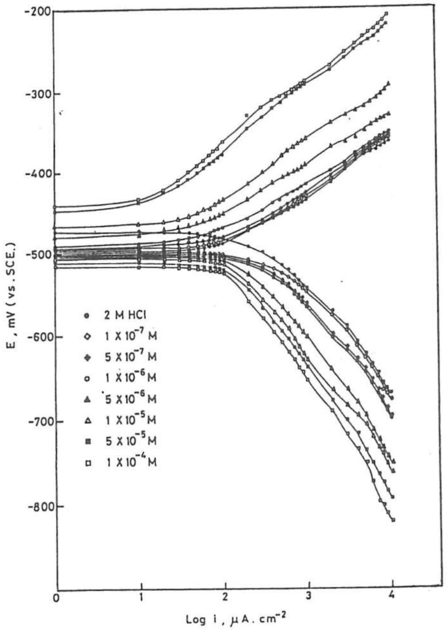


Fig. 2. Galvanostatic polarization curves of C-steel in 2M HCl alone and containing different concentrations of compound (I) at 25 °C

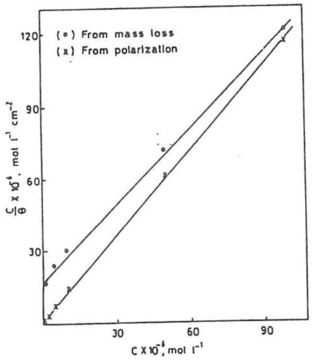


Fig. 3. C/θ vs. C of compound (I)

Effect of temperature

The effect of temperature on the rate of dissolution of C-steel in 2M HCl was studied by galvanostatic polarization method in the range 25-45°C. Arrhenius plot of log $i_{corr.}$ vs. 1/T is shown graphically in Figs. 4 and 5 for first and second group compounds, respectively. The values of activation energy, E_a^* are given in Table 4. These values indicate that the presence of inhibitors increase the activation energy of the metal dissolution reaction. The activation energy, E_a^*, for the corrosion process in free acid solution is found to be 63.56 KJ mol^{-1}. Ateya et al. [24] found that the activation energy of 51.4 KJ mol^{-1} for iron in 5N H_2SO_4 solution which was identical to that reported by Hadson et al. [25], and by Selim et al. [26]. On the other hand, Maitra and Singh [27], found that the activation energy of low carbon steel in 1N H_2SO_4 solution is 4.81 KJ mol^{-1}. Generally, one can say that the nature and concentration of electrolyte affect greatly the activation energy for the corrosion process.

The heat of adsorption (Q) can be obtained from the slopes of the log (θ/1-θ)vs 1/T. The thermodynamic parameters of the inhibitors investigated are listed in Table 4.

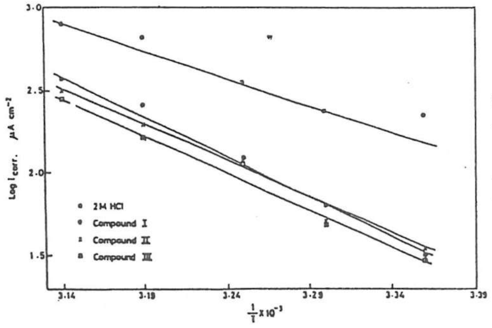


Fig. 4. Log $i_{corr.}$ vs 1/T curves for C-steel in absence and presence of 10^{-4}M of first group compounds.

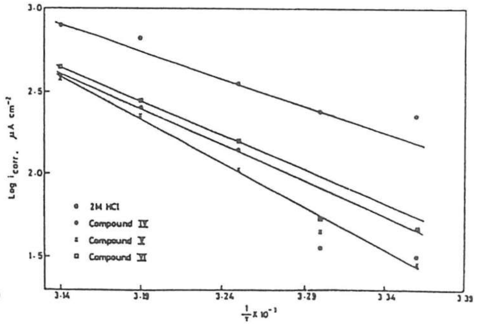


Fig. 5. Log $i_{corr.}$ vs 1/T curves for C-steel in absence and presence of 10^{-4}M of second group compounds

Table 4. Thermodynamic parameters for adsorption of inhibitors on C-steel in 2M HCl containing 10^{-4} M inhibitors.

Inhibitor	E_a^* KJ $mole^{-1}$	-ΔG* KJ mol^{-1}	ΔS* JK^{-1} mol^{-1}	-Q KJ mol^{-1}	Slope of log(θ/1-θ)vs 1/T
Free acid	63.56	-	-	-	-
I	80.34	36.70	85.23	62.01	$3.24x10^3$
II	84.55	37.06	70.44	57.99	$3.03\ x10^3$
III	86.02	37.39	50.54	52.44	$2.74\ x10^3$
IV	87.10	36.37	65.64	55.88	$2.92\ x10^3$
V	100.40	36.68	19.66	42.49	$2.22\ x10^3$
VI	78.20	36.02	94.90	64.30	$3.36\ x10^3$

Chemical structure and corrosion inhibition

Variation in structure of two group compounds (I-VI) takes place through phenylamino side chain but the thiosemicarbazone moiety being the same (unchanged). The electron charge density of the adsorption centers depends on substituents in the phenylamino ring.

Skeletal representation of the mode of adsorption of the compounds is shown in Fig. 6.

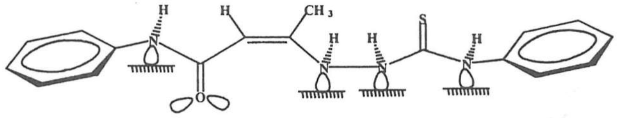


Fig. 6. Skeletal representation of the mode of adsorption of the tested compounds

The obtained results indicate that the order of decreased inhibition efficiency of first and second group compounds can be accounted in terms of obviously operating factors, including the polar effect [28] of the substituents on the phenylamino side chain and the location of substituent group. In the ortho-position both inductive and resonance effects may operate together strongly, but proximity of the group, i.e. steric effect, complicate the availability of active centers for inhibition reaction. In case of the substituted group is located in para-position, the inductive effect is relatively small owing to the presence of four carbon distant.

In our investigation for first group compounds, inhibitor III which contains methyl group as ortho-substituent is more efficient than inhibitor II with contains methoxy group also as ortho- substituent due to the sterric effect of methoxy group present in ortho-position.

For second group compounds, the order of decreased inhibition efficiency runs parallel to the order of decreasing donating character for the different substituted groups as follows: OCH_3 (σ = -0.27) > CH_3 (σ = -0.17) > H(σ = 0.0) > NO_2(σ = +0.78), where σ is the substituent constant in the Hammett equation [29].

Evidence for the validity of the forgiven explanation is gathered from the application of the Hammett equation. A plot of log $i_{corr.}$ vs. σ gives a straight line (Fig. 7) demonstrating the dependence of corrosion rate on the polar character of substituents in the inhibitor molecules.

The ability of the inhibitors to adsorb on metallic surfaces was elucidated from electrocapillary curves determined in their presence and in their absence. Curves for the adsorption of inhibitor I from 2M HCl as an example (Fig. 8) indicates that this ability can be gathered from a decrease in mercury drop time with increase of concentration. Moreover, similar curves for the various inhibitors at a concentration of 10^{-4}M revealed that the order of decrease in this ability is concordant with the order of decrease in inhibition efficiency as indicated by weight loss and polarization measurements. Therefore, inhibition of C-steel in 2M HCl

by the studied inhibitors is directly related to their adsorption at the metal surface.

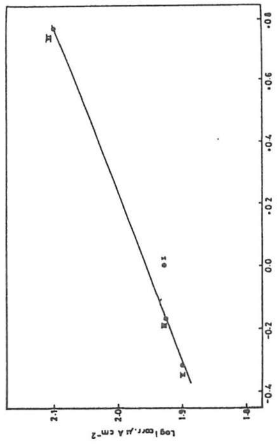


Fig. 7. Log $i_{corr.}$ vs. σ of second group compounds for C-steel in 2M HCl.

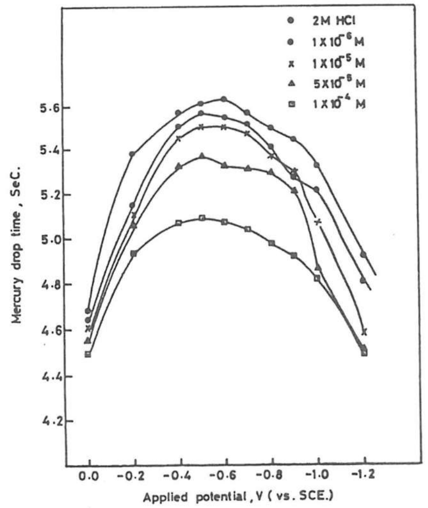


Fig. 8. Electrocapillary curves of 2M HCl solution containing different concentrations of compound (I)

The relation between inhibition characteristics and quantum chemical data show that log $i_{corr.}$ mostly depends upon the energies of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). It is evident from Fig. 9(A&B) that the inhibition efficiency increases with the increase of energy of the HOMO, that is, the increase of the ionization potential. It is further evident that the inhibition efficiency increases with the ease of ionization of the molecule, which means that the molecule acts as an electron doner when blocking the corrosion reaction.

The results of Table 5 show that the energies of HOMO orbital of the 1-arylamino-3-(4-phenylthiosemicarbazone)-butan-1,3-dione derivatives decrease in the order: II > III > I for first group compounds and V > IV > VI for those of second.

The quantum calculations of the inhibition efficiency for second group compounds run parallel to its calculated from chemical and electrochemical methods, but for first group compounds, compound II comes before compound III in inhibition efficiency. This can be interpreted on the basis of steric effect, which can not considered in quantum calculations of HOMO and LUMO orbital.

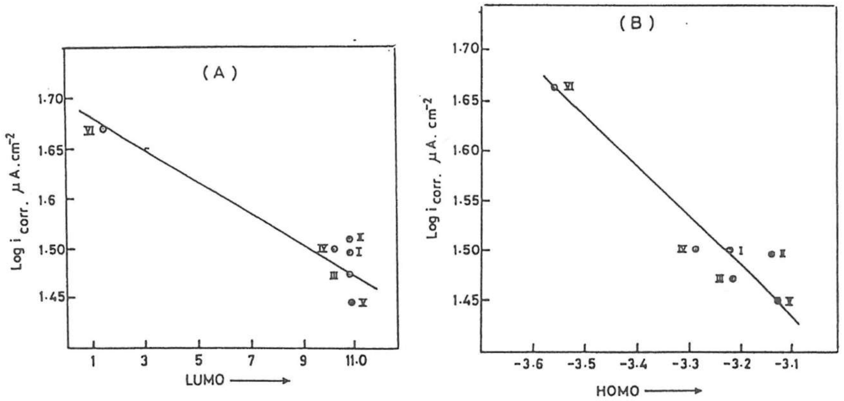


Fig. 9. Correlation between LUMO (A) and HOMO (B) energies with log $i_{corr.}$ for the different compounds

Table 5. Quantum chemical parameters of the investigated compounds.

Inhibitor	log* $i_{corr.}$	Atom**	Charge density	HOMO Kcal mole^{-1}	LUMO Kcal mole^{-1}	% Inh.
I		N(1)	+0.249			
		O(9)	+0.0853			
	1.659	N(8)	+0.242	-3.2229	+10.8898	85.88
		S(10)	+0.109			
III		N(1)	+0.249			
		O(9)	+0.0853			
	1.475	N(8)	+0.242	-3.2159	+10.8865	86.67
		S(10)	+0.109			
II		N(1)	+0.247			
		O(9)	+0.0851			
	1.525	N(8)	+0.242	-3.1367	+10.8761	85.04
		S(10)	+0.109			
VI		N(1)	+0.298			
		O(9)	+0.0844			
	1.675	N(8)	+0.246	-3.5560	+1.3071	78.86
		S(10)	+0.113			
IV		N(1)	+0.187			
		O(9)	+0.0891			
	1.625	N(8)	+0.185	-3.2959	+10.3628	81.16
		S(10)	+0.068			
V		N(1)	+0.246			
		O(9)	+0.0852			
	1.449	N(8)	+0.242	-3.1335	+10.9684	87.45
		S(10)	+0.109			

* Calculated at $1x10^{-4}M$

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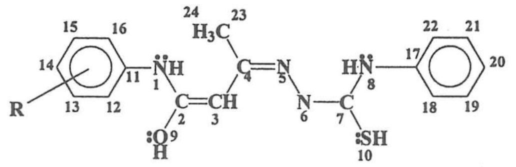

Conclusions

The tested butane-1,3-dione derivatives act as mixed type inhibitors but the cathode is more polarized against pure carbon steel in 2M hydrochloric acid at 25°C. All the compounds are adsorbed on the metal surface following Langmuir adsorption isotherm. Inhibition efficiency increases with increase in the concentration of the inhibitors as well as its electron donor character. The rat eof corrosion was found to increase with increase in temperature and decrease with increase in the HOMO energy.

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