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The synergistic inhibitive effect and the thermodynamic parameters of 2 (2- hydroxylstyryl) pyridinium-N- ethyl iodide and some metal cations on the acid corrosion of low-carbon steel

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The synergistic effect of 2(2-hydroxy styryl) pyridinium -N- ethyl iodide (cyanine dye) and some selected metal cations viz. Zn^{+2} or Cr^{+3} on the corrosion of low carbon steel in 2M H_2SO_4 has been studied by weight loss measurements and galvanostitic polarization technique over the temperature range 30 to 60°C.

The efficiency of combined inhibitor was studied for different concentrations of Zn^{+2} and Cr^{+3} cations ranging from 5×10^{-3} to 10^{-1} M. The obtained results showed that the presence of cyanine dye molecules in the corrosive medium (2M H_2SO_4 solution) inhibits the corrosion process of low-carbon steel and as the concentration of the cyanine dye increases the inhibition efficiency also increased at all the examined temperatures. The presence of Zn^{+2} ions only in the corrosive medium is not favorable for the corrosion of the steel metal but the presence of Cr^{+3} gives a higher inhibition effect. On the other hand, the presence of Zn^{+2} or Cr^{+3} ions together with the cyanine dye increases the inhibition efficiency at all examined concentrations and temperatures, while the synergistic effect of cyanine dye and Cr^{+3} ions is the best one.

The activation energy, heat of adsorption and thermodynamic parameters of the synergistic effect of cyanine dye and metal cations under investigation on the corrosion process have been calculated at the different temperatures, supporting the obtained results. The electronic energies and charge densities for cyanine dye compound were calculated by the MINDO/3 method.

Keywords: Corrosion; transition metal cations; low carbon steel; cyanine dye.

1. INTRODUCTION

Study of organic corrosion inhibitors is an attractive field of research due to its usefulness in various industries. Most of the well-known acid inhibitors are organic compounds that contain nitrogen, sulphur, oxygen and multiple bonds in the molecules through which are adsorbed on the metal surface.[1] Corrosion inhibition of mild steel in acid media by leaf extracts of Occimum viridis (OV) was studied at temperatures of 30 and 60 °C. The results indicate that the extracts inhibit the corrosion process in acid media and inhibition efficiency increased with concentration. Synergistic effects increased the inhibition efficiency in presence of halide additives namely KCl, KBr, KI. Temperature studies revealed a decrease in efficiency with rise in temperature and corrosion activation energies increased in the presence of the extract, probably implying that physical adsorption of cationic species may be responsible for the observed inhibition behavior.[2] The inhibitive capabilities of some organic dyes namely; safranine-o (SO), thymol blue (TB) and fluorescein-Na (F-Na) on the electrochemical corrosion of mild steel in sulphuric acid solution was studied, the results indicate that all of the studied compounds act as inhibitors in the acidic corrodent. Inhibition efficiency increased with concentration for SO and TB but decreased with concentration for F-Na.[3]

The corrosion inhibition of mild steel in hydrochloric acid solution by methylene blue dye (MB) was investigated at 30 and 60 °C. MB was shown to be an inhibitor in the acidic corrodent. Inhibition efficiency increased with MB concentration but decreased with rise in temperature. The corrosion inhibition is attributed to the adsorption of MB at the mild steel surface via a physical adsorption mechanism. These results were further corroborated by kinetic and activation parameters for corrosion and adsorption processes evaluated from experimental data.[4] Methylene blue dye (MB) was investigated as a corrosion inhibitor for mild steel in 2 M sulphuric acid solution. The inhibition efficiency of MB increased with concentration and synergistically increased in the presence of the halide additives, namely KCl, KBr and KI. The MB was found to obey Langmuir and Frumkin adsorption isotherms in the concentration range investigated.[5]

Gonzalez et al [6] found that, mixture of zinc salt and phosphonic acid reduced the corrosion rate of carbon steel and this behavior may be due to the formation of a very thin and homogeneous protective film. The synergistic effect of Zn^{+2} ions and molybdate on the corrosion inhibition of mild steel was studied, [7] it was found that the presence of Zn^{+2} ions and molybdate together in the neutral aqueous environment decrease the corrosion rate by 90% due to the formation of protective film from ferric molybdate, zinc peroxide and γ- FeOOH and this film is semi-conducting and luminescent. On the other hand, the presence of Cu^{+2} cations together with some thiols in the corrosive medium (H_2SO_4) of mild steel increases the inhibition efficiency of corrosion than that in presence of thiol only.[8]

The synergistic effect of mixtures from N-phosphonomethylglycine and Zn^{+2} ions on the corrosion of steel in neutral chloride solutions, was studied and it was found that the inhibition efficiency increase by 85 to 95% and this mixture retarded both the anodic and cathodic partial reaction of the corrosion process.[9]

A study by Onuchukwu et al [10] showed that the presence of a mixture from dichromate and Ni^{+2} ions, reduces the aggressiveness of the corrosive medium for carbon steel by a noble shift of corrosion potential of the metal. Interface and interphase inhibition mechanisms are proposed to suggest explanations for the inhibiting experimental observations of these ions in the corrosion of carbon steel. The influence of chromium additives on the inhibitive efficiency of some organic compounds was studied by Zucchi et al. [11] they found that the inhibitive effect of the investigated compound against corrosion of steels increases with increasing chromium content.

In this communication we aim to study the synergistic effect of (2-hydroxy styryl) pyridinium -N- ethyl iodide (cyanine dye) together with Zn^{+2} and Cr^{+} ions, as representative to the di and tri valent cations on the corrosion inhibition of low carbon steel in 2M H_2SO_4 solution at temperature range (30-60) ^{o}C. The adsorption of mixed inhibitors was analyzed in order to choose the appropriate adsorption isotherm and hence to determine the thermodynamic functions ΔG, ΔH and ΔS.

2. EXPERIMENTAL

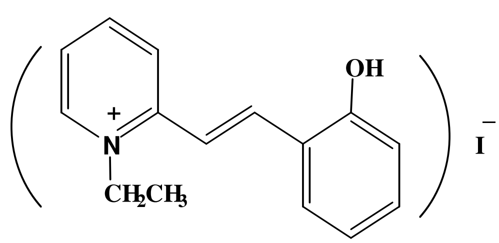
2.1 Reagents

The investigated cyanine dye was prepared as described before, [12] and recrystallized from ethanol. The purity checked by HPLC, elemental analysis and spectral data.

The synergistic effect of the cyanine dye and Zn^{+2} or Cr^{+3} ions [$ZnSO_4$ or $Cr_2(SO_4)_3$] representative to the di and tri-valent cations on the corrosion of low carbon steel in 2M H_2SO_4 was carried out by adding the cyanine dye only and together with metal cations to the corrosive medium.

Low carbon steel samples used [(C (0.17 – 0.23) %, Mn (0.2 – 0.5) %, P 0.35% and Si 0.035%)] having a thickness of 2 mm and dimensions of 1 cm x 5 cm were pretreated to remove any oxide layers (for less than one minute) or corrosion products from the surface (for 15 minutes) using the following solutions respectively: .[13] a) H_2SO_4 (70g/L); b) NaOH (100g/L), Na_2CO_3 (40g/L), Na_2SiO_3 (10g/L).

The effect of cyanine dye and metal cations separately and together on the weight loss (mg/dm^2) of the low– carbon steel in 2M H_2SO_4 solution as corrosive medium was investigated using the technique mentioned elsewhere.[14]



2 (2- hydroxylstyryl) pyridinium -N- ethyl iodide

2.2 Equipments

Anodic and cathodic galvanostitic polarization curves of low – carbon steel electrode have been measured. The polarization cell used for this purpose has been described earlier. [15] Potentials were measured by a digital potentiometer using a saturated calomel electrode (SCE) half cell and platinum counter electrode. The applied current density (I_d) was ranged from (0.45 - 45) mA/cm^2, starting with the lower current density. The corrosion current ($I_{corr.}$) and corrosion potential ($E_{corr.}$) were determined from the intersection of the Tafel lines.

The effect of 2 (2-hydroxy styrylpyridinium -N- etly1 Iodide concentrations ($10^{-5} - 10^{-3}$)M on one hand and 10^{-5} M together with different concentrations ($5x10^{-3}$ - 10^{-1}) M of metal cations (Cr^{+3} and Zn^{+2}) on the other hand, on the galvanostitic polarization curves of low carbon steel electrode in 2M H_2SO_4 solution, as a function of temperature has been measured.
The cyanine dye used has the following molecular structure.

3. RESULTS AND DISCUSSION

3.1. Weight loss measurements

Data recorded in Table (1) represent the effect of cyanine dye concentration $10^{-5} - 10^{-3}$ M, metal cation $5x10^{-3} - 10^{-1}$ M and 10^{-5} M of cyanine dye together with metal cations $5x10^{-3} - 10^{-1}$ M, on the weight loss of low carbon steel in 2M H_2SO_4 solution as a corrosive medium. It is obvious that the presence of cyanine dye or metal cations separately in the corrosive medium (2M H_2SO_4) decreased the loss in weight (except in case Zn^{+2} ions), which mostly decreased as the concentration increased.
On the other hand, the synergism of the dye and the metal cations (Cr^{+3} or Zn^{+2}) increased the inhibition effect, where the inhibition efficiency (I%) and the degree of surface coverage area (**θ**) increase with concentration.

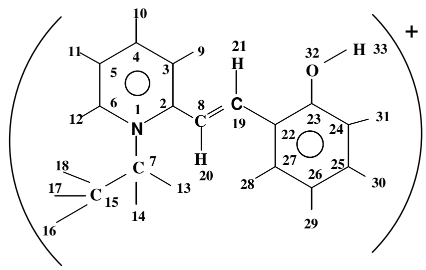
Table 1. The effect of cyanine dye or metal cations separately and together on the weight loss (mg dm^{-2}) of low –carbon steel in 2M H_2SO_4 solution (for 5h.) at 30°C

Cyanine dye				dye (10-5M) + Zn+2				dye (10-5M) + Cr+3			
Conc. M	Wt. loss mg	I%	θ	Conc. M	Wt. loss mg	I%	θ	Conc. M	Wt. loss mg	I%	θ
0.00	743	-	-	0.00	743	-	-	0.00	743	-	-
10^{-5}	360	14.4	0.14	$5x10^{-3}$	543	26.9	0.27	$5x10^{-3}$	470	36.7	0.37
10^{-4}	490	34	0.34	10^{-2}	460	38	0.38	10^{-2}	360	51.5	0.52
$5x10^{-4}$	370	50	0.50	$5x10^{-2}$	377	49	0.49	$5x10^{-2}$	293	60.6	0.61
10^{-3}	260	65	0.65	10^{-1}	327	56	0.56	10^{-1}	210	71.7	0.72

Zn+2 only				Cr+3 only			
Conc. M	Wt. loss mg	I%	θ	Conc. M	Wt. loss mg	I%	θ
0.00	743	-	-	0.00	743	-	-
$5x10^{-3}$	741	0.0	0.0	$5x10^{-3}$	650	12.5	0.12
10^{-2}	745	0.0	0.0	10^{-2}	540	27.3	0.27
$5x10^{-2}$	743	0.0	0.0	$5x10^{-2}$	457	38.5	0.38
10^{-1}	742	0.0	0.0	10^{-1}	377	49	0.49

The corrosion inhibition by cyanine dye or Cr^{+3} ions may be explained via its adsorption at steel surface.[16-18] The observed synergistic effect of cyanine dye and metal cations could be interpreted by considering the co-adsorption of both Cr^{+3} or Zn^{+2} ions and cyanine dye molecules at the metal surface,[19] while the cyanine dye together with Cr^{+3} ions is the best one.

From MINDO/3 electronic energy point of view,[20] the charge densities of the used cyanine dye molecule have been calculated together with some physical characters like the ionization potential, electron affinity, heat of formation, electronic energy and dipole moment. The charge densities have the following values:



2 (2- hydroxylstyryl) pyridinium -N- ethyl iodide (cyanine dye)

Dipole moment = 5.682 D Heat of formation = 173.11006 cal.
Total energy = -2633.99030 ev Core – core repulsion = 13333.37420 ev
Electron affinity = 4.13987 ev Electronic energy = -15967.36449 ev
Ionization potential = 11.12430 ev

The charge density of the cyanine dye molecule

No.	Atom	Charge	No.	Atom	Charge
1	N	0.0721	18	H	0.0241
2	C	0.2232	19	C	0.2285
3	C	-0.0879	20	H	0.0166
4	C	0.1296	21	H	-0.0256
5	C	-0.0437	22	C	-0.1695
6	C	0.1021	23	C	0.0078
7	C	0.1242	24	C	-0.1773
8	C	-0.1822	25	C	0.1355
9	H	0.0580	26	C	-0.0795
10	H	0.0436	27	C	0.0982
11	H	0.0690	28	H	-0.0171
12	H	0.0394	29	H	0.0364
13	H	-0.0142	30	H	0.0140
14	H	0.201	31	H	0.0450
15	C	0.0089	32	O	-0.4473
16	H	-0.0146	33	H	0.2730
17	H	0.0494	-	-	-

From these values, it can be concluded that the higher positive charge is localized at the hydrogen atom number 33 which may be ionizable, and the highest negative charge is concentrated on the oxygen atom at position number 32, accordingly, the cyanine dye molecule can be adsorbed on the steel surface (positively charged), which has incomplete d- shells, from the highest negative center as in position 32 leading to the corrosion inhibition action.

3.2. Polarization studies

The effect of 2 (2- hydroxyl styryl) pyridinium -N- ethyl iodide over the concentration range 10^{-5} – 10^{-3} M, on the anodic and cathodic polarization of low carbon steel in 2M H_2SO_4 at different temperatures (30-60^o C) was studied. The obtained curves at 30^{o}C (shown in Figures 1 -3 in presence of dye , dye together with Zn^{+2} ions and dye together with Cr^{+3} ions respectively) as a representative for the investigation at different temperatures, which all gave the same behavior the corrosion parameters are recorded in Table (2). These curves illustrate that, the addition of cyanine dye with and without metal cations to the corrosive medium (2M H_2SO_4) shifted the electrode potential to the more noble direction (cathodic potential of low carbon steel electrode to more negative values and the anodic potential to less negative ones), and the linear part of the Tafel line is also shifted in a parallel manner with respect to the original line of the blank. as the current density increase. The shift of potential increases as the concentration of additives is increased. This behavior supports the inhibition effect of cyanine dye separately and together with metal cations. This behavior is the same at all examined temperature, but the inhibition efficiency decreased as the temperature increased.

The data recorded in Table (2) show that, the addition of cyanine dye only and together with metal ions to the corrosive medium (2M H_2SO_4) increased the inhibition efficiency which has been calculated (I %) as described earlier,[21] it was found also that the inhibition efficiency increased as the concentration of the added metal cations increased. The inhibition efficiency owing to the presence of cyanine dye and ions Cr^{+3} is higher than that in case of dye and Zn^{+2}.

It is clear from the data recorded in Table 2 that in case of a corrosive medium containing cyanine dye only, the increase of temperature is associated with an increase in a corrosion current (I_{corr}.) and a slight shift of corrosion potential (E_{corr}.) suggests that the inhibition is of a mixed type. Thus the investigated cyanine dye acts on the mechanism of the reaction. On The other hand, the addition of metal cations (Zn^{+2} or Cr^{+3}) to the corrosive medium containing 10^{-5} M from cyanine dye alter the corrosion parameters. The (I_{corr}.) was found to be lower in the presence of metal cation together with dye than in the presence of dye only, the (E_{corr}.) was positively shifted. Consequently the inhibition efficiency increases. Increase of the temperature from 30 to 60 ^{o}C is associated with an increase in (I_{corr}.) in the presence of dye only and dye together with metal cation. The desorption process at a higher temperature may be responsible for the increase of (I_{corr}.)

3.4. Activation energy

Arrhenius plots for low carbon steel in absence and in the presence of cyanine dye only and together with metal cations under investigation are shown in Figure (4). The value of the apparent activation energy (E_a) of the corrosion process, calculated from the slopes of log $I_{corr.}$ vs. 1/T plots, are given in Table (3). It is clear that the E_a values for steel corrosion in the presence of cyanine dye are lower than that in the presence of dye together with metal cations. The presence of Cr^{+3} ions gives the higher effect. This synergism of dye and metal ions is discussed from the view point of a model of co-adsorption of dye molecules and metal cations. On the other hand, the E_a values increase as the concentration of added inhibitors increase. This behavior supports the results obtained from the polarization measurements**.**

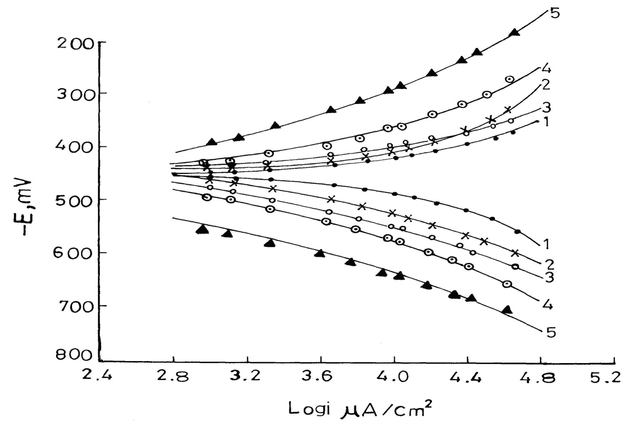


Figure 1. Galvanostatic polarization curves of low carbon steel electrode in 2M H_2SO_4 in presence of cyanine dye at 30°C. 0.00M (1) 10^{-5}M (2) 10^{-4}M (3) $5x10^{-4}$ M (4) 10^{-3} M (5)

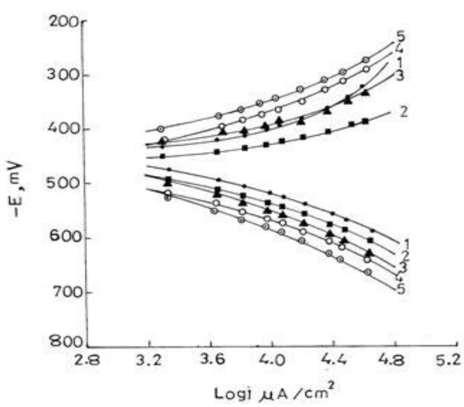


Figure 2. Galvanostatic polarization curves of low carbon steel electrode in 2M H_2SO_4 in presence of cyanine dye + Zinc cations at 30°C.0.00M (1) $5x10^{-3}$M (2) 10^{-2}M (3) $5x10^{-2}$ M (4) 10^{-1}M (5)

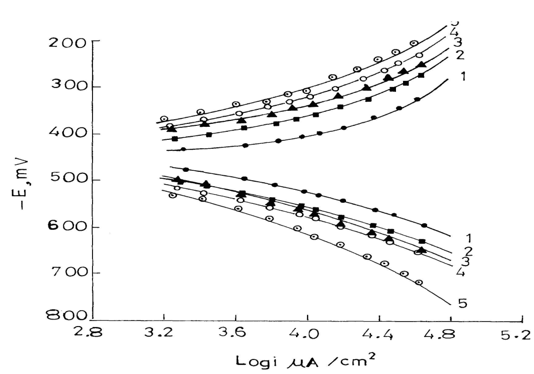


Figure 3. Galvanostatic polarization curves of low carbon steel electrode in 2M H_2SO_4 in presence of cyanine dye + Chromium cations at 30°C. 0.00M (1) $5x10^{-3}$M (2) 10^{-2}M (3) $5x10^{-2}$ M (4) 10^{-1}M (5)

Table (2) The effect of temperature on the corrosion parameters of low carbon steel in $2M\ H_2SO_4$ containing different concentration of cyanine dye (10^{-5}–10^{-3}) M and 10^{-5}M cyanine dye + different concentration of Zn^{+2} or Cr^{+3} ($5x10^{-3}$ – 10^{-1})M.

Temp.°C	Cyanine dye					Cyanine dye + Zn^{+2}					Cyanine dye + Cr^{+3}				
	Conc.	E_{corr}mV	i_{corr} mA	I%	θ	Conc.	E_{corr}mV	i_{corr} mA	I%	θ	Conc.	E_{corr}mV	i_{corr} mA	I%	θ
30	0.00	445	316	-	-	0.00	445	316	-	-	0.00	445	316	-	-
	10^{-5}	430	270	15	0.15	$5x10^{-3}$	455	230	27	0.27	$5x10^{-3}$	450	200	37	0.37
	10^{-4}	435	210	33	0.33	10-2	430	200	37	0.37	10-2	420	152	52	0.52
	$5x10^{-4}$	450	158	50	0.50	$5x10^{-2}$	435	140	49	0.49	$5x10^{-2}$	440	126	60	0.60
	10^{-3}	440	107	66	0.66	10^{-1}	437	160	56	0.56	10^{-1}	438	90	72	0.72
40	0.00	450	457	-	-	0.00	450	457	-	-	0.00	450	457	-	-
	10^{-5}	447	398	13	0.13	$5x10^{-3}$	440	346	24	0.24	$5x10^{-3}$	435	316	31	0.31
	10^{-4}	443	310	32	0.32	10-2	450	295	35	0.35	10-2	410	251		
	$5x10^{-4}$	400	250	45	0.45	$5x10^{-2}$	438	251	45	0.45	$5x10^{-2}$	425	193	45	0.45
	10^{-3}	435	190	58	0.58	10^{-1}	450	200	56	0.56	10^{-1}	445	160	65	0.65
50	0.00	465	630	-	-	0.00	465	630	-	-	0.00	465	630	-	-
	10^{-5}	465	794	20	0.20	$5x10^{-3}$	463	316	20	0.20	$5x10^{-3}$	425	460	27	0.27
	10^{-4}	470	501	27	0.27	10-2	452	501	27	0.27	10-2	400	398	37	0.37
	$5x10^{-4}$	475	398	37	0.37	$5x10^{-2}$	446	457	37	0.37	$5x10^{-2}$	425	290	45	0.54
	10^{-3}	470	316	50	0.50	10^{-1}	435	400	50	0.50	10^{-1}	440	250	60	0.60
60	0.00	478	460	-	-	0.00	478	794	-	-	0.00	478	794	-	-
	10^{-5}	475	700	12	0.12	$5x10^{-3}$	450	457	20	0.20	$5x10^{-3}$	445	590	26	0.26
	10^{-4}	480	660	17	0.17	10-2	435	631	24	0.24	10-2	425	525	34	0.34
	$5x10^{-4}$	485	524	34	0.34	$5x10^{-2}$	425	602	37	0.37	$5x10^{-2}$	425	457	42	0.42
	10^{-3}	475	457	42	0.42	10^{-1}	425	501	42	0.42	10^{-1}	430	365	54	0.54

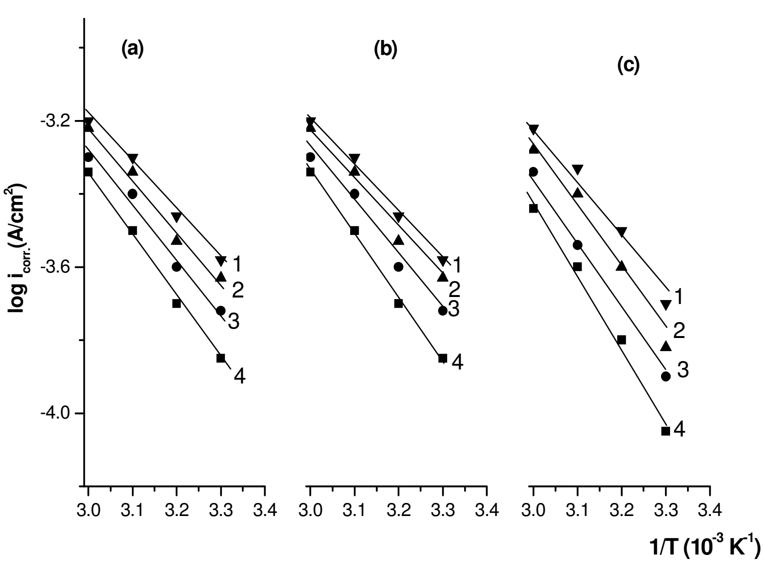


Figure 4. Arhenius plots for inhibited low carbon steel in $2M\ H_2SO_4$ solution:
a) different concentration of cyanide dye 10^{-3}(1), $5x10^{-4}$(2), 10^{-4}(3), 10^{-5}(4)
b) 10^{-5} cyanide dye + different concentration of Zn^{2+} 10^{-1}(1), $5x10^{-2}$(2), 10^{-2}(3), $5x10^{-3}$(4)
c) 10^{-5} cyanide dye + different concentration of Cr^{3+} 10^{-1}(1), $5x10^{-2}$(2), 10^{-2}(3), $5x10^{-3}$(4)

Table (3) The effect of investigated inhibitors on the apparent activation energy (E_a) of the low carbon steel corrosion in 2M H_2SO_4.

Cyanine dye		**10^{-5} M Cyanine dye +Zn^{+2}**		**10^{-5} M Cyanine dye +Cr^{+3}**	
Conc., M	**E_a (KJ mol^{-1})**	**Conc., M**	**E_a (kJ mol^{-1})**	**Conc., M**	**E_a (kJ mol^{-1})**
10^{-5}	5.616	5.10^{-3}	5.183	5.10^{-3}	5.893
10^{-4}	6.019	10^{-2}	5.434	10^{-2}	6.437
$5x10^{-4}$	6.838	5.10^{-2}	6.102	5.10^{-2}	7.900
10^{-3}	8.360	10^{-1}	7.0586	10^{-1}	9.279

3.5. Adsorption isotherms

The degree of coverage area (θ) of the low carbon steel electrode surface by the inhibitors at constant potential is given by .[22-23]

$$\theta = 1 - I/I_o$$

Where I_o and I are the corrosion current in absence and in presence of the inhibitor respectively. The values of θ at the different concentrations of cyanine dye, cyanine dye together with Zn^{+2} and cyanine dye together with Cr^{+3} have been inserted in Table (2). The degree of coverage θ was found to increase as the concentration of the investigated inhibitor increase at all tested temperatures. On the other hand the value of θ at a given concentration ratio is higher in case of Cr^{+3} cyanine dye than that in case of Zn^{+2} + cyanine dye which in turn is higher than that in case of cyanine dye without metal ions.

Also the values of θ decrease as the temperature increase for all investigated inhibitors, this supports the fact that the adsorption of these investigated compounds is monolayer physical adsorption.[8] The Langmuir isotherm for monolayer adsorption is given by the equation .[24]

$$\theta/1-\theta = Ace^{-\Delta H/RT}$$

$$\mathrm{Log}\ (\theta/1-\theta) = \log A + \log C - \Delta H/RT$$

Where A is a temperature independent constant, C is the bulk concentration of the investigated inhibitors, Δ H is the heat of adsorption.

The Δ H values calculated from the slopes of θ /1- θ vs 1/T plots Figure (5) are given in Table (4) , The values of Δ H for all investigated inhibitors show that the heat of adsorption Δ H have the following sequence. Dye + Cr^{+3} > dye + Zn^{+2} > dye.

This behavior give another support to the result obtained in the weight loss measurements.

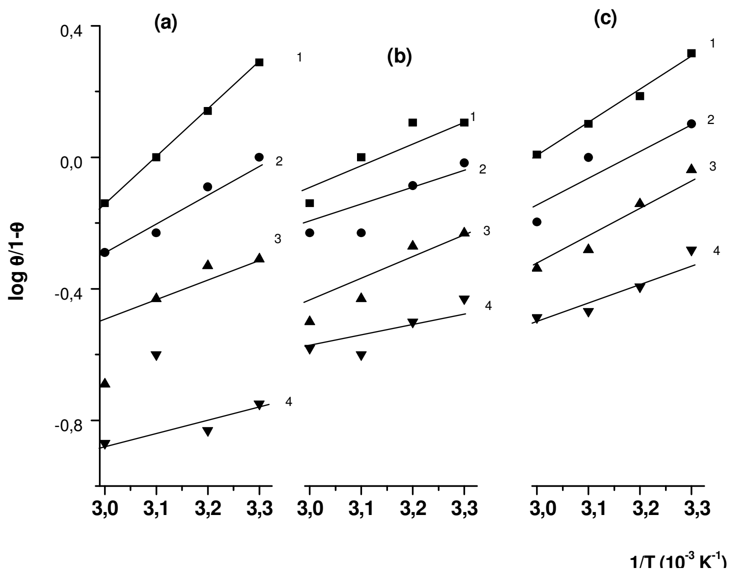


Figure 5. Plot of **log (θ/1-θ) vs. 1/T** for low carbon steel surface
a) different concentration of cyanide dye 10^{-3}M(1), $5x10^{-4}$M(2), 10^{-4}M(3), 10^{-5}M(4)
b) 10^{-5}M cyanide dye + different concentration of Zn^{2+} 10^{-1}M(1), $5x10^{-2}$M(2), 10^{-2}M(3), $5x10^{-3}$M(4)
c) 10^{-5} M cyanide dye + different concentration of Cr^{3+} 10^{-1}M(1), $5x10^{-2}$M(2), 10^{-2}M(3), $5x10^{-3}$M(4)

Table (4) The effect of investigated compounds on the apparent ΔH of low carbon steel in 2M H_2SO_4.

Cyanine dye		**10^{-5} M Cyanine dye +Zn^{+2}**		**10^{-5} M Cyanine dye +Cr^{+3}**	
Conc., M	-ΔH (kJ mol^{-1})	Conc., M	-ΔH (kJ mol^{-1})	Conc., M	-ΔH (kJ mol^{-1})
10^{-5}	200	$5x10^{-3}$	200	$5x10^{-3}$	320
10^{-4}	300	10^{-2}	278	10^{-2}	460
$5x10^{-4}$	450	$5x10^{-2}$	295	$5x10^{-2}$	410
10^{-3}	667	10^{-1}	333	10^{-1}	560

3.6. Thermodynamic parameters

Langmuir adsorption isotherm may be formulated as:

$$\mathbf{C/\theta = 1/K + C}$$

The plot of log C/θ against log C was found to be linear relation for all investigated inhibitors and these are in. Figure (6) and the data are recorded in Table (5). The equilibrium constant for the adsorption- desorption process of the formed cyanine dye, Zn^{+2} + cyanine dye complex and Cr^{+3} + cyanine dye mixture on the low carbon steel surface (K) could be calculated from the reciprocal of the antilogarithm of the intercept of the appropriate plots Figure (6) and recorded in Tables (5). From the above results it was found that, the value of K decrease as the temperature increases due to the increasing of the desorption process.

The free energy (ΔG) and entropy changes (ΔS) of cyanine dye, Zn^{+2} + cyanine dye and Cr^{+3} + cyanine dye complex adsorption on the low carbon steel surface in 2M H_2SO_4 can be calculated

$$\mathbf{K = exp^{(-\Delta G/RT)}, \Delta G = \Delta H - T\Delta S}$$

The calculated values of ΔG and ΔS over temperature range 30 - 60°C have been recorded in Table (5).

The negative values of ΔG indicate the spontaneous adsorption of the cyanine dye together with metal cations. It was also found that as the temperature increases the desorption process also increases and the inhibition effect will be decreased. On the other hand, ΔS decreased with increasing temperature in case of all investigated inhibitors, this indicated that, the adsorption process is an exothermic process and that accompanied by decrease of entropy

Table (5) The effect of investigated compounds on the equilibrium constant and the thermodynamic parameters (ΔG, ΔS) for the acid corrosion of low carbon steel at temperature range (30 - 60)°C.

Temp.°C	Cyanine dye			Cyanine dye +Zn^{+2}			Cyanine dye +Cr^{+3}		
	K	-ΔG KJ/mol	-ΔS KJ/mol	K	-ΔG KJ/mol	-ΔS KJ/mol	K	-ΔG KJ/mol	-ΔS KJ/mol
30	78.1×10^3	28.81	2.1	190	13.291	1.06	275	14.23	1.80
40	60×10^3	28.78	2.03	125	12.634	1.02	200	13.86	1.74
50	40×10^3	28.61	1.98	105	12.567	0.99	158	13.67	1.69
60	28×10^3	25.94	1.93	100	12.820	0.96	126	13.46	1.64

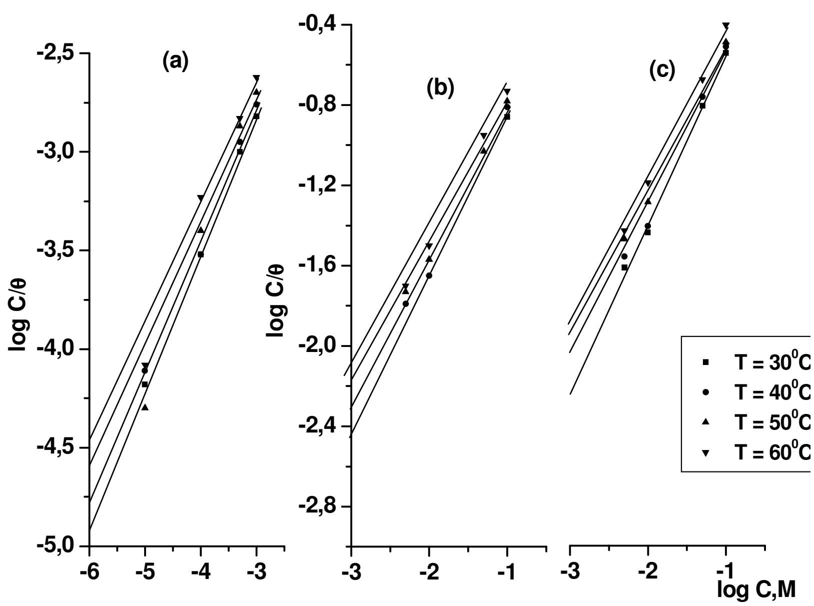


Figure 6. Langmiur adsorption isotherms for corrosive media 2M H_2SO_4 containing
a) different concentration of cyanide dye
b) 10^{-5}M cyanide dye + different concentration of Zn^{2+}
c) 10^{-5} M cyanide dye + different concentration of Cr^{3+}

5. CONCLUSION

The use of 2 (2- hydroxystyryl) pyridinium -N- ethyl iodide (cyanine dye) is highly favorable as an inhibitor for the corrosion of low - carbon steel in 2M H_2SO_4 solution. The inhibition efficiency is correlated to the concentration of cyanine dye in the corrosive medium.

The synergistic effect of cyanine dye together with Zn^{+2} or Cr^{+3} ions increased the inhibition efficiency in which the mixture of cyanine dye and Cr^{+3} ions is the better one.

The inhibition effect of cyanine dye without and with the studied metal cations was found to be a mixed type and occurred via monolayer physical adsorption at anodic sites and conforms approximately to the Langmiur isotherm.

The values of activation energy E_a indicate that, the inhibition of the used low-carbon steel in H_2SO_4 solution by the studied cyanine dye in absence and presence of Zn^{+2} or Cr^{+3} ions becomes less favorable as the temperature increases.

The thermodynamic parameter obtained from this study ΔH, ΔG and ΔS indicate that the presence of higher concentration of Cr^{+3} or Zn^{+2} cations together with cyanine dye increase the activation energy, and the negative values of ΔG indicate a spontaneous adsorption of the inhibitors on the surface of the low- carbon steel.

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