Journal of Materials Science and Engineering with Advanced Technology
Volume 19, Number 1, 2019, Pages 1-27
Available at http://scientificadvances.co.in
DOI: http://dx.doi.org/10.18642/jmseat_7100122019

CORROSION INHIBITION OF 1,4-DIMETHYL PHENYL-N,N-DIMETHYLANILINIUM DIBROMIDE SALT ON MILD STEEL IN HCl SOLUTION

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Abstract

Electrochemically and weight loss measurements were carried out to study the effect of laboratory synthesized 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide salt (DMPMA) on the corrosion inhibition of mild steel in 1.0M HCl solution containing various concentrations $(1.0 \times 10^{-3}\text{M to } 1.0 \times 10^{-7}\text{M})$ at temperatures ranging from 303 K to 343 K.

1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide salt was found to be very efficient inhibitor for mild steel in 1.0 M HCl solution, reaching about 93% at the concentration of $1.0 \times 10^{-3}\text{M}$ at 303 K. The percentage of inhibition in the presence of this inhibitor decreased with temperature which indicating a physical adsorption was the predominant inhibition mechanism. This inhibitor will have application in industries, where hydrochloric acid solutions at elevated temperatures are used to remove scale and salts from steel surfaces, such as acid cleaning of tankage and pipeline, and may render dismantling unnecessary.

Keywords and phrases: corrosion, inhibitor, 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide, Temkin adsorption isotherm.

Received November 15, 2018

1. Introduction

The use of inhibitors to minimize the corrosion of metals is an important subject in industry and research. Corrosion increases the running costs and reduces plant efficiency, availability, and product quality.

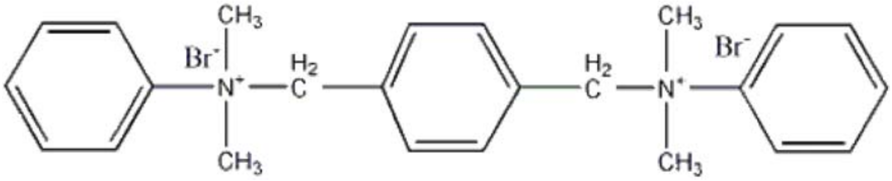
Organic compounds containing aromatic rings, polar groups, and/or N, P, O, S elements are found to be the most efficient inhibitors. The inhibition occurs via adsorption of the inhibitor at the metal/solution interface. This inhibition reduces the corrosion current produced from the adsorption process.

The study of corrosion inhibition of mild steel in aggressive acidic media was widely investigated and became an important industrial topic for research. Acidic HCl solutions are usually used in industry to remove scale and salts from steel surfaces, cleaning tanks and pipelines. This treatment may be prerequisite for coating by electroplating, galvanizing or painting techniques. An inhibitor must be added to the acidic media in order to prevent or minimize the dissolution of the underlying metal. This inhibitor displaces water molecules at the metal surface and adsorbs at the metal/solution interface, so that the metal surface will be protected from corrosion by forming a barrier film on metal surface.

Extensive literatures exist on corrosion inhibition in acidic media; however detailed knowledge of the mode of action and the mechanism of inhibition still needs more investigation.

Organic nitrogen-containing compounds as corrosion inhibitors for different metals were studied widely by many authors [1-18]. Sulphur-containing inhibitors [19-26] and phosphorus organic inhibitors were investigated by other authors [27-30]. The effect of structure on the inhibition of some organic compounds was also studied [30, 31].

The aim of this work was to study the corrosion inhibition efficiency of the synthesized compound 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide (DMPMA) on mild steel in 1.0 M HCl solution (Scheme 1) using electrochemical, and weight loss measurements.

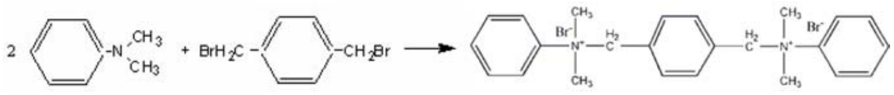


Scheme 1. 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide.

2. Experimental Details

Synthesis of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide

The 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide salt (3) was prepared by refluxing two molar equivalent from N,N-dimethylaniline (1) with one molar equivalent from 1,4-dibromethylbenzene (2) in acetone as shown in the procedure below (Scheme 2):



(1) (2) (3)

Scheme 2. Synthesis of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide.

A mixture of 8.00 grams (0.066 mol) of N,N-dimethylaniline (1), and 8.72 grams of 1,4-dibromethylbenzene (0.033 mol) (2), in 500 mL carbon tetrachloride (CCl_4) was refluxed for 6 hours. After cooling to room temperature, a crystalline off-white precipitate (3) was collected by filtration, then washed with excess diethyl ether and dried. Dissolution in small amount of chloroform and addition of excess diethyl ether gave the pure salt (3) in 80 percent yield with a melting point between 133 °C and 136 °C.

3. Electrochemistry

3.1. Electrode preparation

A 5 mm diameter piece cut from a mild steel rod (IS 226 containing 0.18% C, 0.6% Mn, and 0.35% Si) supplied by “Reliable Steel Traders”, Sharjah, UAE, formed the working electrode; and was mounted, using Araldite epoxy resin, in a glass tube that fits in the electrochemical cell (Figure 1). Prior to each experiment, the working mild steel electrode was abraded using a series of carborundum papers starting with 600 grades and ending with 1200 grades. The electrode surface was then polished with 0.3 μm alumina on cloth, washed with deionized distilled water, and rinsed with pure ethanol before being transferred to the electrochemical cell that contained deaerated fresh electrolyte.

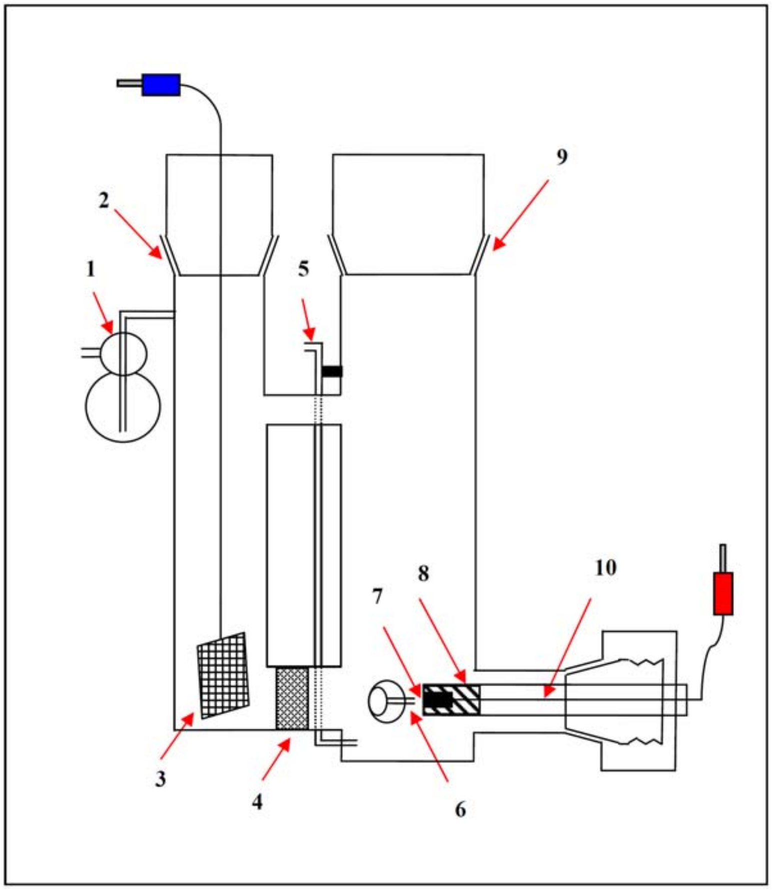


Figure 1. Electrochemical cell. (1) gas bubbler, (2) B 12 glass socket, (3) platinum gauze (counter electrode), (4) glass frit, (5) inlet for nitrogen gas, (6) luggin capillary (reference electrode), (7) iron rod (working electrode), (8) epoxy resin, (9) B 24 glass socket, and (10) copper wire.

3.2. Instrumentation

The electrochemical cell (Figure 1) consisted of a mild steel working electrode (WE), a saturated calomel electrode (SCE) as a reference electrode (RE), and platinum gauze counter electrode (CE). Prior to each experiment, the electrolyte was deaerated by nitrogen bubbling. The cell was designed in a way that the nitrogen was allowed to escape into the solution, precluding its collection at the electrode surface.

In order to protect the working electrode from any substance that may be produced at the counter electrode during the electrochemical reactions, the counter-electrode compartment was separated from the working-electrode compartment with a glass frit.

A PC controlled AUTOLAB PGSTAT128N Modular Potentiostat (electrochemical workstation) (supplied from Metrohm) capable of driving currents up to $\pm$ 800 mA with an output potential across the cell of up to $\pm$ 10 V was used for the measurements.

3.3. Measuring procedure

Electrochemical corrosion measurements (Tafel plots) were carried out on the mild steel electrode, prepared as described before, in 1.0 M HCl and in 1.0 M HCl containing various concentrations of the prepared DMPMA inhibitor. The concentration of the inhibitor ranged from 1.0×10^{-7} M to 1.0×10^{-3} M. Owing to the restricted solubility of DMPMA inhibitor in 1.0 M HCl, higher concentrations could not be prepared.

The electrochemical cell was filled with 60 mL of the electrolyte. The solution was deaerated with nitrogen gas and the WE equilibrium potential was monitored and recorded vs. SCE until it reached a steady state. The electrode potential was scanned between overpotentials of $-$ 100 mV to +100 mV vs. SCE at a sweep rate of 1 mV.s^{-1}.

Replicate measurements were carried out in order to ensure reproducibility of the results.

3.4. Results and discussions

Figure 2 shows the anodic and cathodic polarization curves (Tafel plot) of the mild steel electrode in deaerated 1. 0 M HCl solution with and without the addition of various concentrations of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide (DMPMA). The presence of the inhibitor affected both the anodic and cathodic branches of the curve as it can be clearly seen in Figure 2. It is clearly noticed that the corrosion current decreased with the increase of the concentration of DMPMA inhibitor (Table 1). In the absence of inhibitor (in 1.0 M HCl), the corrosion current was found to be 0.80606 mA, and reached 0.10949 mA at $1.0 \times 10^{-3}\,\mathrm{M}$ of DMPMA inhibitor in 1.0 M HCl (Table 1).

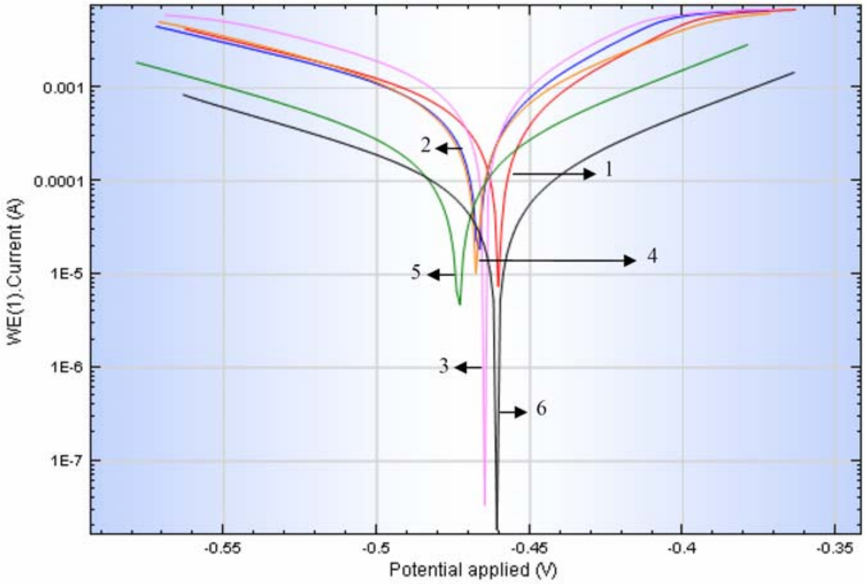


Figure 2. Anodic and cathodic polarization curves of mild steel in an uninhibited 1.0 M HCl solution and in 1.0 M HCl containing various concentrations of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide salt.

(1) 1.0 M HCl; (2) $1.0\,\mathrm{M\ HCl} + 1.0 \times 10^{-7}\,\mathrm{M}$ inhibitor; (3) $1.0\,\mathrm{M\ HCl} + 1.0 \times 10^{-6}\,\mathrm{M}$ inhibitor; (4) $1.0\,\mathrm{M\ HCl} + 1.0 \times 10^{-5}\,\mathrm{M}$ inhibitor; (5) $1.0\,\mathrm{M\ HCl} + 1.0 \times 10^{-4}\,\mathrm{M}$ inhibitor; and (6) $1.0\,\mathrm{M\ HCl} + 1.0 \times 10^{-3}\,\mathrm{M}$ inhibitor.

Table 1. Tafel corrosion currents and percent inhibitions of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide various concentrations in 1.0 M HCl at room temperature

	1.0 M HCl	**1.0 M HCl $+1.0\times10^{-7}$M**	**1.0 M HCl $+1.0\times10^{-6}$M**	**1.0 M HCl $+1.0\times10^{-5}$M**	**1.0 M HCl $+1.0\times10^{-4}$M**	**1.0 M HCl $+1.0\times10^{-3}$M**
OCP/V vs. SCE	– 0.463	– 0.472	– 0.469	– 0.471	– 0.479	– 0.463
b_a/(mV/dec)	0.035564	0.054028	0.056219	0.065312	0.060943	0.059797
b_c/(mV/dec)	0.069716	0.10021	0.087065	0.079336	0.85116	0.074415
$E_{corr.}$/V	– 0.46016	– 0.46693	– 0.46478	– 0.4674	– 0.47332	– 0.46082
$I_{corr.}$/mA	0.80606	0.72840	0.55179	0.35070	0.22850	0.10949
Polarity Resistance Ω	27.581	25.695	16.384	27.545	94.633	201.46
% Inhibition at 25 °C	0.000	9.63	31.54	56.49	71.65	86.42

The percentage inhibition values of DMPMA at various concentrations in 1.0 M HCl were calculated according to the following equation and the results are shown in Table 1:

$$\text{Percentage Inhibition} = \frac{(I_{\text{Corr.}})_{\text{Uninh.}} - (I_{\text{Corr.}})_{\text{Inh.}}}{(I_{\text{Corr.}})_{\text{Uninh.}}} \times 100, \tag{1}$$

where:

$(I_{\text{Corr.}})_{\text{Uninh.}} =$ Corrosion current in the uninhibited solution,

and

$(I_{\text{Corr.}})_{\text{Inh.}} =$ Corrosion current in inhibited solution.

Figure 3 shows the plot of the percentage inhibition versus the concentration of DMPMA. In this figure, the percentage inhibition increase gradually from about 10% with a concentration of 1.0×10^{-7} M inhibitor and reached a maximum value of about 86% with 1.0×10^{-3} M.

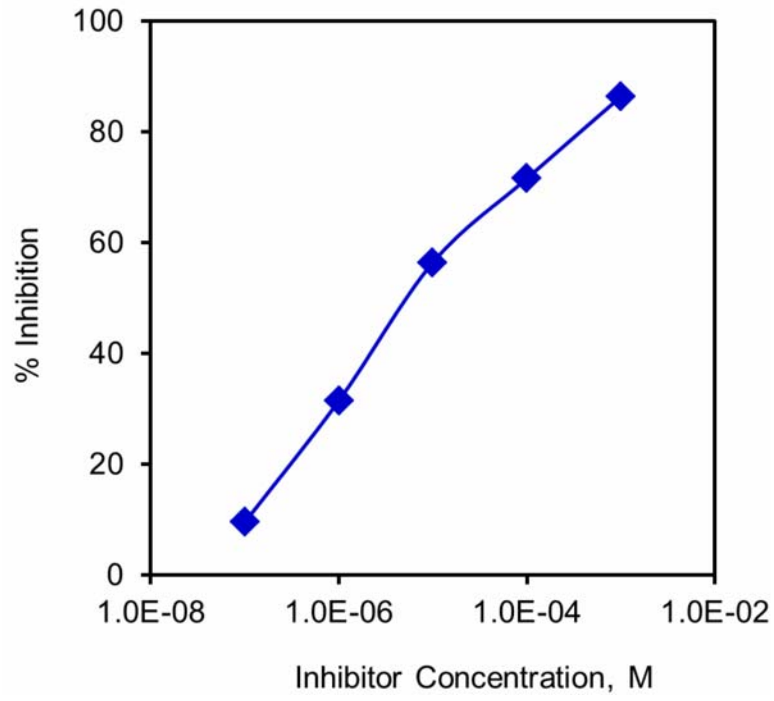


Figure 3. Percentage inhibition of different concentrations of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on mild steel surface in 1.0 M HCl solution obtained from anodic and cathodic polarization curves.

4. Effect of Temperature

4.1. Specimen preparation

Rectangular specimens (1.0 cm × 2.3 cm × 0.3 cm) cut from large sheet of 3.0 mm thick mild steel (IS 226 containing 0.18% C, 0.6% Mn, and 0.35% Si) supplied by "Reliable Steel Traders", Sharjah, UAE; were used for weight loss measurements. A 2 mm diameter hole was drilled close to the upper edge of the specimen and served to be hooked with a glass rod for immersion purposes. Prior to each experiment, the specimens were polished with 600 grade emery paper, rinsed with distilled water, degreased with acetone, dried, and finally weighed precisely on an accurate analytical balance.

4.2. Instrumentation

For the weight-loss measurements, a 250 mL round bottom flask fitted with a reflux condenser and long glass rod which served to hook and immerse the specimen and in turn immersed in a thermally controlled water bath was used.

4.3. Measuring procedure

The flask was filled with 100 mL of 1.0 M HCl solution with and without (DMPMA) of various concentrations, then placed in water bath held at the desired temperature. The mild steel samples were immersed in the solution, and left there for exactly six hours, after that the samples were removed, rinsed with distilled deionized water, degreased with acetone, dried, and finally weighed precisely using an accurate analytical balance. This procedure was repeated with all samples with various concentrations of inhibitor $(1.0 \times 10^{-7}\,\mathrm{M} - 1.0 \times 10^{-3}\,\mathrm{M})$ and at various temperatures (303 K–343 K).

Three replicate measurements were carried out in order to ensure reproducibility of the results and the average values were reported.

4.4. Results and discussions

Weight loss measurements were carried out on the mild steel in 1.0 M HCl in the absence and presence of (DMPMA) over a period of 6 hours. Table 2 represents the corrosion rates $[\mathrm{mg.cm^{-2}.h^{-1}}]$, and the percentage efficiencies [%] for the studied inhibitor with different concentrations $(1.0 \times 10^{-7}\,\mathrm{M} - 1.0 \times 10^{-3}\,\mathrm{M})$ at 303 K, 313 K, 323 K, 333 K, and 343 K, respectively. The percentage efficiency was calculated according to the following equation:

$$\%\ \text{Inhibition} = \frac{W_{\text{Uninh.}} - W_{\text{Inh.}}}{W_{\text{Uninh.}}} \times 100, \tag{2}$$

where: $W_{\text{Uninh.}}$ = corrosion rate without inhibitor; and

$W_{\text{Inh.}}$ = Corrosion rate with inhibitor.

Table 2. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on the corrosion rate $(\mathrm{mg.cm^{-2}.h^{-1}})$ and percentage efficiency of mild steel in 1.0M HCl at various temperatures

	Temperature / K									
	303		313		323		333		343	
Concentration of inhibitor	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency	Corr. Rate	% Efficiency
1.0 M HCl	0.446	–	0.910	–	2.244	–	4.812	–	9.537	–
1.0 M HCl $+1.0 \times 10^{-7}$M	0.349	21.87	0.825	9.39	2.044	8.90	4.535	5.78	9.278	2.72
1.0 M HCl $+1.0 \times 10^{-6}$M	0.260	41.30	0.605	33.54	1.681	25.08	4.084	15.14	8.229	13.71
1.0 M HCl $+1.0 \times 10^{-5}$M	0.075	83.18	0.183	79.94	0.585	73.95	2.226	53.75	5.689	40.35
1.0 M HCl $+1.0 \times 10^{-4}$M	0.028	93.70	0.070	92.31	0.196	91.25	0.548	88.62	2.138	77.58
1.0 M HCl $+1.0 \times 10^{-3}$M	0.010	97.80	0.030	96.70	0.085	96.23	0.213	95.58	0.505	94.70

Figures 4 and 5 show the plots of the corrosion rate of mild steel with and without the inhibitor (DMPMA) versus the concentration of inhibitor at 303 K, 313 K, 323 K, 333 K, and 343 K. At 303 K (Figure 4), the corrosion rate dropped from $0.446\ \mathrm{mg.cm^{-2}.h^{-1}}$ (1.0 M HCl without inhibitor) to $0.349\ \mathrm{mg.cm^{-2}.h^{-1}}$ with $1.0 \times 10^{-7}\ \mathrm{M}$ of (DMPMA) inhibitor. Then the corrosion rate decreased slightly to reach $0.260\ \mathrm{mg.cm^{-2}.h^{-1}}$ (41.30% inhibition) with $1.0 \times 10^{-6}\ \mathrm{M}$, followed by a steep decrease to reach $0.075\ \mathrm{mg.cm^{-2}.h^{-1}}$ with $1.0 \times 10^{-5}\ \mathrm{M}$; and finally, at higher concentrations ($1.0 \times 10^{-4}\ \mathrm{M}$ and $1.0 \times 10^{-3}\ \mathrm{M}$) the decrease in the corrosion rate was slight and reached $0.028\ \mathrm{mg.cm^{-2}.h^{-1}}$ and $0.010\ \mathrm{mg.cm^{-2}.h^{-1}}$ (93.7% and 97.8% inhibition), respectively (Table 2).

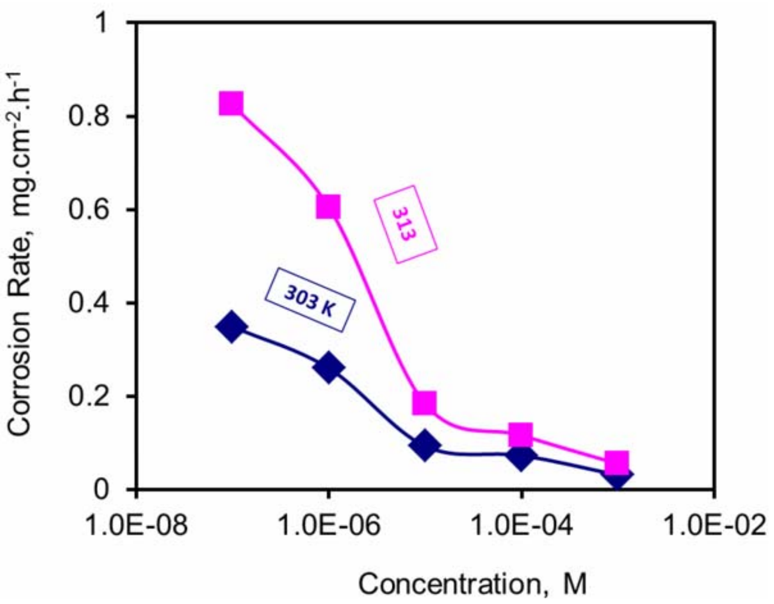


Figure 4. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on the corrosion rate ($\mathrm{mg.cm^{-2}.h^{-1}}$) of mild steel in 1.0 M HCl at various temperatures.

◆ 303 K ■ 313 K

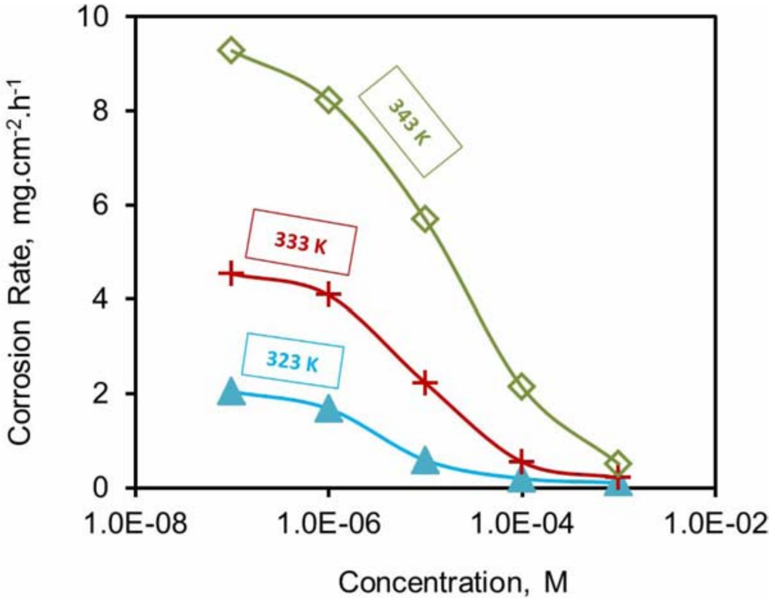


Figure 5. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on the corrosion rate $(\text{mg.cm}^{-2}.\text{h}^{-1})$ of mild steel in 1.0 M HCl at various temperatures.

▲ 323 K ✚ 333 K ◇ 343 K

At 313 K (Figure 4), the curve showed a similar shape as that obtained at 303 K. At concentrations greater than 1.0×10^{-7} M, the corrosion rate decreased steeply and reached about $0.070\ \text{mg.cm}^{-2}.\text{h}^{-1}$ (92.3%) at 1.0×10^{-4} M.

The corrosion rate at 323 K, 333 K, and 343 K with different concentrations of the (DMPMA) inhibitor are shown in Figure 5. It is clearly noticed that the presence of the (DMPMA) inhibitor at these high temperatures still acted as an excellent corrosion inhibitor reaching a maximum percent inhibition of 94.7% with 1×10^{-3} M inhibitor at 343 K.

There was a slight effect on the corrosion rate at low and high concentrations of the inhibitor (between $1.0 \times 10^{-7}\,\mathrm{M}$ and $1.0 \times 10^{-6}\,\mathrm{M}$) and (between $1.0 \times 10^{-4}\,\mathrm{M}$ and $1.0 \times 10^{-3}\,\mathrm{M}$) at all temperatures; whereas this rate was large at intermediate concentrations (from $1.0 \times 10^{-6}\,\mathrm{M}$ to $1.0 \times 10^{-4}\,\mathrm{M}$).

The plots of the percentage of inhibition as a function of the inhibitor concentration at various temperatures (303 K–343 K) are shown in Figure 6. This figure showed that the percentage of inhibition decreases with the increase of temperature.

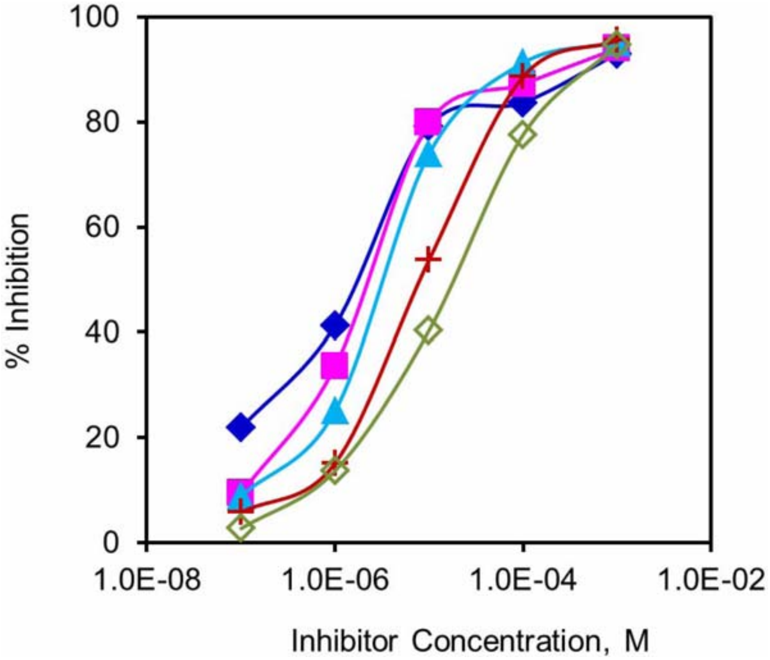


Figure 6. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on the percent inhibition of mild steel in 1.0 M HCl at various temperatures.

◆ 303 K ■ 313 K ▲ 323 K ✚ 333 K ◇ 343 K

The data obtained from the weight loss measurements were plotted in accordance to Arrhenius equation:

$$\ln \text{ rate } = -\frac{E_a}{RT} + \text{const.}, \tag{3}$$

where: $E_a =$ activation energy $[\text{kcal.mol}^{-1}]$, $R =$ gas constant $[\text{kcal.mol}^{-1}]$, T = absolute temperature [K], and const. = constant.

The Arrhenius plot of the corrosion of mild steel in 1.0 M HCl solution (Ln corrosion rate as a function of $1/T$, Table 3) with and without the presence of (DMPMA) at various concentrations $(1.0 \times 10^{-7}\text{M} - 1.0 \times 10^{-3}\text{M})$ is shown in Figure 7. From this figure, the activation energy was calculated according to Equation (3), and taking $\text{R} = 1.987 \times 10^{-3}$ kcal.mol^{-1} (Table 4). It was found the activation energy increases with the increase of concentration of (DMPMA) as tabulated in (Table 4). This means that as the temperature increases the adsorption of the inhibitor on the metal surface decreases. This also suggests that the corrosion rate increases due to the greater exposed area of the metal surface to the acidic media.

Table 3. The data obtained from the weight loss measurements for Arrhenius equation: $(1/T)$ against Ln corrosion rate

	Ln corrosion rate $(\mathbf{mg.cm^{-2}.h^{-1}})$					
$(1/T) \times 10^3 \mathrm{K}^{-1}$	**1.0 M HCl**	**1.0 M HCl** $+ 1.0 \times 10^{-3}$**M**	**1.0 M HCl** $+ 1.0 \times 10^{-4}$**M**	**1.0 M HCl** $+ 1.0 \times 10^{-5}$**M**	**1.0 M HCl** $+ 1.0 \times 10^{-6}$**M**	**1.0 M HCl** $+ 1.0 \times 10^{-7}$**M**
3.30	– 0.807	– 4.605	– 3.576	– 2.590	– 1.347	– 1.053
3.19	– 0.094	– 3.507	– 2.659	– 1.700	– 0.502	– 0.192
3.10	0.8083	– 2.465	– 1.630	– 0.536	0.519	0.715
3.00	1.5711	– 1.546	– 0.601	0.800	1.407	1.512
2.92	2.2552	– 0.683	0.750	1.773	2.108	2.228

Table 4. The activation energy (E_a) for the corrosion of mild steel in 1.0 M HCl with and without 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide inhibitor at various concentrations

System	**Activation energy, E_a(kcal.mol^{-1})**				
	1.0×10^{-3}M	**1.0×10^{-4}M**	**1.0×10^{-5}M**	**1.0×10^{-6}M**	**1.0×10^{-7}M**
1.0 M HCl	16.09	16.09	16.09	16.09	16.09
1.0 M HCl + Inhibitor	14.25	17.01	22.09	18.19	17.09

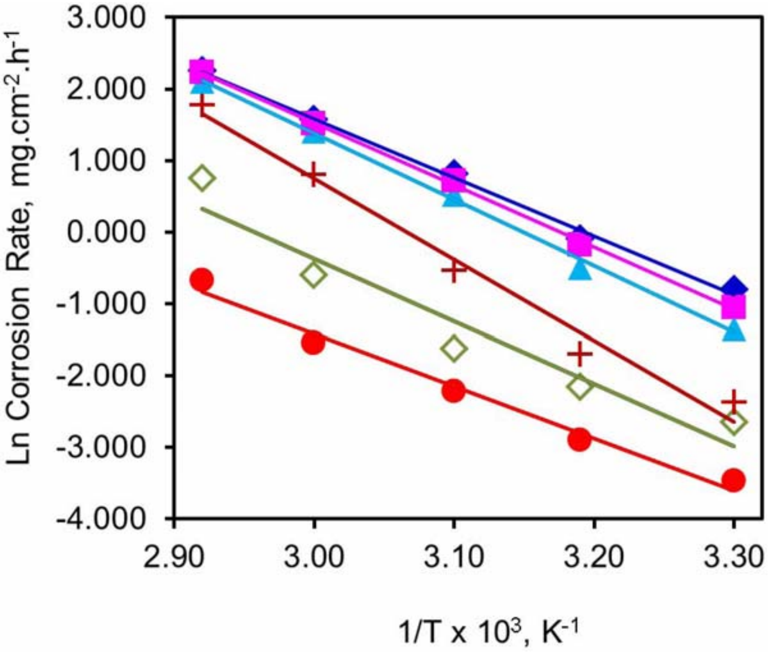


Figure 7. Effect of temperature on the corrosion rate of mild steel in 1.0 M HCl solution with and without the presence of various concentrations of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide.

◆ 1.0 M HCl ■ 1.0×10^{-7}M ▲ 1.0×10^{-6}M

✚ 1.0×10^{-5}M ◇ 1.0×10^{-4}M ● 1.0×10^{-3}M

It has been noticed that the activation energy (E_{a}) values for the corrosion of mild steel in the presence of the inhibitor are higher than the values in the absence of inhibitor at all concentrations $(1.0 \times 10^{-3}\text{M} - 1.0 \times 10^{-7}\text{M})$. This behaviour may be attributed to the physisorption process, whereas unchanged or lower values of E_{a} in inhibited solution suggest a chemisorption process [33].

Table 5. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on surface coverage for mild steel in 1.0 M HCl at various temperatures

	Temperature / K				
	303	**313**	**323**	**333**	**343**
Concentration of inhibitor	**Surface coverage θ**	**Surface coverage θ**	**Surface coverage θ**	**Surface coverage θ**	**Surface coverage θ**
$1.0\,\text{M HCl} + 1.0 \times 10^{-7}\text{M}$	0.219	0.094	0.089	0.058	0.027
$1.0\,\text{M HCl} + 1.0 \times 10^{-6}\text{M}$	0.413	0.335	0.251	0.151	0.137
$1.0\,\text{M HCl} + 1.0 \times 10^{-5}\text{M}$	0.792	0.799	0.740	0.538	0.404
$1.0\,\text{M HCl} + 1.0 \times 10^{-4}\text{M}$	0.937	0.923	0.913	0.886	0.776
$1.0\,\text{M HCl} + 1.0 \times 10^{-3}\text{M}$	0.978	0.967	0.962	0.956	0.947

The surface coverage values, θ, of various concentrations $(1.0 \times 10^{-3}\text{M} - 1.0 \times 10^{-7}\text{M})$ of (DMPMA) on mild steel surface at various temperatures are tabulated in Table 5. These values were extracted from the corresponding % efficiency values reported earlier in Table 2. The plot of surface coverage, θ, against the natural logarithm of the concentration, ln*C*, for mild steel in the presence of the various inhibitor concentrations is shown in Figure 8. After examining the data and adjusting them to different theoretical adsorption isotherms, it was concluded that all inhibitors were adsorbed on the mild steel surface according to Temkin isotherm:

$$-2a\theta = \ln KC, \tag{4}$$

where: a = molecular interaction constant,

θ = degree of coverage,

K = equilibrium constant for the adsorption reaction, and

C = concentration of the inhibitor.

The equilibrium constant for the adsorption reaction, K, is related to the standard free energy of adsorption via the following Equation (5) [34]:

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G}{RT}\right), \tag{5}$$

where: K = equilibrium constant for the adsorption reaction,

55.5 = concentration of water $[\text{mol.L}^{-1}]$,

ΔG = standard free energy $[\text{kcal.mol}^{-1}]$,

R = gas constant $[\text{kcal.mol}^{-1}]$, and

T = absolute temperature [K].

According to Equation (4), the straight lines shown in Figure 4 will have the following slopes and intercepts:

$$\text{Slope} = -\frac{1}{2a}; \tag{6}$$

$$\text{Intercept} = -\frac{1}{2a}\ln K. \tag{7}$$

Combination of Equations (6) and (7) leads to the following relationship:

$$\text{Intercept} = \text{Slope}.\ (\ln K), \tag{8}$$

from which the equilibrium constant for the adsorption reaction, K, can be calculated:

$$K = e^{\left(\frac{\text{Intercept}}{\text{Slope}}\right)}. \tag{9}$$

The values of the standard free energy of adsorption of the inhibitor, ΔG^0, were calculated from the results in Figure 8 and using the previous Equation (5) at various temperatures (303 K–343 K), see Table 6.

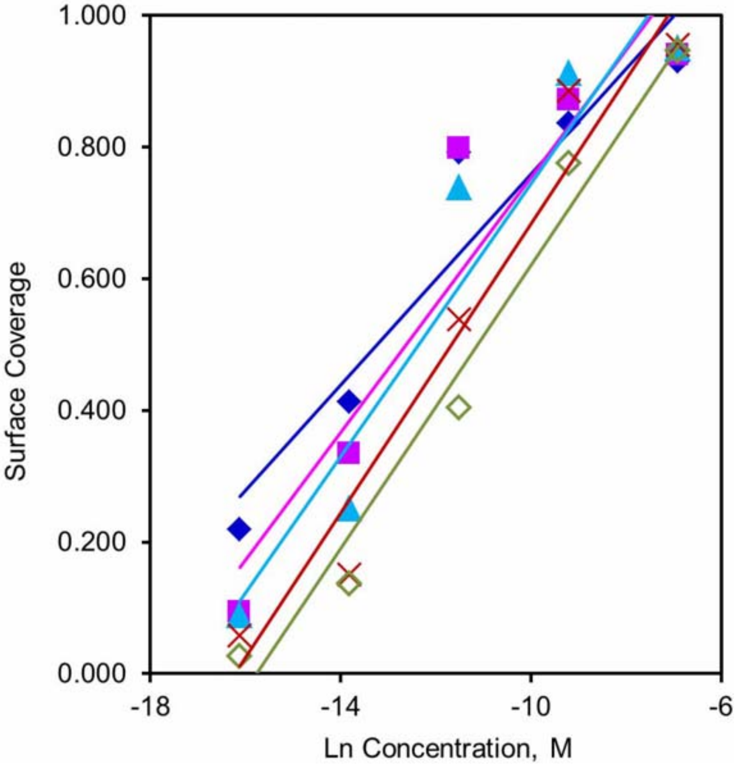


Figure 8. Effect of concentration of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide on the surface coverage of mild steel in 1.0 M HCl at various temperatures.

◆ 303 K ■ 313 K ▲ 323 K ✚ 333 K ◇ 343 K

Table 6. The free energy of adsorption (ΔG_{ads}) for mild steel in 1.0 M HCl in the presence of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide at various temperatures (303 K–343 K).

ΔG, kcal.mol^{-1}				
303 K	**313 K**	**323 K**	**333 K**	**343 K**
– 14.14	– 13.57	– 13.62	– 13.39	– 13.49

The values of the enthalpy of adsorption, ΔH^0, (Table 7), for the inhibitor were calculated from the following equation:

$$\Delta H^0 = E_a - RT. \tag{10}$$

Table 7. The enthalpy of adsorption (ΔH) for mild steel in 1.0 M HCl in the presence of 1.0×10^{-3} M 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide at various temperatures (303 K–343 K)

ΔH, kcal.mol^{-1}				
303 K	**313 K**	**323 K**	**333 K**	**343 K**
13.65	13.63	13.61	13.59	13.57

The values of entropy, ΔS^0, (Table 8), were calculated at various temperatures for the inhibitor using the following equation:

$$\Delta G^0 = \Delta H^0 - T\Delta S^0. \tag{11}$$

Table 8. The change in entropy (ΔS) for mild steel in 1.0 M HCl in the presence of 1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide at various temperatures (303 K–343 K)

ΔS, kcal.K^{-1}.mol^{-1}				
303 K	**313 K**	**323 K**	**333 K**	**343 K**
0.092	0.087	0.084	0.081	0.079

Tables 6 to 8 show the thermodynamic data obtained in the presence of the inhibitor at 1.0×10^{-3} M. These thermodynamic quantities represent the algebraic sum of the values for adsorption and desorption. The spontaneity adsorption of the inhibitor on the mild steel surface was noticed from the negative sign of ΔG^0 values. The standard free energy, ΔG^0, varies from -14.14 kcal.mol^{-1}.K^{-1} at 303 K to -13.49 kcal.mol^{-1}.K^{-1} at 343 K. The absolute of these values is less than 20 kcal.mol^{-1}.K^{-1}, which also indicates a physisorption process. The positive enthalpy values, indicates that the adsorption process is an exothermic and associated with a decrease in entropy (ΔS) of solute, while the opposite is true for the solvent resulting in a net increase of entropy for the whole system. The gain in entropy which accompanies the substitutional adsorption process is attributed to the increase in the solvent entropy. This is in agreement with the general suggestion that the values of ΔG^0 increase with the increase of inhibition efficiency due to adsorption desorption process [23, 35].

The high inhibition efficiency may be attributed to the preferred flat orientation of this compound on the metal surface. The interaction occurs between the π-electrons of the three benzene rings.

5. Conclusion

1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide (DMPMA) was found to be a very efficient inhibitor for mild steel in 1.0 M HCl solution, reaching about 98% with inhibitor concentration 1.0×10^{-3} M at 303 K.

1,4-dimethyl phenyl-N,N-dimethylanilinium dibromide (DMPMA) is a potential corrosion inhibitor since it contains three phenyl rings. It was apparent from the molecular structure that this compound would be adsorbed on the metal surface through the π-electrons of the three benzene rings.

The decrease of the percentage inhibition in the presence of this inhibitor with the increase of temperature, as well as the values of activation energy and free energy, suggested that the physical adsorption was the predominant inhibition mechanism.

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