

View Article Online View Journal

# NJC

Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Maleki, A. Davoodi, M. V. Azghandi, E. Akbarzadeh, M. Baghayeri, H. Veisi, S. Sedigh Ashrafi and M. Raei, *New J. Chem.*, 2015, DOI: 10.1039/C5NJ02707A.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/njc

# Facile Synthesis and Investigation of 1,8-Dioxooctahydroxanthene Derivatives as Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution

Behrooz Maleki,<sup>\*a</sup> Ali Davoodi,<sup>b</sup> Mojtaba Vakili Azghandi,<sup>c</sup> Mehdi Baghayeri,<sup>a</sup> Elahe Akbarzadeh,<sup>d</sup> Hojat Veisi,<sup>e</sup> Samaneh Sedigh Ashrafi,<sup>a</sup> Massomeh Raei<sup>a</sup>

<sup>a</sup>Department of Chemistry, Hakim Sabzevari University, Sabzevar, 96179-76487, Iran

E-mail:b.maleki@hsu.ac.ir, Tel: +98-571-4002643 Fax: +98-571-4410300

<sup>b</sup>Materials and Metallurgical Engineering Department, Faculty of Engineering, Ferdowsi University of Mashhad, Mashhad 91775-1111, Iran

<sup>c</sup>Materials Science and Engineering Department, Faculty of Engineering, Bu-Ali Sina University, Hamadan, Iran

<sup>d</sup>Young Researchers and Elite Club, Islamshahr Branch, Islamic Azad University, Islamshahr, Iran

<sup>e</sup>Department of Chemistry, Payame Noor University(PNU), 19395-4697 Tehran, Iran

# Abstract

An environmentally friendly and facile method for preparation of 1,8-dioxooctahydroxanthene between aldehydes with dimedone or cyclohexane-1,3-dione is presented in the presence of trichloromelamine (TCM) under solvent-free condition. Also, for the first time the corrosion inhibitive performance of some 1,8-dioxooctahydroxanthene derivatives on mild steel in 0.1 M

HCl was investigated by AC and DC electrochemical techniques and quantum chemical method. Efficiency more than 97% was obtained with 1 mmol/L 1,8-dioxooctahydroxanthene. Density functional calculations showed that the lone pair electrons of oxygen in the structure of 1,8dioxooctahydroxanthene are suitable sites to interact with the metal. Finally in presence of 1,8dioxooctahydroxanthene, a decrease in surface roughness and corrosion attacks were demonstrated by microscopic examinations, respectively.

**Key words:** Inhibitors, 1,8-Dioxooctahydroxanthene, Corrosion, Quantum chemistry, DFT, Potentiodynamic polarization.

# 1. Introduction

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

Xanthene derivatives as heterocyclic compounds have been interested because of their various pharmacological properties such as antibacterial, antiviral and anti-inflammatory activities.<sup>1-4</sup>

1,8-dioxooctahydroxanthenes contain reactive pyran ring system and have applications in medicinal chemistry<sup>5-7</sup> and fluorescent materials.<sup>8</sup> Interestingly, this structurally complex molecule can be synthesized by a simple one pot tandem reaction between an aldehyde (1 equiv) and dimedone or cyclohexane-1,3-dione (2 equiv) in the presence of a catalyst.<sup>9-12</sup> However, in absence of a catalyst the reaction produce Knoevenagel type adducts, to give an open chain intermediate, 2,2'-aryl/alkyl methylene-bis(3-hydroxy-5,5-dimethyl-2-cyclohexene-1-one).<sup>13,14</sup> Thus, value of a synthetic method for this important class of heterocycles depends mainly on identifying a simple, cost effective, and eco-friendly catalyst and a simple work-up procedure.

*N*-halo reagents have the potential to promote important reactions such as halogenation, oxidation, and protection as well as formation of C-X, C-O, and C=O bonds. Chloramines such as trichloromelamine (TCM) are used as bleaching agents, disinfectants and bactericides, due to their function as chlorinating agents and oxidants. It was registered by EPA as an active

## New Journal of Chemistry

ingredient for food contact surface sanitizer, 3rd sink sanitizer and hard surface disinfectant. It was first used by the US Military as a fruit and vegetable disinfectant.<sup>15-18</sup>

On the other hand, many industrial sections such as acid cleaning bath, water cooling system, various refinery units, pipelines, chemical operations, steam generators, ballast tanks, oil and gas production units are involved with inhibitors due to high corrosion rates in these parts.<sup>19-24</sup> Recently attention was made to study more environmental friendly chemical compounds as green corrosion inhibitors. The adsorption of organic molecules at the metal/solution interface is a great interest in surface science and can remarkably change the corrosion resistance of the metal.<sup>25</sup> It is generally accepted that the first step in the adsorption of an organic inhibitor on a metal surface usually involves replacement of one or more water molecules adsorbed at the metal surface.<sup>26</sup>

$$inhibitor_{(sol)} + xH_2O_{(ads)} \rightarrow inhibitor_{(ads)} + xH_2O_{(sol)}$$

The inhibitor may combine with freshly generated Fe<sup>2+</sup> ions on steel surface, forming metal inhibitor complexes.<sup>27,28</sup>

$$Fe^{2+}+inhibitor_{(ads)} \rightarrow [Fe*inhibitor]^{2+}_{(ads)}$$

Most of the well known acid inhibitors are organic compounds containing nitrogen, sulfur and/or oxygen atoms.<sup>29,30</sup>

Our studies mainly focuses on facile chemical synthesis of 1,8-dioxooctahydroxanthene derivatives. Moreover, its corrosion inhibiting as a green compound on mild steel in hydrochloric acid solution is investigated by electrochemical techniques. The advantages of this compound as corrosion inhibition are the less solubility and large molecule size. Less soluble molecules have a greater tendency to be adsorbed and have more stability than soluble molecules. Because 3,3,6,6-tetramethyl-9-)4-nitrophenyl(-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione is a less soluble

molecule, so has greater stability and better inhibitive behavior than completely soluble molecule. In general, the molecules having the larger area create the better the inhibitive behavior. However, with very large molecules (such as 3,3,6,6-tetramethyl-9-)4-nitrophenyl(-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione), there may be steric hindrance problems when a large molecule attempts to fit onto a surface already partially occupied with previously adsorbed molecules.

# 2. Experimental

# 2.1. Materials

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

Chemicals were obtained from Merck, Sigma-Aldrich and Fluka. IR spectra were recorded on a Shimadzu 435-U-04 spectrophotometer (KBr pellets). <sup>1</sup>H NMR spectra were obtained using Jeol FT NMR 90 MHz and spectrometer in CDCl<sub>3</sub> using TMS as an internal reference. Melting points were determined in open capillary tubes in a Stuart BI Branstead Electrothermal Cat No:IA9200 apparatus and uncorrected. Trichloromelamine (TCM) was commercially available and used **as** received. Electrochemical behavior was investigated by IVIUM Potentiostat. Corrosion attack morphology investigations were conducted by OLYMPUS optical microscopy. Quantum chemical chemical studies were performed by Gaussian 98 software.

# 2.2. General Procedure for Synthesis of 1,8-Dioxooctahydroxanthene

To a mixture of aldehydes (1 mmol) and cyclic 1,3-dicarbonyl compounds (2 mmol), trichloromelamine (TCM, 20 mol%) was added and the mixture was heated in an oil bath at 110°C with good stirring for the appropriate time as indicated in Table 2. The progress of the reaction was monitored by TLC (n-hexane:ethyl acetate, 8:2). After completion of the reaction, hot EtOH (1 mL, 96%) was added and the mixture stirred for 5 min. Then, the catalyst (TCM)

separated by filtration. The residue was washed with ice-water. A solid precipitated which collected by filtration and washed with  $H_2O$  and then dried to give the corresponding 1,8-dioxooctahydroxanthenes (**3a-o**). Finally, the obtained product was recrystallized from ethanol.

**2.2.1.** Spectral Data for 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2Hxanthene-1,8-dione (*3e*): Yellow solid; mp: 224-226 °C (lit. 222-223 °C); IR (KBr, cm<sup>-1</sup>): 3035, 2980, 1685, 1670, 1620, 1533, 1360, 1213, 1173, 1010, 860, 780, 745, 703; <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>): δ 0.998 (s, 6H), 1.12 (s, 6H), 2.15-2.24 (m, 4H), 2.54 (s, 4H), 4.83 (s, 1H), 7.47 (d, 2H), 8.11 (d, 2H); <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>): 196.26, 162.93, 151.49, 146.48, 129.35, 123.44, 114.54, 50.59, 40.84, 32.35, 32.23, 29.25, 27.27.

# 2.3. Specimen and Corrosive Media

The specimen (working electrode) was selected from a mild steel rod with following chemical composition (in wt%): 0.17% C, 0.3% Si, 0.4% Mn and Fe balance. The sample was then mounted in a self-cure epoxy resin resulting in 0.785 cm<sup>2</sup> exposed area. Before each test, the specimen was ground down to 1200 grit emery paper, then washed with ethanol and dried with warm air. The electrolyte solution in all experiments was 0.1 M HCl prepared by Merck reagent and deionised water. Also, the inhibited solutions were prepared with direct adding of various concentrations of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione which was in emulsion form in 0.1 M HCl. To control the cell temperature at constant condition while running the experiments, a water bath with accuracy within  $\pm 1$  °C was employed.

# 2.4. Electrochemical Measurements

The electrochemical measurements were carried out in a conventional three-electrode cell in which the working electrode was the described mild steel sample and the saturated calomel electrode (SCE) and a platinum wire were as reference and counter electrode, respectively. An IVIUM Potentiostat was employed to perform all electrochemical measurements. In order to reach a steady state, the working electrode was immersed in the prepared solution which was open to air in stagnant condition for 30 min. To measure linear polarization resistance (LPR), the potential of the electrode was perturbed from -20 to +20 mV around corrosion potential with 0.5 mV/s scan rate. Also, potentiodynamic polarization was carried out with a constant sweep rate of 1 mV/s in the range of -300 to +300 mV with respect to corrosion potential. The impedance measurement was performed using AC signals with 10 mV amplitude in the frequency range from 100 KHz to 0.1 Hz at corrosion potential. EIS Analyzer software was used to fit the experimental results of EIS measurements using appropriate equivalent circuit.

# 2.5. Corrosion Attack Morphology Investigation

Optical microscopy was accomplished in order to investigate corrosion attack morphology in absence and presence of inhibitor. The surface of specimens was mechanically polished with down to 0.05  $\mu$ m alumina slurry until a mirror-like surface was acquired. Subsequently, they were immersed in 0.1 M HCl in absence and presence of 0.8 ppm (mmol/L) inhibitor for 150 min at room temperature. After bringing out of each specimen, it was washed and cleaned by ethanol and immediately dried at warm air.

## 2.6. Quantum chemical study

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

In order to investigate the effect of molecular structures of monomers, quantum chemical studies were carried out. The optimized structure and the highest occupied molecular orbital (HOMO) of

three monomers were geometrically calculated by DFT method using B3LYP level and 3–21G<sup>\*\*</sup> basis set with Gaussian 98 software.

# **3.** Result and discussion

# 3.1. Chemistry and Synthesis

In recent years, trichloromelamine (TCM) has been used as an effective catalyst in organic synthesis due to its safety, low-price, easy availability and handling with a considerable low amounts. According to our recent studies on the development of efficient and environmentally benign procedures using reagents and catalysts,<sup>31-45</sup> it has been decided to examine the possibility of synthesizing 1,8-dioxooctahydroxanthenes derivatives via various aldehydes, dimedone or cyclohexane-1,3-dione using trichloromelamine (TCM) as a highly efficient reagent under solvent-free conditions (Scheme 1).





Initially, in the presence of a catalytic amount of TCM (20 mol%) under solvent-free conditions at 110°C for 30 minute was produced 3,3,6,6-tetramethyl-9-(phenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (**3a**) in the two-component reaction of benzaldehyde (**1a**),

dimedone (2) and a catalytic amounts of TCM (20 mol%) under solvent-free conditions at 110°C, 3,3,6,6-tetramethyl-9-(phenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione (3a) was produced in 30 minutes (Table 1, entry 1). The effect of temperature on the rate of the reaction was studied (entries 2-3). Decreasing in in temperature leads to decreasing product yields (entry 2). Next, the optimum amount of TCM was evaluated (entries 4-5). The highest yield was obtained with 20 mol% of the catalyst at 110 °C (entry 1). It was observed that the reaction did not proceed at 110 °C in absence of TCM (entry 6).



Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55



<sup>a</sup>Isolated yields. <sup>b</sup>No reaction.

Product

l

 $C_6H_5$ 

Η

40

78

272-273

270-271

R

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55.

#### View Article Online DOI: 10.1039/C5NJ02707A

Based on the optimized reaction conditions, the reactions of dimedone or cyclohexane-1,3dione, and various aromatic aldehydes were investigated as well. As shown in Table 2, aromatic aldehydes carrying either electron-withdrawing or electron-donating substituents afforded good yields of products with high purity at 110 °C under solvent-free conditions.

Time

Yield (%)<sup>a</sup>

Mp (°C)

(3)(min) Reported Found 203-204  $C_6H_5$ CH<sub>3</sub> 82 203-205 30 a  $4-ClC_6H_4$ CH<sub>3</sub> 30 84 233-235 230-232 b  $2-ClC_6H_4$ CH<sub>3</sub> 40 80 225-227 225-227 с d 2-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> CH<sub>3</sub> 30 80 251-253 252-254  $4-NO_2C_6H_4$ CH<sub>3</sub> 20 86 224-226 222-223 e f 3-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub> CH<sub>3</sub> 20 88 168-170 170-172 4-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub> CH<sub>3</sub> 50 80 218-219 217-218 g  $4-BrC_6H_4$ CH<sub>3</sub> 30 84 237-239 239-238 h i  $4-FC_6H_4$ CH<sub>3</sub> 30 79 226-227 226-227 j  $2-NO_2C_6H_4$ Η 40 80 240-242 245-247 k  $4-NO_2C_6H_4$ Η 30 82 263-265 263-265

Table 2. Preparation of	f 1,8-Dioxooctah	ydroxanthene	using TCM	(20 mol%)
-------------------------	------------------	--------------	-----------	-----------

 $R_1$ 

View Article Online DOI: 10.1039/C5NJ02707A

m	4-ClC <sub>6</sub> H <sub>4</sub>	Н	30	76	289-291	288-290
n	$4-CH_3C_6H_4$	Н	60	74	262-263	262-263
0	$4\text{-BrC}_6\text{H}_4$	Н	30	80	229-231	228-231

<sup>a</sup>Isolated yields.





Scheme 2. Proposed mechanism.

# 3.2. Investigation of 1,8-Dioxooctahydroxanthene Derivatives as Green Corrosion Inhibitors

# 3.2.1. Potentiodynamic Polarization

The effect of the concentration of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione on the mild steel corrosion rate in 0.1 M HC1 solution at 25 °C has been studied by potentiodynamic polarization. The polarization curves have been depicted in Fig. 1 and also the electrochemical parameters including corrosion potential ( $E_{corr}$ ), corrosion current density ( $i_{corr}$ ), cathodic and anodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) obtained by the extrapolation of Tafel slopes have been presented in Table 3.



Figure. 1. Potentiodynamic polarisation curves of inhibitor in different concentrations at 25°C.

**Table 3.** Potentiodynamic polarization parameters of mild steel in 0.1 M HCl solution in absence and presence of various concentration of inhibitor.

Concentration	$E_{corr}$	<i>i</i> <sub>corr</sub>	$\beta_a$	$\beta_c$	Α	η
(ppm)	(mV vs. SCE)	$(mA/cm^2)$	$A/cm^2$ ) (mV/decade) (mV/decade)		U	(%)
Blank	-562	1.24	420	392	-	-
0.001	-561	0.94	335	377	0.24	24.2
0.01	-555	0.53	288	316	0.57	56.9
0.1	-538	0.09	120	186	0.93	92.9
1	-509	0.05	80	157	0.96	96.4

Also, the values of surface coverage ( $\theta$ ) and inhibition efficiency have been calculated using the following equations.<sup>46</sup>

$$\theta = \frac{i_{corr}^0 - i_{corr}}{i_{corr}^0}$$
(1)  
$$\eta = \theta \times 100$$
(2)

Where  $(i^{\circ}_{corr})$  and  $(i_{corr})$  represents the corrosion current densities in absence and presence of inhibitor, respectively.

Figure 1 indicates that 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2Hxanthene-1,8-dione is capable to significantly decrease both anodic and cathodic current densities. Table 3 shows that the inhibitor concentration has a positive effect on inhibitive behaviour of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8dione so that the efficiency values considerably increase with increasing in 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione concentration (i.e. 24.2% in 0.001 mmol/L to 96.4% in 1 mmol/L). It is believed that 3,3,6,6-tetramethyl-9-(4-nitrophenyl)- New Journal of Chemistry Accepted Manuscript

3.4.5.6.7.9-hexahydro-2H-xanthene-1.8-dione molecules adsorb onto metal surface and consequently slow down metal dissolution and hydrogen evolution by blocking many available active sites. Although, the presence of defects on organic layer created by inhibitor adsorption cannot be ruled out, therefore hydrogen evolution and metal dissolution may occur from these regions where there is no inhibitor coverage (i.e. 1-  $\theta$ ).<sup>20</sup> In addition. The polarization curves shown in Figure 1 reveal a fact that, in the case of lower concentration (<0.01 ppm), the inhibitor decreased the cathodic current density more strongly than the anodic current density that in lower concentrations of inhibitor, 3,3,6,6-tetramethyl-9-)4-nitrophenyl(-3,4,5,6,7,9-hexahydro-2Hxanthene-1,8-dione has a tendency to more block the cathodic sites which act as suitable sites for hydrogen evolution. In contrast, in the case of higher concentration (>0.01 ppm), the inhibitor decreased the anodic current density more strongly than the cathodic current density that in longer concentrations of inhibitor the cothodic site has covered by inhibitor molecules and 3,3,6,6-tetramethyl-9-)4-nitrophenyl(-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione has а tendency to more block the anodic sites which act as suitable sites for anodic dissolution.<sup>47-49</sup>

Also, Table 3 reveals that in presence of inhibitor, the values of anodic and cathodic Tafel slopes ( $\beta_a$  and  $\beta_c$ ) have been significantly diminished and also the corrosion potential slightly shifted toward more positive values. The variation of Tafel slopes refers to change in reaction kinetics. This can be explained that with anodic and cathodic polarizing of the sample, the reaction kinetics speed up in inhibited solution in comparison with uninhibited one. This is a negative effect of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione on corrosion rate of mild steel. However, the considerable decrease in active area is the main reason for diminishing net corrosion current density in inhibited solution.<sup>50</sup> Considering

New Journal of Chemistry Accepted Manuscript

that 1,8-dioxooctahydroxanthene decreases both anodic and cathodic current densities while it has no effect on corrosion potential, this compound can be classified as mixed-type inhibitors.

# **3.2.2. Electrochemical Impedance Spectroscopy (EIS)**

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55.

Electrochemical impedance spectroscopy (EIS) is a valuable method which has been widely used to study the inhibitive behavior of many compounds.<sup>20</sup> It provides information on both the resistive and capacitive behavior at interface and makes possible to assess the performance of the tested compounds as inhibitors for metals.<sup>51</sup> In this part, the effect of inhibitor concentration on inhibitive behavior of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione on mild steel in 0.1 M HCl has been investigated using EIS measurement after 1 hr immersion time at 25 °C. Figure 2 depicts Nyquist plots in absence and presence of different inhibitor concentrations.



**Figure. 2.** Nyquist plots in absence and presence of different inhibitor concentrations at 25 °C. Inserted image shows the equivalent circuit model.

As seen, Nyquist plots consist of a depressed semicircle in inhibited and uninhibited solutions. This capacitive loop is attributed to the double-layer capacitance in parallel with the charge transfer resistance. In addition, Figure 2 shows that a rise in 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione concentration results in increasing the semicircle diameter, indicating the inhibition of the corrosion process.<sup>52-54</sup>

The impedance parameters have been obtained by EIS analyser software using appropriate equivalent circuit (see inserted image in Fig. 2) for metal-electrolyte interface and presented in Table 4.  $R_s$ ,  $R_{ct}$ , and CPE represent solution resistance, charge transfer resistance and constant phase element, respectively. A small inductive or quasi inductive loop at very low frequency was observed. Several reasons have been proposed for this observation such proton adsorption/desorption process, etc. Here this has been neglected since its contribution to the total impedance was negligible.

**Table 4.** EIS parameters of mild steel electrode in 0.1 M HCl solution in absence and presence of various concentrations of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione at 25 °C.

Concentration	EIS	IS				LPR		
(ppm)	R <sub>s</sub>	R <sub>ct</sub>	Р	n	C <sub>dl</sub>	η%	R <sub>p</sub>	η
	$(\Omega.cm^2)$	$(\Omega.cm^2)$	(µF.cm <sup>-2</sup> )		(µF.cm <sup>-2</sup> )		$(\Omega.cm^2)$	(%)
Blank	13.8	19.6	540	0.86	257	-	41.24	-
0.001	14.1	30.1	430	0.88	238	35	52.41	21
0.01	16	73.3	8.2	0.89	41	73	104	60
0.1	20	217.9	6.3	0.89	35	91	270	84
1	15.7	355	6.1	0.89	37	95	417	90

Also, the percentage of inhibitor efficiency  $\eta$  has been calculated by the charge transfer resistance by means of following formula:<sup>49</sup>

$$\eta = \frac{R - R^0}{R} \times 100 \tag{3}$$

Where,  $R^{\circ}$  and R are the charge transfer resistance of mild steel in absence and presence of inhibitor, respectively. In addition, the values of double-layer capacitance have been calculated by Eq. 4:<sup>47</sup>

$$C_{dl} = P^{\frac{1}{n}} R_{ct}^{1-\frac{n}{n}}$$
(4)

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

In above expressions, *P*, *n* and  $R_{ct}$  are the constant phase element (CPE) parameter, CPE exponent and charge transfer resistance of mild steel, respectively. As known, the CPE element is a non-ideal capacitance which is generally used to simulate experimental data.<sup>20,29</sup> Deviations from the ideal semi-circle can partly be due to the surface inhomogeneities and mass transport processes. Thus, in these situations, pure double layer capacitors are better described by a transfer function with CPE.<sup>21,55,56</sup>

Evaluation of Table 4 revealed that with increasing in 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione concentration, the values of  $R_{ct}$  increase while the double layer capacitance values decrease. An increase in  $R_{ct}$  refers to more block of the active area at the metal surface as a result of increasing inhibitor concentration. Also, the decrease in double-layer capacitance indicates that in presence of various inhibitor concentrations, the double layer reinforced onto the surface. Since, the double-layer between the charged metal surface and the solution is considered as an electrical capacitor. In addition, the values of *n* show an increase with increasing inhibitor concentration. This can be attributed to the decrease in

## **New Journal of Chemistry**

surface roughness and the slightly improvement of surface homogeneity due to inhibitor adsorption on the most active sites.<sup>20,29,57</sup>

The 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione adsorption on the iron surface decreases its electrical capacity due to displacing the water molecules and other ions which are originally adsorbed on the surface with inhibitors molecules. According to Helmholtz model, double layer capacitance is related to structural parameters as follows:<sup>57</sup>

$$C_{dl} = \frac{\varepsilon_0 \varepsilon}{d} S \tag{5}$$

Where *d* is the thickness of the film, *S* is the surface area of the electrode,  $\varepsilon^{\circ}$  is the permittivity of the air and  $\varepsilon$  is the local dielectric constant. The decrease in  $C_{dl}$  is probably due to a decrease in local dielectric constant and/or an increase in the thickness of a adsorb layer at electrode surface in 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione.<sup>58</sup> Although, by increasing in inhibitor concentration, a decrease in the surface area which act as a place for surface charging may also be as other reason for  $C_{dl}$  decreasing.<sup>59</sup>

It should be mentioned that the efficiency calculated by EIS results in absence and presence of different concentration of investigated 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione are in close correlation with those of polarization in. In addition, EIS measurement confirms that this compound has a good inhibitive behaviour for mild steel in 0.1 M HCl media.

# **3.2.3.** Linear Polarization Resistance (LPR)

The effect of inhibitors concentration on corrosion behavior of mild steel in 0.1 M HCl solution at 25 °C has been studied by LPR method which is a useful and fast method. The LPR values and also efficiency calculated by Equation 3 have been presented in Table 4. LPR results confirm the inhibitive properties of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione, also conclusions obtained from potentiodynamic polarization and EIS results.

# 3.2.4. Thermodynamic Calculations of Inhibitor Adsorption

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

The primary step in the action of inhibitors in acid solutions is adsorption onto the metal surface, which is usually an oxide-free surface. It has been reported that the inhibition mechanism of an inhibitor may vary with factors such as concentration, pH, nature of the anion of the acid, and nature of the metal.<sup>60</sup> Thus, basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. In order to obtain the thermodynamic parameters, the relation between surface coverage ( $\theta$ ) values and inhibitor concentration (*C*) must be considered. So far, several attempts were made to find the relation between  $\theta$  and *C* such as Langmuir, Temkin, Frumkin and Flory–Huggins.<sup>61,62</sup> Langmuir adsorption isotherm was generally found to be the appreciable description of the adsorption behavior of the inhibitor. According to Langmuir isotherm, the relation between  $\theta$  values and inhibitor concentration, *C*, is considered as follows.<sup>63</sup>

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \tag{6}$$

Where  $K_{ads}$  is the equilibrium constant of the adsorption process and *C* is the inhibitor concentration. Figure 3 shows  $C/\theta$  variations as a function of *C*. The obtained plot of the inhibitor is perfectly linear with a correlation coefficient higher than 0.999 and it shows that the 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione obeys Langmuir isotherm (Fig. 3). Since we have used the percentage of surface coverage values, the

slope is 0.01 which in turn gives unit value by multiplying at 100 as unit slope for Langmuir isotherm in Eq. 6.



Figure. 3. Langmuir adsorption isotherm of inhibitor in 0.1 M HCl at 25 °C.

The equilibrium constant of adsorption  $K_{ads}$  is related to the standard free energy of adsorption ( $\Delta G^{\theta}_{ads}$ ) with the following equation.<sup>20</sup>

$$\Delta G_{ads}^{0} = -RT \ln(55.5K_{ads}) \tag{7}$$

In this expression, *R* is gas constant, *T* is absolute temperature and 55.5 is concentration of water in solution in mol/1.  $\Delta G^{\theta}_{ads}$  value corresponding to 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione has been calculated ( $\Delta G^{\theta}_{ads}$ = -38.74 kJ/mol). The negative sign of  $\Delta G^{\theta}_{ads}$  refers to the adsorption of inhibitors onto the metal surface.<sup>64</sup> In general, the magnitude of  $\Delta G^{\theta}_{ads}$  approximately -20 kJ/mol or less negative is assumed for existing electrostatic interactions between inhibitor and the charged metal surface (i.e., physisorption). Those  $\Delta G^{\theta}_{ads}$  around -40 kJ/mol or more negative are an indication of charge sharing or charge transferring from an organic species to the metal surface to form a coordinate type of metallic

bond (i.e., chemisorption).<sup>25</sup> Considering above notifications and the  $\Delta G^{0}_{ads}$  value of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione ( $\Delta G^{0}_{ads}$ = -38.74 kJ/mol), it can be claimed that 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione has a nearly chemical adsorption onto mild steel surface.

# 2.2.5. Corrosion Attack Morphology

Published on 20 November 2015. Downloaded by New York University on 21/11/2015 13:57:55

The corrosion attack morphology of the mild steel samples immersed in inhibited and uninhibited (blank) solutions for 150 min, has been studied by optical microscopy and the metallographic result have been presented in Fig. 4. As seen from Fig. 3, the polished surface of mild steel immersed in blank solution has been rough and severely corroded so that several pits are dispersedly observed at the surface (Fig. 4 (a)). While in the case of inhibited solution, a less corrosion attack is detected and the specimen surface is nearly unchanged. In this micrograph (Fig. 4 (b)), pearlite phase has been partially etched and the grain boundaries of ferrite phase is not observed.



**Figure. 4.** Corrosion attack morphology obtained by optical microscope; A) blank solution and B) in presence of 1 mmol/L 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione.

# 2.2.6. Effect of Molecular Structure

First estimation for the ability of inhibitive behavior of a compound is to act as an electron donor. The adsorption of the inhibitor on the metal surface can be considered on the basis of donor-acceptor interaction between inhibitor molecules and the metal surface. Organic compounds are protonated in acidic solutions but, as the one molecule approaches the metal surface, the molecule loses its proton so that the lone pair of electrons on the heteroatoms can interact with the metal surface.<sup>65,66</sup> In order to determine this effect, quantum chemical study method was employed and the results were presented in Fig. 5.



**Figure. 5.** A) Molecular structure and highest occupied molecular orbital (HOMO), B) Molecular structure and lowest unoccuped molecular orbital

HOMO and LUMO of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2Hxanthene-1,8-dione optimized by DFT method using B3LYP level and 3–21G<sup>\*\*</sup> basis set with Gaussian 98 reveals that oxygen atoms existing in Xanthene have a large electron density. Lone pair electrons of oxygen can be suitable sites to adsorb onto metal surface. It is reported that these electrons are an agent for charge sharing or charge transferring, resulting in chemisorptions. In addition, surface chelates are formed involving bonding between a surface cation and heteroatom atom in the chelating molecule (i.e. chelates between heteroatom such as oxygen, sulphur, nitrogen and the metal cation such as Fe<sup>+2</sup>).<sup>61,67</sup>

A second factor in determining the effectiveness of a chemisorbed organic the inhibitor is the molecular size. In general, the molecules having the larger area create the better inhibitive behavior. However, with very large molecules (such as 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione), there may be steric hindrance problems when a large molecule attempts to fit onto a surface already partially occupied with previously adsorbed molecules. Thus, complete coverage of the surface by large molecules may sometimes be difficult to achieve.<sup>68</sup> Competitive adsorption, in inhibited solution, is assumed to occur at low carbon steel surface between the aggressive Cl ions and the inhibitor molecules in this study. As known, the predominant reason for corrosion process of mild steel in HCl solution is due to the adsorption of Cl ions onto its bare metallic surface sites. The mobility of Cl is higher than 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione, therefore the 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione cannot compete with Cl ions, but 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2Hxanthene-1,8-dione adsorption can prevent Cl ions to reach the steel surface sites by steric effect. Also, in relation to corrosion inhibition, when an inhibited solution contains adsorbable anions, such as halide ions, these adsorb on the metal surface by creating oriented dipoles and consequently increase the adsorption of the organic cations on the dipoles. In these cases, a

positive synergistic effect arises; therefore, the degree of inhibition in the presence of both adsorbable anions and inhibitor cations is higher than the sum of the individual effects.<sup>69</sup> Therefore, this process could explain the higher inhibition efficiency of various organic inhibitors in hydrochloric acid solutions compared to sulfuric acid solutions. In this work, in order to examine this phenomenon, several electrochemical tests including potentiodynamic polarization and EIS measurement were carried out in  $H_2SO_4$  media (the results were not shown here). It was observed that the inhibitor efficiency of 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione unexceptionally decreased and approached to 40% values.

The third factor affecting chemisorption, and thus inhibition, is the solubility of the organic soluble molecule. Less soluble molecules have a greater tendency to be adsorbed and has more stability than soluble molecules.<sup>57,58</sup> Because 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione is a less soluble molecule, so has greater stability and better inhibitive behavior than completely soluble molecule.

# 4. Conclusion

In conclusion, we have successfully developed a practical, operationally simple, economical, and environmentally friendly procedure for the synthesis and Investigation of 1,8-dioxooctahydroxanthene derivatives as corrosion inhibitors. Moreover, the final results of this research including: Electrochemical measurements showed that the 3,3,6,6-tetramethyl-9-(4-nitrophenyl)-3,4,5,6,7,9-hexahydro-2H-xanthene-1,8-dione increases charge transfer resistance of double layer on the surface and functions as a mixed-type inhibitor. Thermodynamic data

extracted by Longmuir isotherm is showing the chemisorption adsorption and adsorption process happen by lone pair electrons of oxygen in xanthenes.

# Acknowledgements

Partial financial support from the Research Council of Hakim Sabzevari University is greatly appreciated.

# References

- 1. R. D. Jonathan, K. R. Srinivas and E. B. Glen, Eur. J. Med. Chem., 1988, 23, 111.
- 2. S. Samantaray, P. Kar, G. Hota and B. G. Mishra, Ind. Eng. Chem. Res., 2013, 52, 5862.
- 3. H. K. Wang, S. L. Morris-Natschke and K. H. Lee, Med. Res. Rev., 1997, 17, 367.
- A. V. Rukavishnikov, M. P. Smith, G. B. Birrell, J. F. W. Keana and O. H. Griffith, *Tetrahedron Lett.*, 1998, **39**, 6637.
- A. Naya, M. Ishikawa, K. Matsuda, K. Ohwaki, T. Saeki, K. Noguchi and N. Ohtake, Bioorg. Med. Chem. Lett., 2003, 11, 875.
- 6. H. Wang, L. Lu, S. Zhu, Y. Li and W. Cai, Curr. Microbiol., 2006, 52, 1.
- N. Mulakayala, P. V. N. S. Murthy, D. Rambabu, R. Adepu, G. R. Krishna, C. M. Reddy, K. R. S. Prasad, M. Chaitanya, C. S. Kumar, M. V. B. Rao and M. Pal, *Bioorg. Med. Chem. Lett.*, 2012, 22, 2186.
- 8. C. G. Knight and T. Stephens, *Biochem. J.*, 1989, 258, 683.
- B. Maleki, S. Barzegar, Z. Sepehr, M. Kermanian and R. Tayebee, J. Iran. Chem. Soc., 2012, 9, 757.
- 10. B. Maleki, M. Gholizadeh and Z. Sepehr, Bull. Korean Chem. Soc., 2011, 32, 1697.

- 11. F. Shirini and N. Ghaffari Khaligh, Dyes Pigm., 2012, 95, 789.
- A. Ilangovan, S. Malayappasamy, S. Muralidharan and S. Maruthamuthu, *Chem. Cent. J.*, 2011, 5, 81.
- 13. M. Bayat, H. Imanieh and S. H. Hossieni, Chin. Chem. Lett., 2009, 20, 656.
- 14. J. T. Li, Y. W. Li, Y. L. Song and G. F. Chen, Ultrason. Sonochem., 2012, 19, 1.
- 15. H. Veisi and R. Ghorbani-Vaghei, Tetrahedron., 2010, 66, 7445.
- A. Bamoniri, M. A. Zolfigol, B. F. Mirjalili and F. Fallah, *Rus. J. Org. Chem.*, 2007, 43, 1393.
- 17. S. Kondo, M. Ohira, S. Kawasoe, H. Kunisada and Y. Yuki, J. Org. Chem., 1993, 58, 5003.
- B. F. Mirjalili, A. Bamoniri and H. R. Akrami, *Digest J. Nanomat. Biostruct.*, 2009, 4, 763.
- 19. S. A. Ali, M. T. Saeed and S. U. Rahman, Corrosion Sci., 2003, 45, 253.
- A. Kosari, M. Momeni, R. Parvizi, M. Zakeri, M. H. Moayed, A. Davoodi and H. Eshghi, *Corrosion Sci.*, 2011, **53**, 3058.
- M. Lagrenée, B. Mernari, M. Bouanis, Traisnel and F. Bentiss, *Corrosion Sci.*, 2002, 44, 573.
- 22. M. A. Quraishi, F. A. Ansari and D. Jamal, Chem. Physic., 2003, 77, 687.
- 23. M. A. Quraishi and R. Sardar, Mater. Chem. Physic., 2003, 78, 425.
- 24. M. A. Quraishi and S. K. Shukla, Mater. Chem. Physic., 2009, 113, 685.
- R. Solmaz, G. Kardaş, M. Çulha, B. Yazıcı and M. Erbil, *Electrochimica Acta.*, 2008, 53, 5941.
- 26. J. O. Bockris and D. A. J. Swinkels, *Electrochem. Soc.*, 1964, 111, 743.

- 27. V. Branzoi, F. Branzoi and M. Baibarac, Mater. Chem. Physic., 2000, 65, 288.
- 28. E. E. Oguzie, Y. Li and F. H. Wang, J. Colloid Interface Sci., 2007, 310, 90.
- 29. F. Bentiss, M. Lebrini, M. Lagrenée, M. Traisnel, A. Elfarouk and H. Vezin, *Electrochimica Acta.*, 2007, **52**, 6865.
- 30. M. A. Migahed, A. M. Abdul-Raheim, A. M. Atta and W. Brostow, *Mater. Chem. Physic.*, 2010, **121**, 208.
- B. Maleki, S. Hemmati, A. Sedrpoushan, S. Sedigh Ashrafi and H. Veisi, *RSC Adv.*, 2014, 4, 40505.
- 32. B. Maleki, E. Rezaee-Seresht and Z. Ebrahimi, Org. Prep. Proced. Int., 2015, 47, 149.
- 33. B. Maleki, Org. Prep. Proced. Int., 2015, 47, 173.

- 34. R. Tayebee, S. J. Ahmadi, E. Rezaei Seresht, F. Javadi, M. A. Yasemi, M. Hosseinpour and B. Maleki, *Ind. Eng. Chem. Res.*, 2012, **51**, 14577.
- 35. B. Maleki and F. Taimazi, Org. Prep. Proced. Int., 2014, 46, 252.
- 36. B. Maleki, S. Sedigh Ashrafi and R. Tayebee, RSC Adv., 2014, 4, 41521.
- B. Maleki, D. Azarifar, H. Viesi, S. F. Hojati, H. Salehabadi and R. Nejat Yami, *Chin. Chem. Lett.*, 2010, **21**, 1346.
- H. Veisi, B. Maleki, F. Hosseini Eshbala, H. Veisi, R. Masti, S. Sedigh Ashrafi and M. Baghayeri, *RSC Adv.*, 2014, 4, 30683.
- 39. B. Maleki and S. Sedigh Ashrafi, RSC Adv., 2014, 4, 42873.
- 40. M. Baghayeri, H. Veisi, B. Maleki, H. Karimi-Maleh and H. Beitollahi, *RSC Adv.*, 2014,
  4, 49595.
- 41. R. Tayebee, M. Jarrahi, B. Maleki, M. Kargar Razi, Z. B. Mokhtari and S. M. Baghbanian, *RSC Adv.*, 2015, **5**, 10869.

- 42. H. Veisi, B. Maleki, M. Hamelian and S. Sedigh Ashrafi, RSC Adv., 2015, 5, 6365.
- 43. B. Maleki, S. Barat Nam Chalaki, S. Sedigh Ashrafi, E. Rezaee Seresht, F. Moeinpour,
  A. Khojastehnezhad, and R. Tayebee, *Appl. Organomet. Chem.*, 2015, 29, 290.
- 44. B. Maleki and S. Sheikh, RSC Adv., 2015, 5, 42997.
- 45. B. Maleki, S. Babaee and R. Tayebee, Appl. Organomet. Chem., 2015, 29, 408.
- 46. Q. Qu, L. Li, W. Bai, S. Jiang and Z. Ding, Corrosion Sci., 2009, 51, 2423.
- 47. B. Hirschorn, M. E. Orazem, B. Tribollet, V. Vivier, I. Frateur and M. Musiani, *Electrochimica Acta.*, 2010, **55**, 6218.
- 48. K. F. Khaled and M. M. Al-Qahtani, Chem. Physic., 2009, 113, 150.
- 49. E. A. Noor, Mater. Chem. Physic., 2009, 114, 533.
- 50. E. Mc Cafferty and N. Hackerman, J. Electrochem. Soc., 1972, 119, 146.
- 51. D. A. López, S. N. Simison and S. R. de Sánchez, Electrochimica Acta., 2003, 48, 845.
- 52. M. Keddam, O. Rosa Mottos and H. Takenouti, Electrochem. Soc., 1981, 128, 257.
- 53. K. F. Khaled, K. Babic-Samardzija and N. Hackerman, Corrosion Sci., 2006, 48, 3014.
- 54. W. J. Lorenz and F. Mansfeld, Corrosion Sci., 1981, 21, 647.
- 55. J. R. Macdonald, J. Electroanalytic. Chem. Interfac. Electrochem., 1987, 223, 25.
- O. Olivares-Xometl, N. V. Likhanova, M. A. Domínguez-Aguilar, E. Arce, H. Dorantes and P. Arellanes-Lozada, *Mater. Chem. Physic.*, 2008, **110**, 344.
- 57. H. Hamdy and H. Perchlorate, *Electrochimica Acta.*, 2006, 51, 5966.
- 58. A. K. Singh and M. A. Quraishi. Corrosion Sci., 2010, 52, 152.
- 59. F. Bentiss, M. Traisnel and M. Lagrenee, Corrosion Sci., 2000, 42, 127.
- 60. H. D. Leçe, K. C. Emregül and O. Atakol, Corrosion Sci., 2008, 50, 1460.

- 61. L. Herrag, B. Hammouti, S. Elkadiri, A. Aouniti, C. Jama, H. Vezin and F. Bentiss, *Corrosion Sci.*, 2010, **52**, 3042.
- 62. L. M. Vracar and D. M. Drazic, Corrosion Sci., 2002, 44, 1669.
- 63. F. Bentiss, M. Lebrini and M. Lagrenée, Corrosion Sci., 2005, 47, 2915.
- 64. G. Avci, Colloids Surfaces A: Physicochem. Engin. Aspects., 2008, 317, 730.
- 65. J. J. Fu, S. N. Li, Y. Wang, X. D. Liu and L. D. Lu, J. Mater. Sci., 2011, 46, 3550.
- 66. J J. Fu, H. S. Zang, Y. Wang, S. N. Li, T. Chen and X. D. Liu, *Ind. Eng. Chem. Res.*, 2012, **51**, 6377.
- 67. G. Gökhan, Corrosion Sci., 2008, 50, 2981.

- 68. S. Rajendran, S. P. Sridevi, N. Anthony, A. John Amalraj and M. Sundearavadivelu, *Anti-Corrossion Methods Mater.*, 2005, **52**, 102.
- 69. E. E. Sridevi, Mater. Chem. Physic., 2004, 87, 212.

# **Graphical Abstract**

```
Facile Synthesis and Investigation of 1,8-Dioxooctahydroxanthene Derivatives as
Corrosion Inhibitors for Mild Steel in Hydrochloric Acid Solution
```

Behrooz Maleki, Ali Davoodi, Mojtaba Vakili Azghandi, Mehdi Baghayeri, Elahe Akbarzadeh, Hojat Veisi, Samaneh Sedigh Ashrafi, Massomeh Raei



For the first time, the corrosion inhibitive performance some of 1,8-dioxooctahydroxanthene derivatives is proposed.