Int. J. Electrochem. Sci., 12 **(2017)** 4134 – 4149, doi: 10.20964/2017.05.10

International Journal of
ELECTROCHEMICAL
SCIENCE
www.electrochemsci.org

Electrochemical and Quantum Chemical Investigations of some Cyanoacetamide Derivatives as Eco-Friendly Corrosion Inhibitors for Aluminum-Silicon Alloy in Acidic Solution

A. S. Fouda[1,*], *A.M.Eldesoky*[2] , *F.Sh.Mohamed*[3] *and M. W. El-Sherbeni*[1]

[1]Department of Chemistry, Faculty of Science, El-Mansoura University, El-Mansoura-35516, Egypt
[2] Engineering Chemistry Department, High Institute of Engineering &Technology (New Damietta), Egypt and Al-Qunfudah Center for Scientific Research (QCSR), Chemistry Department, Al-Qunfudah College, Umm Al-Qura University, KSA.
[3]Department of Chemistry, Faculty of Science, Damietta University, Damietta, Egypt.
[*]E-mail: asfouda@hotmail.com

Received: 27 December 2016 / *Accepted:* 28 February 2017 / *Published:* 12 April 2017

Cyanoacetamide derivatives (CyD) were investigated as eco-friendly corrosion inhibitors at various doses for alloy (Al/Si) in one molar HCl utilized Tafel polarization (TP), (EFM) electrochemical frequency modulation and (EIS) impedance method. The temperature influence on corrosion behaviour with appending of various doses was carried out in range of temperature of 25-45ºC by EFM technique. TP plots revealed that the investigated CyD were of mixed-type. The protection efficiency (% η) was found to rise with increasing the concentration of investigated CyD but decrease with improving the medium temperature. CyD adsorption on Al/Si alloy surface was found to obey Temkin isotherm. Some adsorption and activation thermodynamic functions were measured and explained. The order of the % η of CyD is given: (**1**) > (**2**) > (**3**). It was noted that the data of quantum chemical calculations run parallel to the rise in % η given which support the preceding order.

Keywords: Cyanoacetamide derivatives, Al-Si alloy, HCl, TP, EIS, EFM

1. INTRODUCTION

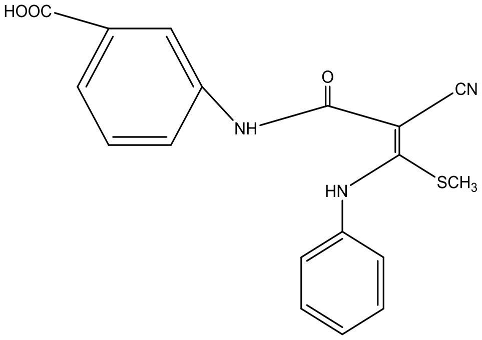
Corrosion is a basic process playing an important role in safety and economics , particularly for metals. Corrosion of Al and its alloys has been a find on different work because increase the technological significant, their electrical conductivity, powering, and many applications on industrial expressly in electronics, building, transportation and packing [1]. Even if Al alloy has a protective adhesive passivation by amphoteric oxide film, and dissolves when the alloy is encounter to higher dose of bases or acids [2]. The higher study aim to disconnection of metal from corrosive medium, corrosion inhibitors is added to inhibit dissolution of metal and lower acid exhaustion [3]. The utilized of inhibitors is the important technique for prevent corrosion, expressly in corrosive medium [4]. Most of inhibitors are organic assembled that include O, S, and N atoms and large protection efficiency and production easy [5-8]. Heterocyclic assembled have been utilized for the iron protection [9-12], Cu [13], Al [14-16], and other alloys [17-18] in various medium. Even if these assembled have bigger protection efficiencies, no side effects, even in very small doses, due to their toxicity to humans, deleterious environmental effects, and increase-cost [19]. Universally, the first step is inhibitors adsorption on the alloy surface. Many mechanisms have occurred by formed the passive oxide film when Cl^- arrived to interface of metal film. Finally, the Cl^- does not come in the oxide film but it is attached chemically on the surface [20]. The inhibitors choice depends on two mechanisms: I: synthesized relatively low cost raw materials; II: include cloud of electron on the electro-negative atoms or aromatic ring contain long-chain assembled. Universally, organic assembled include O, S, and/or N as polar groups and connect to double bonds in their structures have been classified as best corrosion protection for higher metals and alloys in acidic solution [21-39]. Functional include polar groups are esteem the reaction site that fixed the adsorption process [40]. From this processes rely on a small effect, such as the kind and charge of the metal surface, the adsorption type, and the kind of the electrolyte solution [41].

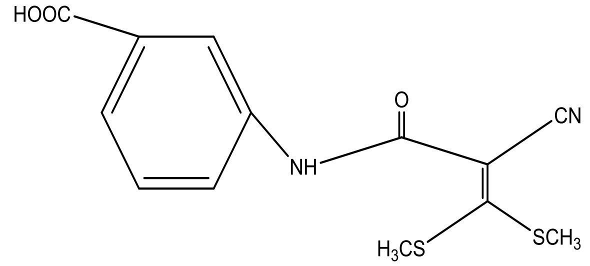
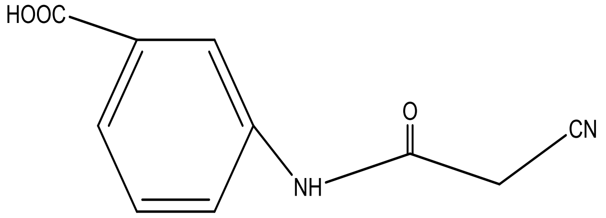
The point of paper is to research the inhibiting effect of these CyD (1-3) on the corrosion habit of alloy Al-Si in HCl one molar solution utilized on different electrochemical methods.

2. EXPERIMENTAL METHODS

2.1. Reagents & solutions

Table 1. Formulas, structures & molecular weights and the studied CyD (1-3)

Cpd. No.	Compound	Mol. F& Mol. Wt
(1)	 (*E*)-3-(2-cyano-3-(methylthio)-3-(phenylamino)acrylamido)benzoic acid	$C_{18}H_{15}N_3O_3S$ 353.08

(2)	 3-(2-cyano-3,3-bis(methylthio)acrylamido)benzoic acid	$C_{13}H_{12}N_2O_3S_2$ 308.37
(3)	 3-(2-cyanoacetamido)benzoic acid	$C_{10}H_8N_2O_3$ 204.19

Alloy Al/Si that utilized here is of composition: Al 92.48%, Si 7.03%, Mn 0.004%, Fe 0.110%, Ni 0.002%, Mg 0.369%, Zn 0.003%, Cr 0.001%, Ti 0.007% and Na 0.003%. CyD (1-3) with molecular weights, molecular formulas & structures are record in Table1. Appropriate doses of hydrochloric acid (37.5%) was prepared using bidistilled water. $1x10^{-3}$ molar stock solutions from the investigated CyD (1-3) were found by liquefaction the suitable weights of the tested pure solid assembled in ethanol absolute [42].

2.2. Electrochemical measurements

2.2.1. TP technique

TP calculation were performed utilized an ordinary three-compartment cell glass of a capacity 100 ml that contain three different types of electrodes; Al-Si alloy specimen as working electrode (WE), calomel electrode saturated type (SCE) as a reference electrode, and a platinum sheet was used as the counter electrode (CE). The counter electrode area was larger with respect to the area of the WE. This can exert a uniform potential field on the WE and minimize polarization effect on the CE. The working electrode was a Al/Si rod encapsulated in Teflon with an exposed cross section of 1 cm^2 diameter. The surface of the working electrode was polished exactly to mirror finish and degreased with acetone. This WE was dipped into the cell of polarization, with time 35 min was specified for the WE to reach a steady state OPC. All the tests were take place at 25^oC by using an ultra-circulating thermostat. The TP current potential plots were recorded by exchanging the potential of electrode automatically from -0.8 to 0.8 mV against (E_{ocp}) open circuit potential with a rate of scan 1 mV/s.

2.2.2. EIS technique

EIS tests have performed at AC frequency varied from 10 kHz to 10 mHz with amplitude of 5 mV peak-to-peak using AC signals at open circuit potential. The EIS data was analysed and discussed based on the circuit equivalent. Cell and apparatus used in EIS technique is the same as used in TP.

2.2.3. EFM technique

In this method one uses the larger peaks to measure the causality factors CF-2 & CF-3, (i_{corr}), and TP (β_c & β_a). Measurements were occurred utilized Gamry apparatus PCI4G750 Galvanostat / Potentiostat /ZRA. A Gamry framework system was used. Echem Analyst software 5.58 was utilized for drawing, data fitting, and graphing.

2.4. Quantum study

For quantum chemical calculations, Material Studio Version 4.4 software was used.

3. RESULTS AND DISCUSSION

3.1. Analysis of TP study

Potentiodynamic polarization study is used to validate the corrosion behavior and also used to calculate the kinetics of the electrode reactions. [43]. Fig. 1 depicts the current-potential relationship of alloy Al/Si at unlike tests solutions of CyD (1) [as the good inhibitor], similar curves were obtained for CyD 2 &3 (not shown). The electrochemical functions like current of corrosion (i_{corr}), (E_{corr}.), anodic Tafel slopes (β_a) , cathodic (β_c), θ and % η for alloy in HCl one molar solution in existence and nonexistence of various doses of CyD are presented in Table 2. These tabulated data indicated that, by increasing the doses of CyD gave a consistent break down in both cathodic and anodic current. Also, there is no appreciable shift in E_{corr} was noted. These results clearly indicate that these inhibitors acting as mixed inhibitors kind [44]. The TP of β_a and β_c at 25ºC do not exchange significant upon appending of CyD, which lead to the presence of these additives attendance of these additives not exchange the alloy corrosion process and the mechanism of cathodic reaction. These inhibitors effect on both cathodic reactions and anodic [45], i.e. it is mixed kind inhibitors. % η and θ were measured utilized the following Eq. (1):

$$\% \eta = \theta \times 100 = [1 - (i_{corr} / i^{o}_{corr})] \times 100 \qquad (1)$$

Where i_{corr} and i^{o}_{corr} are the current corrosion attendance and Lake of CyD, continually. The order % η was given as follow: (1) > (2) > (3).

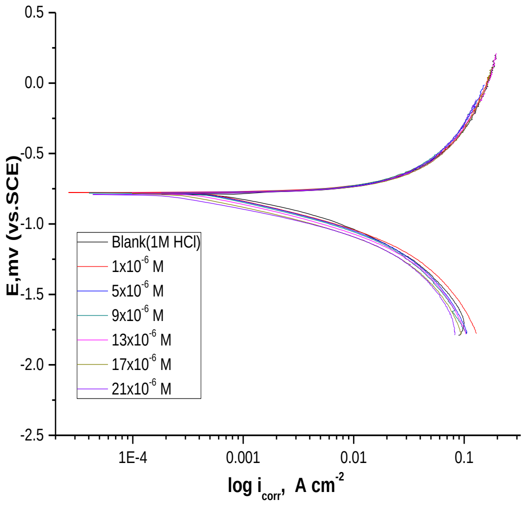


Figure 1. TP diagrams for the Al/Si corrosion in hydrochloric acid one molar in the nonexistence & existence of various doses of substance (1) at 25^{o}C

Table 2. Corrosion parameters of Al-Si alloy immersed in hydrochloric acid one molar at unlike doses of CyD obtained by polarization method at 25^{o}C

Cpd. No.	Conc. x10^{6} M	-E_{corr} mV vs CE	i_{corr} mA cm^{-2}	β_c mV dec^{-1}	β_a mV dec^{-1}	Θ	% η	CR mmy^{-1}
Blank	0.0	787	881.0	233	45	---	---	759.3
(1)	1	779	302.3	204	31	0.657	65.7	403.3
	5	781	289.4	213	34	0.672	67.2	364.4
	9	780	246.2	199	30	0.720	72.0	316.6
	13	783	210.6	201	29	0.761	76.1	263.9
	17	786	170.7	197	27	0.806	80.6	223.5
	21	791	131.2	161	20	0.851	85.1	186.3
(2)	1	754	398.4	213	48	0.548	54.8	478.2
	5	785	387.6	189	53	0.560	56.0	421.1
	9	741	335.9	174	51	0.619	61.9	362.4
	13	693	283.1	211	45	0.679	67.9	311.9
	17	684	222.7	196	36	0.747	74.7	257.8
	21	680	158.2	224	42	0.820	82.0	212.1
(3)	1	654	442.8	187	33	0.497	49.7	503.4
	5	650	402.9	191	38	0.543	54.3	461.2
	9	648	363.7	174	49	0.587	58.7	440.1
	13	641	328.2	170	53	0.627	62.7	396.3
	17	659	272.3	181	50	0.691	69.1	378.2
	21	652	221.9	190	37	0.748	74.8	323.9

3.2. AC impedance spectra analysis

EIS measurements were utilized to estimate the deposited film performance on the metal or alloy surface. The equivalent circuit model is shown in Figure 2. A similar example of EIS value given for CyD (1) [as good inhibitor] is record as Bode and Nyquist curves in Figures. (3a & 3b). The same plots were given for other compounds (not shown).

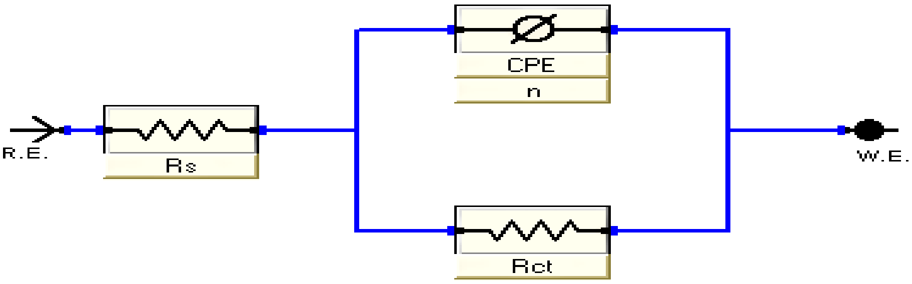


Figure 2. Equivalent circuit model utilized for EIS value recorded for Al/Si alloy

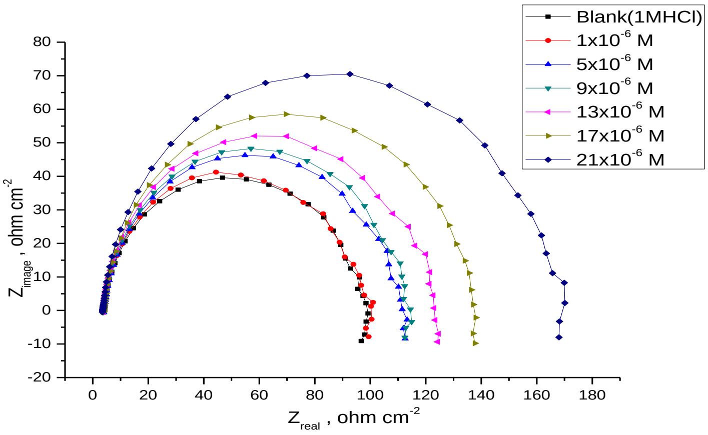


Figure 3a. Nyquist diagrams for alloy Al-Si in one molar HCl in the nonexistence & existence of unlike doses of inhibitor (1) at 25°C

The spectra of the impedance include a Nyquist semicircle kind without appearance of diffusive contribution to the total impedance (Z) which led to that the dissolution goes mainly under charge-transfer control [46-47]. In the existence of CyD the diameter of the capacitive loops increases, this led to the degree of protection of corrosion process, contrary to the lower of the (C_{dl}) which is known from Eq. (2):

$$C_{dl} = (2\,\pi\, f_{max} R_{ct})^{-1} \qquad (2)$$

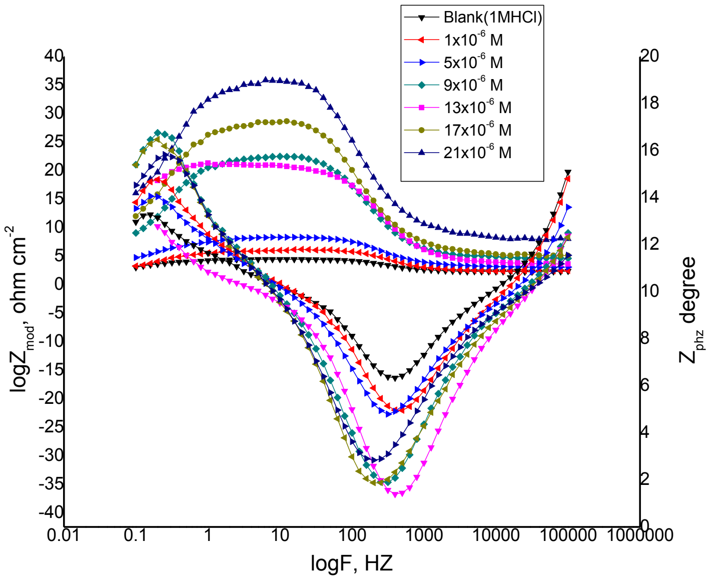


Figure 3b. The Bode curves for alloy Al/Si in the nonexistence & Existence of unlike doses of CyD (1) at 25°C

Table 3. Parameters of Al/Si alloy immersed in 1 molar HCl in the nonexistence & existence of unlike doses of CyD given from EIS technique at 25°C

Cpd. No.	Conc.x10^{-6} M	C_{dl}x10^{-6}, μF cm^{-2}	R_{ct}, Ω cm^2	θ	% η
Blank	0.0	10.8	11.60	---	---
(1)	1	11.4	64.89	0.821	82.1
	5	9.8	78.71	0.853	85.3
	9	10.2	81.42	0.857	85.7
	13	11.3	93.48	0.876	87.6
	17	9.4	114.63	0.899	89.9
	21	10.9	125.84	0.908	90.8
(2)	1	12.1	61.47	0.811	81.1
	5	11.5	73.83	0.843	84.3
	9	12.4	78.31	0.852	85.2
	13	10.9	86.22	0.865	86.5
	17	11.2	107.64	0.892	89.2
	21	10.7	121.78	0.905	90.5
(3)	1	11.9	51.38	0.774	77.4
	5	12.8	64.12	0.819	81.9
	9	12.1	71.54	0.838	83.8
	13	10.3	82.97	0.860	86.0
	17	10.8	89.78	0.871	87.1
	21	11.7	97.41	0.881	88.1

Y_o = magnitude CPE, f_{max} = the frequency imaginary at the EIS maximum and $\omega = 2\pi f_{max}$. The obtained % η were measured from Eq. (3):

$$\% \eta = 100 \times \theta = [1 - (R^o_{ct} / R_{ct})] \times 100 \quad (3)$$

Where R^o_{ct} and R_{ct} are the resistance of the charge-transfer data in nonexistence and existence inhibitors, continually. The lower capacitive semicircles are often depending on the roughness of surface and non-homogeneity, since this capacitive semicircle is combining with thickness and dielectric properties of the barrier oxide film. The data of C_{dl} lower with raising the dose of inhibitors, because the gradual exchange of molecules water in the double layer by the inhibitor molecules had adsorbed [48]. This lower in C_{dl} and rise in R_{ct} confirms that the liquefaction of Al/Si alloy are reduced, due to inhibitors adsorption on the surface of metal. EIS values are given in Table 3, the order of % η as before: (1) > (2) > (3).

3.3. Analysis of EFM study

The EFM is a safe and accurate corrosion tests that can directly give the i_{corr} without knowing Tafel constants and with only a small polarizing signal [49]. The measured corrosion kinetic functions at various doses of the CyD are obtain in Table 4.

Table 4. EFM parameters for alloy Al-Si in one molar HCl attendance and nonattendance of unlike doses of CyD 25°C

Cpd. No.	Conc.x10^{-6}, M	$i_{corr.}$, µA cm^2	β_a, mV dec^{-1}	β_c, mV dec^{-1}	CF-2	CF-3	% η
Blank	0.0	898.4	86.9	217.4	2.07	3.06	---
(1)	1	197.8	69.3	165.9	1.89	2.94	77.9
	5	163.9	91.4	194.1	2.01	2.85	81.8
	9	155.0	65.0	172.5	1.99	3.22	82.7
	13	86.7	75.6	261.8	1.83	2.98	90.3
	17	82.8	81.5	183.4	1.96	2.66	90.8
	21	60.1	72.4	186.0	1.33	2.48	93.3
(2)	1	347.2	78.6	86.9	1.65	2.97	61.4
	5	256.1	81.3	141.2	1.71	2.84	71.5
	9	248.5	93.4	96.4	1.99	2.35	72.3
	13	227.7	72.5	72.2	2.04	2.91	74.7
	17	218.7	66.9	124.8	1.81	2.21	75.6
	21	179.7	98.7	98.5	1.82	2.25	79.9
(3)	1	412.2	89.4	97.5	1.86	2.45	54.1
	5	388.5	65.8	76.8	1.93	2.88	56.8
	9	349.3	43.9	126.1	2.03	3.07	61.1
	13	319.4	97.3	98.4	2.05	3.41	64.4
	17	275.7	63.2	139.8	1.83	2.96	69.3
	21	253.9	78.6	91.9	1.53	2.93	71.7

From Table 4, the i_{corr} lowered by raising the dose of CyD and so the % η improvement. The causality factors are very close to the theoretical data which given best quality of data [50]. The declination of CF from their ideal data may carry out due to the lower amplitude perturbation or due to the spectrum frequency resolution is not enough high. The outcome data showed agreement best for corrosion kinetic functions given with the TP and EIS techniques.

3.4. Adsorption isotherms

The adsorption provides the interaction with the surface of metal alloy and also gave data for the reaction among the adsorbed molecules on the surface of alloy [51]. To know the adsorption mechanism of heterogeneous reactions adsorption isotherms were applied [52]. Several trials were made to fit experimental data to different isotherms contain Temkin, Langmuir, Frumkin, and Freundlich isotherms, it was obtain from data that the best isotherm for the research CyD on the surface of Al-Si is the Temkin [53] as follow:

$$a/2.303\Theta = \log K_{ads} + \log C \qquad (4)$$

K_{ads} = constant adsorption equilibrium, and C = inhibitor doses. The plots of Θ against log C for compound (1) at unlike temperatures are given in Figure 4. Similar plots were given for the other CyD (not shown). Some thermodynamic adsorption functions such as, ΔH°_{ads} adsorption heat, ΔS°_{ads}, ΔG°_{ads} standard free energy. These parameters can be measured by unlike mathematical tests rely on K_{ads} data from adsorption isotherms at temperatures different [54]. ΔG°_{ads} obtain from next Eq. 5:

$$K_{ads}=(1/55.5)\ e^{(-\Delta G^\circ ads\ /\ RT)} \qquad (5)$$

Where 55.5 = water dose. ΔH°_{ads} could be estimated from the following Eq.:

$$\text{Log } K_{ads} = (-\ \Delta H^\circ_{ads}\ /\ 2.303RT) + \text{constant} \qquad (6)$$

In order to measured ΔH°_{ads}, log K_{ads} was draw versus 1/T as given in Figure 5. Which similar with the basic equation:

$$\Delta G^\circ_{ads} = \Delta H^\circ_{ads} - T\Delta S^\circ_{ads} \qquad (7)$$

Table 5 given the parameters on Al-Si alloy surface, and given that: higher data of K_{ads} led to good % η and large interaction among the adsorbent and the adsorbate.

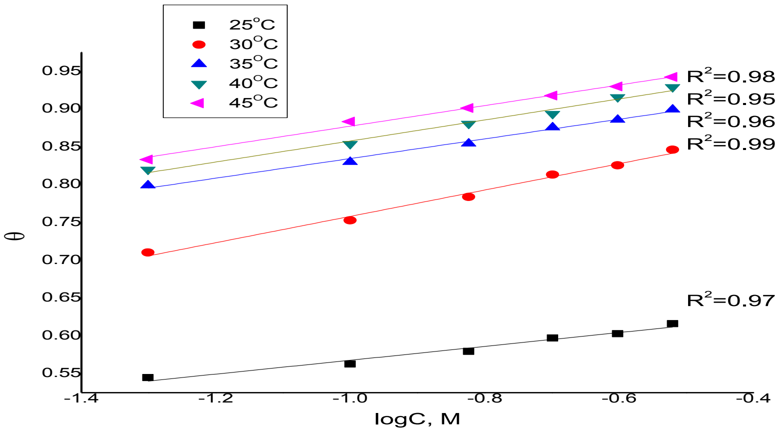


Figure 4. Temkin of CyD (1) on surface of Al-Si in acidic medium

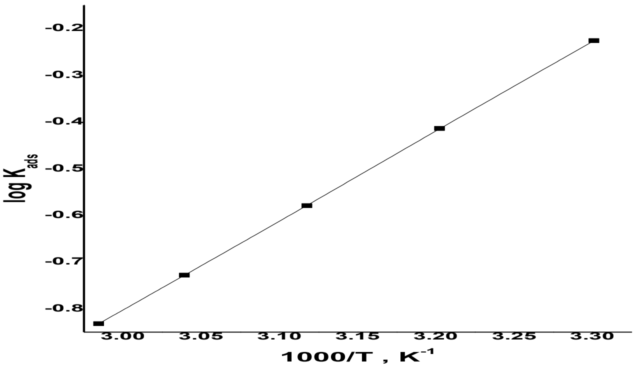


Figure 5. 1/T vs. Log K_{ads} for Al /Si alloy attendance of CyD (1) at unlike temperatures.

The –ve sign ΔG°_{ads} illustrate the spontaneous adsorption of the process [55]. From the outcome data of ΔG°_{ads} it was found the attendance of chemical adsorption. Exothermic adsorption ($\Delta H^{o}_{ads} < 0$) may involve either chemisorption or physisorption or mixture of among processes, an endothermic adsorption process ($\Delta H^{o}_{ads} > 0$) include chemisorption [56]. The + ve sign ΔS°_{ads} this indicates that the disorder was decreased on the direction of formation of the the metal-adsorbed reaction complex.

Table 5. Parameters of the CyD adsorbed on Al/Si alloy at various temperatures

Cpd. No.	Temp. ^{o}C	K_{ads} M^{-1}	$-\Delta G^{\circ}_{ads.}$ kJ mol^{-1}	$\Delta H^{\circ}_{ads.}$ kJ mol^{-1}	$\Delta S^{\circ}_{ads.}$ J $mol^{-1}K^{-1}$
(1)	25	254.5	66.7	36.3	21.9
	30	240.6	67.5		21.4
	35	171.4	60.4		18.6
	40	164.0	61.2		18.2
	45	138.1	53.1		16.8
(2)	25	129.3	52.9	33.4	16.3
	30	124.3	50.3		15.9
	35	123.5	50.1		15.7
	40	116.4	51.6		15.4
	45	114.2	49.6		15.2
(3)	25	107.3	47.9	26.3	14.6
	30	97.2	22.7		15.3
	35	82.9	23.0		10.1
	40	78.3	40.6		12.1
	45	54.6	30.6		9.1

3.5. Temperature effect

The influence of temperature in range (25 to 45˚C).Draw (log k) with (1/T) at various dose of CyD (1) [as the best inhibitor] is given in Figure 6, the same plots for other CyD (not shown). From the slope of lines one can measure E_a^* according to equation of Arrhenius:

$$k = A \exp(-E_a^* / RT) \qquad (8)$$

Where A = constant rely on electrolyte and a metal kind, k = corrosion rate constant, T = kelvin temperature**.** Plot of 1/ T vs. log (k/ T) at various dose of CyD (1) is given in Figure 7. From Figure one can measure (ΔS^*) and (ΔH^*) using transition equation:

$$\text{Rate} = TR/\,Nh\; e^{(-\Delta H^*/\,RT)}\, e^{(\Delta S^*/\,R)} \qquad (9)$$

Where h = Plank's constant, N = Avogadro's number.

All parameters were record in Table 6. it could be shown from the obtained data that the apparent $E_a^*$for the reaction in 1M HCl of Al-Si alloy lower in the attendance of the utilized inhibitors, this break down in $E^*{}_a$ led to the chemical bonds formed were strengthen by the temperature improving [57]. However, the degree of the rate rise in the protected solution is minimum than that blank solution. Therefore, the protection efficiency of the CyD rise with temperature rose. This outcome data supports the idea that the adsorption of the CyD on the Al-Si alloy surface may be nature chemical. Thus, as the rise temperature the numbers of molecules adsorbed improve leading to improve in the protection efficiency. The data obtained illustrated that these CyD coating the corrosion reaction by lowering its $E^*{}_a$. This illustrated by the adsorption on the surface of Al-Si alloy that make charge transfer and a barrier for mass. The kinds of inhibitors perform excellent protection at maximum temperature with considerable rise in protection efficiency at temperatures elevated [58]. Moreover, the relatively maximum data of $E^*{}_a$ in existence of these CyD suggests adsorption chemical process.

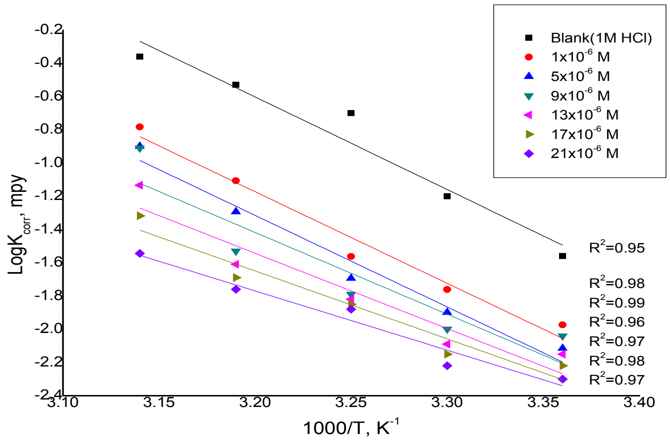


Figure 6. 1/ T vs. log k_{corr} for Al-Si alloy in 1 M hydrochloric acid in the nonexistence & existence of different doses of compound (1).

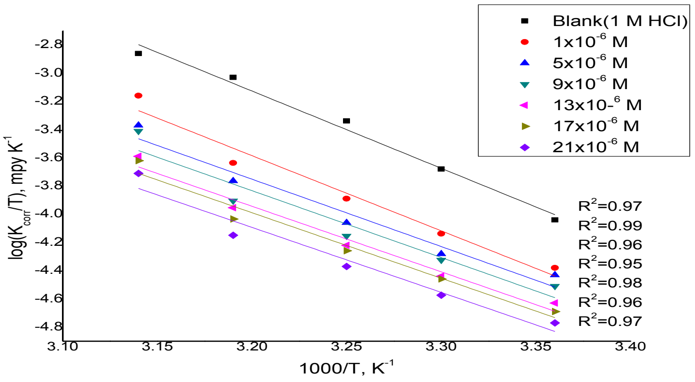


Figure 7. Transition state plots for corrosion of Al/Si alloy in the nonexistence & existence of doses of CyD (1)

Table 6. Parameters for corrosion of Al/Si alloy in the nonexistence & existence of unlike doses of CyD

Conc. M	E_a^* kJ mol^{-1}	ΔH^* kJ mol^{-1}	ΔS^* J mol^{-1} K^{-1}
Blank	48.6	46.5	110.2
Compound (1)			
$1x10^{-6}$	66.9	65.8	52.7
$5x10^{-6}$	70.3	69.1	44.9
$9x10^{-6}$	73.6	72.4	36.3
$13x10^{-6}$	81.7	80.2	14.1
$17x10^{-6}$	91.3	89.9	5.9
$21x10^{-6}$	105.3	39.7	23.2
Compound (2)			
$1x10^{-6}$	54.4	52.5	92.8
$5x10^{-6}$	56.5	54.9	86.2
$9x10^{-6}$	58.4	56.4	82.7
$13x10^{-6}$	66.3	63.4	58.1
$17x10^{-6}$	67.1	64.2	61.8
$21x10^{-6}$	78.1	38.5	10.7
Compound (3)			
$1x10^{-6}$	51.5	49.1	96.8
$5x10^{-6}$	53.2	54.7	86.6
$9x10^{-6}$	57.6	55.6	84.8
$13x10^{-6}$	62.9	60.1	72.5
$17x10^{-6}$	64.1	62.9	61.9
$21x10^{-6}$	69.2	76.3	37.6

The + ve sign of ΔS^* for the inhibitors, indicates that there is an increase in disorder of the activated complex in the rate determining step. This represents dissociation rather than an association step [59]. All data of $E_a^*$are higher than the analogous data of ΔH^* lead to that the corrosion process must contain a gaseous reaction, simply the evolution of hydrogen reaction [60]. Continually, the endothermic processes have signifies chemisorptions process.

3.7. Theoretical calculations

Figure 8 portrays the molecular orbital curves and Mulliken charges of CyD (1-3). Theoretical analysis was making it for only the uncharged forms, in order to obtain further insight into the outcome experimental. Data of quantum chemical parameters such as energies of lowest unoccupied molecular orbital's (E_{LUMO}) and energy of highest occupied molecular orbital's (E_{HOMO}) and energy gap (ΔE) are measured and record in Table 7. It has been known that the bigger or lower -ve E_{HOMO} is related to inhibitor, the higher the trend of offering electrons to unoccupied d orbital of the metal, and the improve the corrosion protection efficiency, in appending, the brought down of E_{LUMO}, the gain of electrons easier from alloy surface [61]. From Table 7, the ΔE given by the different methods in condition of composite (3) is decrease than (1), which improve the assumption that substance (1) molecule will deposit more best on Al-Si alloy surface than substance (3), due to facilitating of electron transfer among molecular orbital HOMO and LUMO which occur due its adsorption on the alloy surface and thereafter attendance the higher %η. Also the E_{HOMO} rise from substance (1) to substance (3) facilitates the adsorption and the PE by supporting the transport process through the adsorbed layer. Reportedly, perfect corrosion inhibitors are utilized from organic assembled that are not only offer electrons to unoccupied orbital of the alloy, but also gain electrons free from the alloys [62]. From all quantum calculation parameters validate this outcome experimental.

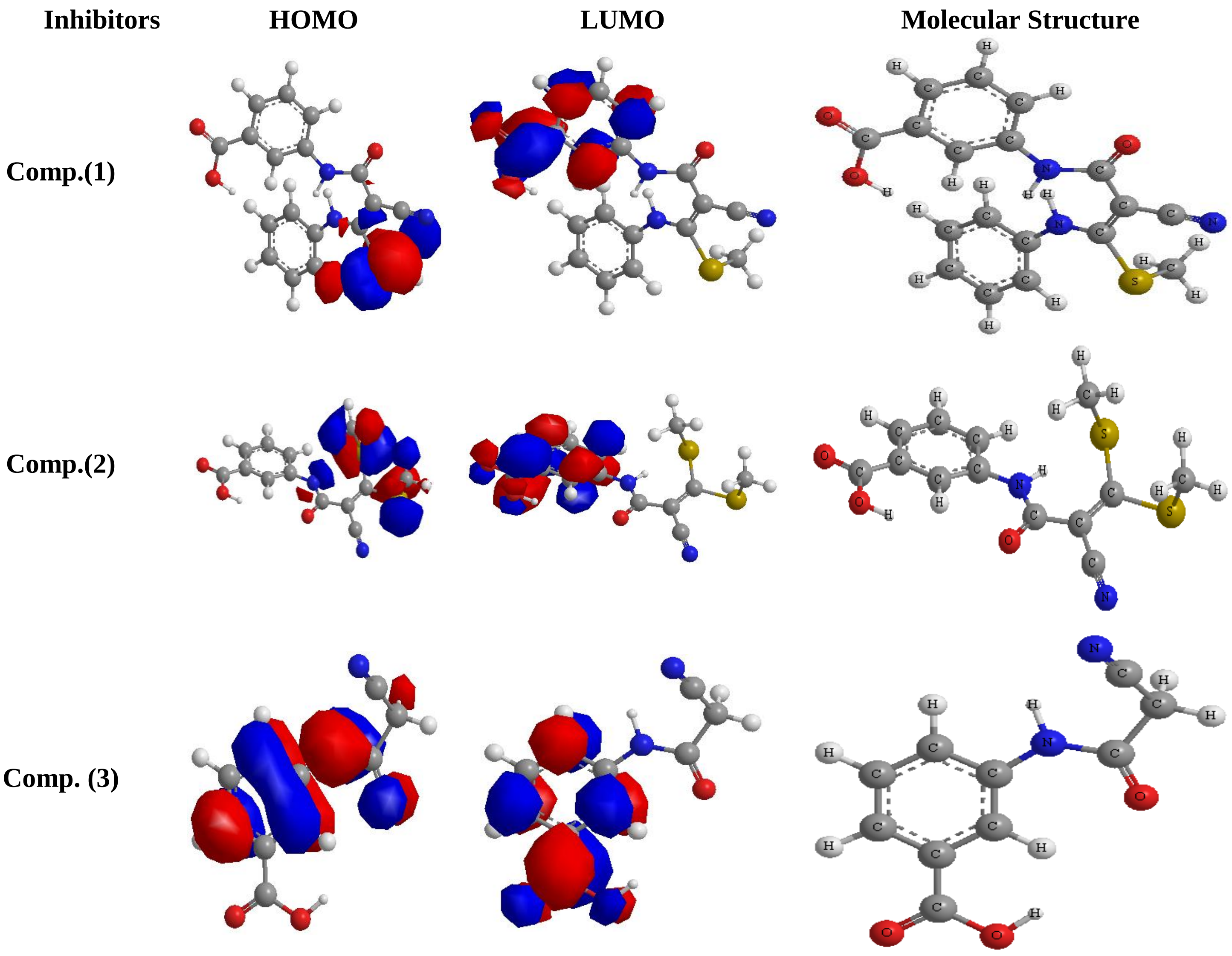


Figure 8. Molecular orbital plots of investigated CyD (1-3)

Table 7. Theortical calculated properties for investigated CyD (1-3)

	substance (1)	substance (2)	substance (3)
$-E_{HOMO}$ (eV)	6.271	7.194	11.663
$-E_{LUMO}$ (eV)	3.786	3.764	3.784
ΔE (eV)	2.485	4.150	7.879

3.9. Corrosion protection mechanism

Adsorption of organic compounds which is the essential mechanism of corrosion inhibition which can be explained by two basic kinds of interactions: chemisorption and physisorption. Physical adsorption need the attendance of both charged species in solution and electrically charged metal surface. The metal charge surface of the alloy is due to the electric field attendance at the solution / metal interface. On the other side, chemisorption process, include sharing charge or transfer charge from the CyD molecules to the alloy surface to form a coordinate kind bond[63]. In case of adsorption, this contains the water molecules change from the alloy and sharing electrons among the hetero-atoms and Al. Also, the CyD molecules can adsorb on alloy surface on the main of donor-acceptor attractions among π-electrons of aromatic rings and vacant p-orbital of surface Al atoms. Thus, we can conclude that corrosion protection for Al-Si alloy in HCl is mainly due to interaction chemical and electrostatic adsorption. The order of lowering % η of the tested CyD from all method utilized is as follows: (1) > (2) > (3).

Substance (1) has excellent PE due to: (i) its higher molecular size (353.40) that may facilitate better adsorption on the alloy surface and hence, it covers larger molecular area (ii) its deposition via seven active centers (3-O, 3-N and 1- S atoms). Substance (2) comes after substance (**1**) in % η due to, it has lower molecular size (308.37) and also it has seven active centers (3-O , 2-N and 2- S atoms). Substance (3) is the least effective substance in % η, this due to, it has lesser molecular size (204.19), and less active centers (3-O and 2-N atoms).

4. CONCLUSIONS

All the tested CyD are best corrosion protection for alloy Al-Si in HCl solution. Double layer capacitances lower than blank solution when the added inhibitor. This can illustrated by adsorption of the CyD on the Al-Si alloy surface. The % η of these investigated assembleds is: (**1**) > (**2**) > (**3**). The adsorption of the CyD was found to obey the adsorption Temkin isotherm led to that the protection process take place via adsorption. The % η given from EFM, PP, and EIS tests are in excellent agreement.

References

1. W. Rosliza, Wan Nik, H. Senin, *Mater. Chem. Phys.*, 107 (2008) 281.
2. I.Obot, N.Obi-Egbedi, *J. Colloids Surf. A: Physicochem. Eng. Asp.* 330 (2008) 207.

3. A. Aytac, *J. Mater. Sci.*, 45 (2010) 6812.
4. G. Trabanelli , *Corrosion*, 47 (1991) 410.
5. D. N.Singh, A. K.Dey, *Corrosion*, 49 (1993) 594.
6. G. Banerjee, S. N. Malhotra, *Corrosion*, 48 (1992) 10.
7. S. T. Arab, E. A. Noor, *Corrosion*, 49 (1993) 122.
8. I. A. Raspini, *Corrosion*, 49 (1993)821.
9. A. Khadraoui , A. Khelifa , L. Touafri, H. Hamitouche, R. Mehdaoui, *J. Mater. Environ. Sci.* 4 (2013) 663.
10. M. Elachouri, M. S. Hajji, M. Salem, S. Kertit , R. Coudert , E. M. Essassi, *Corros.Sci.*, 37 (1995) 381.
11. H. Luo, Y. C. Guan, K. N. Han, J. *Corrosion*, 54 (1998) 619.
12. M. A. Migahed, E. M. S. Azzam , A. M. Al-Sabagh, J. *Mater.Chem.Phys*, 85 (2004) 273.
13. R. F. V. Villamil, P. Corio, J. C. Rubim, M. L. Siliva Agostinho, *J. Electroanal. Chem.*, 472 (1999) 112.
14. H.Kumar and S. Karthikeyan., *J. Mater. Environ. Sci*. 3 (5) (2012) 925–934.
15. Z.M. Hadi, S.K. Al-Mubarak, M. HaddadI, *J. Mater. Environ. Sci.* 1 (4) (2010) 227-238.
16. S. S. Abd El Rehim, H.Hassan, M. A.Amin, *Mater.Chem.Phys.* 78 (2003) 337.
17. R.Guo, T. Liu, X.Wei, *J. Colloids Surf. A*, 209 (2002) 37.
18. V.Branzoi, F.Golgovici, F.Branzoi, *Mater.Chem.Phys*, 78 (2002) 122.
19. K. S.Parikh, K. J.Joshi,J. *Trans. SAEST*, 39 (2004) 29.
20. E. Foad El-Sherbini, S.M. Abd-El-Wahab, M.A. Deyab, *Mater. Chem. Phys.*,82 (2003) 631
21. S.Deng, X.Li, X.Xie, *Corros. Sci.*, 80 (2014)276.
22. Haleem, Wanees, Aal, Farouk, *Corros. Sci.*, 68 (2013)1.
23. M.Jeepa, G.V.Prabhu, M.S.Boobalan and C.M.Rajesh, J.Phys.Chem.,C. 119(38)(2015)22025
24. J.Qian, S.Zhang and L. Liu, Chem. Bull., 77(2) (2014)170
25. S.M. Mousavifard, P. Malek Mohammadi Nouri, M.M. Attar, B. Ramezanzadeh, *Engineering Chemistry*, 19 (2013) 1031.
26. E.M. Sherif, S. M. Park, *J. Electrochem. Soc.*152 (2005) 205-211.
27. A.Hamdi, M.B.Taouti, D.Benbertal, *J. Mater. Environ. Sci.* 6(1) (2015) 93.
28. E.S.M. Sherif, *Int. J. Electrochem. Sci*., 6 (2011) 479.
29. K.Barouni, A.Kassale, L.Bazzi, R.Salghi, B.Hammouti,and A. Elbourine, *Res Chem Intermed*, 40(3)(2014) 991
30. N.A. Ogurtsov, A.A. Pud, P. Kamarchik, G.S. Shapoval, *J. Synthetic Metals*, 143 (2004) 43.
31. M.Mahdi, *Int.J.Adv.Res.Eng.Technol.*, 1(5)(2014) 30
32. E.S.M. Sherif, A.A. Almajid, *J. Appl. Electrochem.*, 40 (2010) 1555.
33. E.S.M. Sherif, *Int. J. Electrochem. Sci.*, 7 (2012) 1482.
34. E. S.M. Sherif, *Int. J. Electrochem. Sci*. 7 (2012) 1884.
35. E. S.M. Sherif, R.M. Erasmus, J.D. Comins, *J. Colloid and Interface Sci.*, 306 (2007) 96.
36. *K.Uma, and S.Rekha*, *J.Chem.Pharm.Res.*, 7(4) (2015) 165
37. E. S.M. Sherif, R.M. Erasmus, J.D. Comins, *J. Colloid and Interface Sci.*, 311 (2007) 144.
38. E.S.M. Sherif, R.M. Erasmus, J.D. Comins, *J. Appl. Electrochem.*, 39 (2009) 83.
39. E.S.M. Sherif, R.M. Erasmus, J.D. Comins, *Corros. Sci.*, 50 (2008) 3439.
40. De-Oliveira, V.W. Faria, G.F.de-Andrade, E.Delia, M.F.Cabral and A.B.Cotrim, Phosphorous, sulphur, Silicon and the related elements, 190 (2015) 1366.
41. E.M. Sherif, S.-M. Park, *Corros. Sci.*, 48 (2006) 4065.
42. E. S.M. Sherif, *Appl. Surf. Sci.*, 252 (2006) 8615.
43. W. P.Smith, L. S. Sollis, D. P.Howes, C. P. Cherry, D.I. Starkey, N.K.Cobley, *J. Med. Chem.*,41(1998) 787.
44. Z. Bikadi, E. Hazai, *J. Chem. Inf.* 11 (2009) 1.
45. T. A. Halgren, *J. Comput. Chem*. 17 (1998) 490.

46. G.M. Morris, D.S. Goodsell, *J. Comput. Chem.* 19 (1998) 1639.
47. A.S. Fouda, A.Al-Sarawy, E.El-Katori, *European J. Chem.*, 1(4) (2010) 312.
48. Li X., Deng, Fu H. and Mu G., *Corros. Sci.* 51(2009)620.
49. J. Bessone, C. Mayer, K. Tuttner, W. J. lorenz, *J. Electrochim. Acta*, 28 (1983) 171.
50. A.S.Fouda , F. El-TaibHeakal and M.S.Radwan, *J. Appl. Electrochem.*, 39 (2009) 391
51. A.S.Fouda, H.A.Mostafa, F. El-TaibHeakal and G.Y.Elawady, *Corros. Sci.* 47 (2005) 1988.
52. F. Bentiss, M. Bouanis, B. Mernari, M. Traisnel, H. Vezin, M. Lagrenee, *Appl. Surf. Sci.*, 253 (2007) 3696.
53. E. Kus, F. Mansfeld, *Corros. Sci.*, 48 (2006) 965.
54. E. McCafferty, H. Leidheiser (Ed.), "Corrosion Control by Coating", Science Press, Princeton, NJ (1979) 279.
55. E.E Oguzie, E.E. Ebenso, *J. Pigm. Resin Technol.*, 1 (2006) 35
56. M. Kliskic, J. Radosevic, S. Gridic, *J. Appl. Electrochem.*, 27 (1997) 947
57. K. Aramaki, N. Hackerman, *J. Electrochem. Soc.*, 116 (1969) 568.
58. P.C. Okafor, M.E. Ikpi, I.E. Uwah, E.E. Ebenso, U.J. Ekpe, S.A. Umoren, *Corros. Sci.*, 50 (2008) 2310.
59. E.E. Oguzie, *Corros. Sci.*, 49 (2007) 1527.
60. A.S. Fouda, A.A.Al. Sarawy, E.E.El. Katori, *Desalination*, 201 (2006) 1.
61. S. Martinez, M. Matikos-Hukovic, *J. Appl. Electrochem.*, 33 (2003) 1137.
62. F. Samie, J. Tidblad, V. Kucera, C. Leygraf, *Atmos. Environ.* 40 (2006) 3631.
63. I. Lukovits, K. Palfi, I. Bako, E. Kalman, *Corrosion* 53 (1997) 915.
64. P. Zhao, Q. Liang, Y Li., *Appl. Surf. Sci.* 252 (2005) 1596.