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Alanine as Corrosion Inhibitor for Iron in Acid Medium: A Molecular Level Study

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Density functional theory (DFT) calculations have been used to investigate the minimum energy structures of alanine molecules on iron (111). Adsorption of alanine molecule on iron (111) surface has been studied computationally to generate adsorption configurations and to use the force field method to obtain a ranking of the energies for each generated configuration, thereby indicating the preferred adsorption sites. In this article Monte Carlo simulation searches of the configurational space of iron (111) (substarte) – alanine (adsorbate) system as the temperature of the system is slowly decreased is used in order to find low energy adsorption sites on both adsorbate and substrate system. The results indicated that alanine could adsorb on Fe surface through the nitrogen/oxygen atoms with the lone pair electrons in its molecule.The inhibition performance of alanine on iron in normal hydrochloric acid medium (1.0 M HCl) at 25±1 °C was tested by potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. Alanine inhibits the acidic corrosion even at very low concentrations, reaching a value of inhibition efficiency up to 80% at a concentration of 50 mM. The results obtained from the different corrosion evaluation techniques are in good agreement. Polarization curves indicate that the studied alanine is mixed-type inhibitors, affecting both cathodic and anodic corrosion currents. Data, obtained from EIS measurements, were analyzed to model the corrosion inhibition process through appropriate equivalent circuit model, a constant phase element (CPE) has been used.

Keywords: Monte Carlo ; EIS; Tafel polarization; Alanine ; Molecular dynamics simulations

1. INTRODUCTION

Nowadays the study of steel corrosion phenomena has become an important industrial as well as academic topic [1]. The use of corrosion inhibitors is one of the most effective methods to protect metal surfaces against corrosion, especially in acid media[2].

The corrosion inhibition efficiency of organic compounds is related to their adsorption properties. Adsorption depends on the nature and the state of the metal surface, on the type of corrosive medium and on the chemical structure of the inhibitor [3].

In recent years, a number of eco-friendly corrosion inhibitors have been exploited as green alternative to toxic and hazardous compounds [4-8] . The amino acids which contain carboxyl and amino functionalities bonded to the same carbon atom are non-toxic, relatively cheap and easy to produce in purities greater than 99%. It has been shown by various authors that some amino acids can act as corrosion inhibitors, which has generated an increasing interest in these compounds as substitute to conventional corrosion inhibitors that are usually toxic [9-13].

Computer modeling techniques have been successfully applied to corrosion problems as summarized in review articles by Zamani, Porter , Mufti and Munn [14, 15]. The application of computer modeling techniques to corrosion systems requires an understanding of the physical phenomenon of corrosion and the mathematics which govern the corrosion process. In addition, knowledge of the numerical procedures which are the basis of computer modeling techniques is necessary for accurate computational analyses. Verification of assumptions by comparison of computer analysis results with experimental or other measured data is a fundamental requirement in the creation of an accurate analysis. Simulation is a prognostic computational tool for complex scientific and engineering problems. The simplest simulation methods have been used for decades, but, with the increase in computational memory and speed simulation, have become the prevalent tool for analysis [16-18].

In this work, the adsorption behavior of alanine at Fe surface will investigated by the molecule dynamics simulation method and density functional theory. A survey of literature indicates that only limited numbers of references are available dealing with the corrosion inhibition effect of alanine on iron. The present work was undertaken to investigate the corrosion inhibition behavior of alanine on iron in 1.0 M HCl solution. The experimental techniques used are potentiodynamic polarization and electrochemical impedance spectroscopy, EIS measurements.

2. EXPERIMENTAL PROCEDURE

All chemicals used were of AR grade and purchased from Aldrich chemical company. Corrosion tests have been carried out on electrodes cut from sheets of mild steel. Steel strips containing 0.07% P, 0.36% Si, 0.01% Al, 0.04% Mn, 0.20% C, 0.06% S and the remainder iron were used for the measurement of electrochemical studies. The surface preparation of the specimens was carried out using emery paper Nos. 600 and 1200, they were degreased with ethanol under ultrasound and dried at room temperature before use. The solutions (1.0 M HCl) were prepared by dilution of an analytical reagent grade 37% HCl with doubly distilled water.

The electrochemical cell used has been described in a previous paper [19, 20]. The reference electrode was a saturated calomel electrode. All the reported potential values are referred to this type of electrode. Polarization experiments were carried out under stirred conditions with a fine Luggin capillary to avoid ohmic polarisation. The procedure adopted for the polarization measurements was the same as described elsewhere [19].

The electrode potential was allowed to stabilize 60 minutes before starting the measurements. All experiments were conducted at 25 ± 1 °C. Measurements were performed using Gamry Instrument Potentiostat/Galvanostat/ZRA. This includes a Gamry Framework system based on the ESA400, Gamry applications that include dc105 for dc corrosion measurements, EIS300 for electrochemical impedance spectroscopy measurements along with a computer for collecting data. Echem Analyst 5.58 software was used for modeling, plotting, graphing and fitting data.

Tafel polarization curves were obtained by changing the electrode potential automatically from (-800 to -100 mV_{SCE}) at open circuit potential with scan rate of 1.0 m V s^{-1}. Impedance measurements were carried out in frequency range from 10 kHz to 40.0 mHz with an amplitude of 10 mV_{SCE} peak-to-peak using ac signals at open circuit potential.

Alanine compound studied was put in the 1.0 M HCl at concentration of $5 \cdot 10^{-6}$ M, 10^{-5} M, $5 \cdot 10^{-5}$ M, 10^{-4} M, $5 \cdot 10^{-4}$ M and 10^{-3} M.

3. COMPUTATIONAL DETAILS

An adsorption phenomenon is of a key importance in understanding corrosion problems. Monte Carlo simulation techniques help in finding the preferential adsorption sites on iron surface through finding the low-energy adsorption sites or to investigate the preferential adsorption of mixtures of adsorbate components on iron surface. Materials studio 6.0, distributed by Accelrys, Inc. [21] has been used to build alanine molecule, iron surface and solvent molecules (water molecules). Molecular mechanics (force field) tools are used to investigate the simulated corrosion system. The key approximation in these studies that the potential energy surface, on which the atomic nuclei move, is represented by a classical force field, which are developed by parameterising data from experiments and high level quantum mechanical calculations. COMPASS force field stands for condensed-phase optimised molecular potentials for atomistic simulation studies [18], which is used to optimise the structures of all components of the corrosion system (iron substrate/solvent/inhibitor). It is the first ab initio force field that enables accurate and simultaneous prediction of chemical properties (structural, conformational, vibrational, etc.) and condensed-phase properties (equation of state, cohesive energies, etc.) for a broad range of chemical systems. It is also the first high-quality force field to consolidate parameters of organic and inorganic materials. The first step in this computational study is the preparation of a model of molecules, which will adsorb on the surface with optimised geometry (i.e. energy minimised). Among the different steps involved in the modelling approach is the construction of the iron surface from the pure crystal, the addition of the alanine molecule near to the surface, the definition of the potentials (i.e. the force field) to study the liquid–solid interaction, followed by the geometry optimization calculation.

This particular case, the use of molecular mechanics can be seen as a precursor to computationally more expensive quantum mechanical methods: Once the model has been optimised with suitable force field (COMPASS), we will be able to simulate a substrate (iron surface) loaded with an adsorbate (alanine molecules), taking into consideration the solvent effect. This computational study aims to find low-energy adsorption sites to investigate the preferential adsorption of alanine molecule on iron surface aiming to find a relationship between the effect of its molecular structure and its inhibition efficiency. To build iron surface, amorphous cell module has been used to create solvent/alanine cell on iron surface. The behaviour of the alanine on the surface was studied using molecular dynamics simulations and the COMPASS force field. The MD simulation of the interaction between the alanine molecule dissolved in H_2O and the iron surface (111) was carried out in a simulation box (3.0 ×3.0 ×2.1 nm) with periodic boundary conditions in order to simulate a representative part of an interface devoid of any arbitrary boundary effects. A cut off distance of 1.0 nm with a spline switching function was applied for the non-bond interactions, i.e. for coulombic, van der Waals and hydrogen bond interactions. The cut off used to select the spline width, which specifies the size of the region within which nonbond interactions are splined from their full value to zero. For the actual computation of this interaction, energy charge groups are used. Cut off distance specifies the distance at which to exclude interactions from the nonbond list. The iron crystal is cleaved along with the (111) plane, thus representing the iron surface. For the MD simulation, all the spatial positions of the iron atoms in the simulation box are fixed because the thermal vibrations of the interaction with an adsorbed molecule and not in the physical behaviour of the crystal itself. The MD simulation simulates a substrate loaded with an adsorbate. A low-energy adsorption site is identified by carrying out a Monte Carlo search of the configurational space of the substrate–adsorbate system as the temperature is slowly decreased. This process is repeated to identify further local energy minima. During the course of the simulation, adsorbate molecule are randomly rotated and translated around the substrate. The configuration that results from one of these steps is accepted or rejected according to the selection rules of the Metropolis Monte Carlo method [22]. The force field used is COMPASS, charge is force field assigned, quality is fine and summation method is group- and atom based. All structures used in this study are minimised in order to ensure that the energy results used in calculating the adsorption energy are accurate; it is critically important that when we optimise the structures, we use the same energy minimization settings as we intend to use for calculating the adsorption energy of alanine. This includes not only the force field, atomic charges, and non-bond summation methods but also the quality of the energy and geometry optimization calculations and the convergence tolerances used for the minimization. Quantum chemical calculations carried out using Dewar’s linear combinations of atomic orbitals–self-consistent field–molecular orbital (LCAO–SCF–MO) [23]. We used PM3 semi-empirical method in commercially available quantum chemical software Hyperchem, release 8.06 [24]. A full optimization of all geometrical variables without any symmetry constraint was performed at the restricted Hartree–Fock level. It develops the molecular orbitals on a valence basis set and also calculates electronic properties and the optimised geometries of the alanine molecules. As an optimization procedure, the built-in Polak–Ribiere algorithm was used [25].

4. RESULTS AND DISCUSSIONS

4.1 Molecular level Study:

4.1.1 Simulated annealing

The simulated annealing task in performed in this study enables us to simulate a substrate, Fe (111) loaded with a set number of adsorbate molecules (alanines). Low energy adsorption sites are identified by repeatedly searching the configurational space of the substrate-adsorbate system as the temperature is slowly decreased and then reset to the maximum through a number of temperature cycles. Alanine molecules are confined to a defined adsorption region in the vicinity of the substrate such that the number of alanine molecules on the surface does not change. The Metropolis Monte Carlo method is used to search for adsorption configurations. In this method, only the positions and orientations of the alanine molecules are sampled; each conformation is treated as a rigid body. The Metropolis method assumes that the alanine molecules do not have a high degree of torsional flexibility and ignores any internal degrees of freedom that the alanine molecules may possess on the iron surface.

Geometry optimization is based on reducing the magnitude of calculated force until they become smaller than defined convergence tolerances. The forces on an atom are calculated from the potential energy expression and will, therefore, depend on the forcefield that is selected. Geometry optimization is carried out for the studied system using an iterative process in which the atomic coordinates are adjusted until the total energy of a structure is minimized, i.e., it corresponds to a local minimum in the potential energy surface.

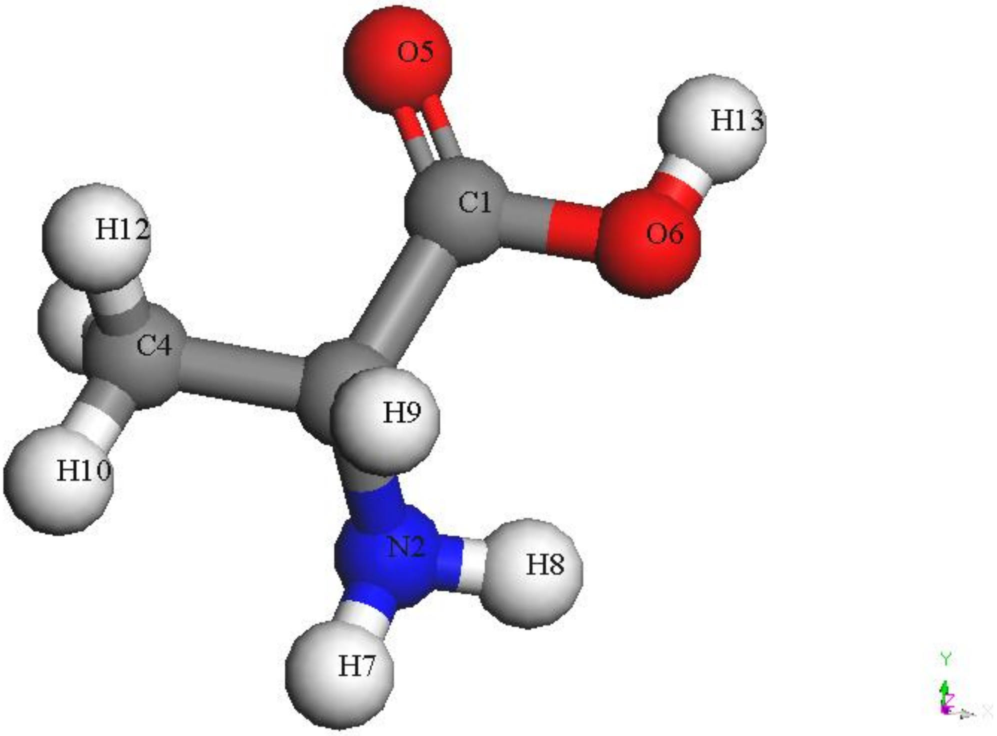

Figure 1. Geometry optimized structure of alanine molecule.

The following algorithms which are available in Materials Studio software include (Steepest descent, Polak-Ribiere variant only, Quasi-Newton, Adjusted basis set Newton-Raphson, Smart) are used for geometry optimization. Different algorithms are better suited to certain circumstances, for example if the structure is far from equilibrium, it is best to use steepest descent. It is, therefore, often beneficial to combine algorithms in a cascade, such that, as the potential minimum is approached, a more appropriate method is used. The Smart algorithm is a cascade of the steepest descent, ABNR, and quasi-Newton methods. Figure 1 shows the geometry optimized structured for alanine molecule.

4.1.2 Metropolis Monte Carlo method

Using the Adsorption locator simulation module distributed by Accelrys, the alanine molecule – iron (111) configuration are sampled from a canonical ensemble. In the canonical ensemble, the loading of all alanine molecules on the iron (111) substrate, as well as the temperature, are fixed.

The probability of a configuration, *m*, in the canonical ensemble is given by equation 1[26]:

$$P_m = C\ \mathrm{e}^{-\beta \mathrm{E_m}} \qquad (1)$$

where *C* is an arbitrary normalization constant, *β* is the reciprocal temperature, and E_m is the total energy of configuration m.

The reciprocal temperature is given by:

$$\beta = \frac{1}{k_B T} \qquad (2)$$

where k_B is the Boltzmann constant and *T* is the absolute temperature.

The total energy of configuration m is calculated according to the following sum:

$$E_m = E_m^{AA} + E_m^{AS} + U_m^{A} \qquad (3)$$

where E_m^{AA} is the intermolecular energy between the alanine molecules, E_m^{AS} is the interaction energy between the alanine molecules and the iron (111), and U_m^{A} is the total intramolecular energy of the alanine molecules. The intramolecular energy of the alanine is not included as its structure is fixed throughout the simulation; thus, this energy contribution is fixed and vanishes, since only energy differences play a role in Adsorption Locator calculations.

The total intramolecular energy, U^A, is the sum of the intramolecular energy of all adsorbates of all components:

$$U^A = \sum_{\{N\}_m} u_{\mathrm{int}ra} \qquad (4)$$

Where $\{N\}_m$ denotes the set of adsorbate loadings of all components in configuration m.

An Adsorption Locator simulation always starts with a clean substrate. The first stage is to adsorb the specified number of alanine molecules. This is accomplished by a random series of insertion steps and equilibration moves (only moves that do not change the loading are permitted) until the specified loading has been reached. During this stage, only insertion steps that do not create structures with intermolecular close contacts and that pass all adsorbate location constraints are accepted.

The starting configuration will take several steps to adjust to the current temperature. A simulation is, therefore, separated into an equilibration and a production stage. The properties returned at the end of the run are based on the production stage only.

In the equilibration and production stages of an Adsorption Locator simulation, each step starts with the selection of a step type using the weights set at the start of the run. The step type can be either a translation or a rotation. After a step type is selected, a random component is chosen and the step type is applied to a random adsorbate of that component. The Metropolis Monte Carlo method is then used to decide whether to accept or reject the change.

The Metropolis Monte Carlo method in Adsorption Locator provides four step types for a canonical ensemble: conformer, rotation, translation, and regrowth[27].

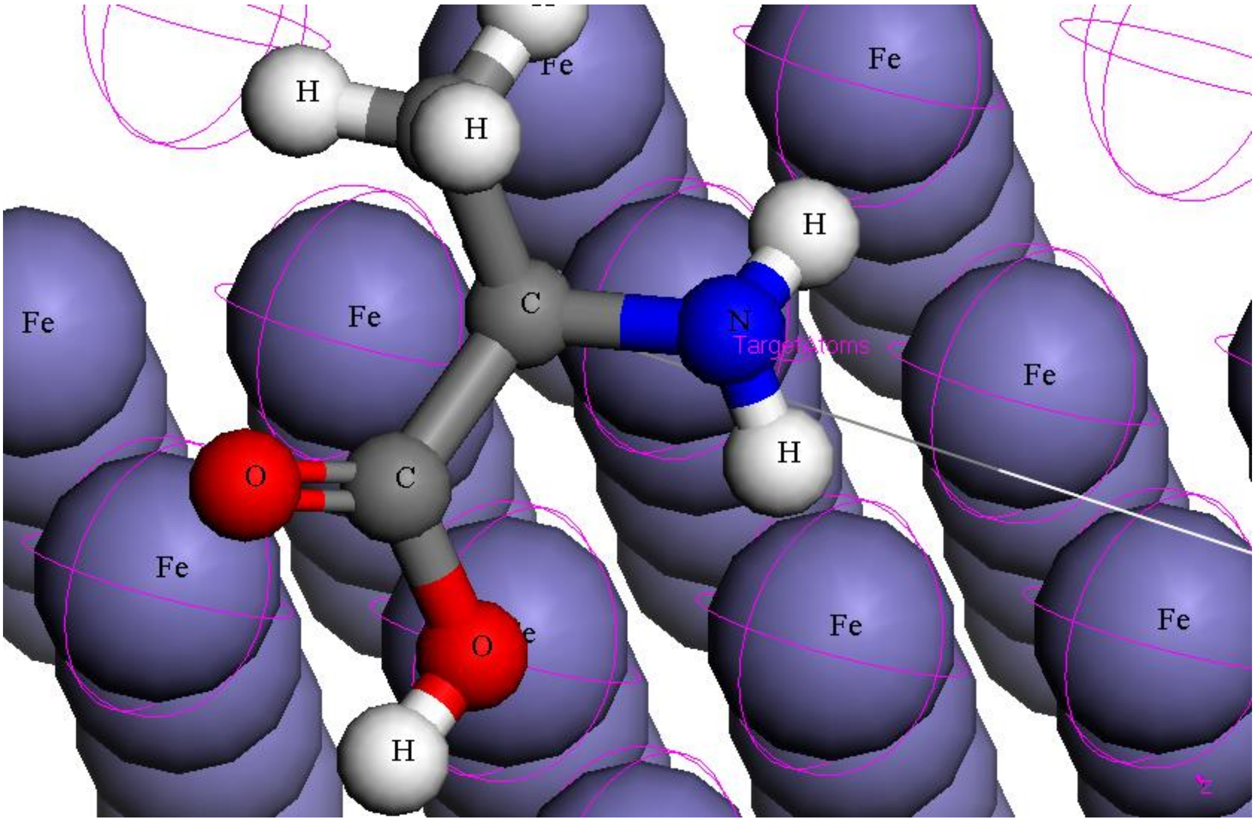

Figure 2. Most suitable configuration for adsorption of alanine on Fe(111) substrate obtained by adsorption locator module[22, 28, 29]

Figure 2 shows the most suitable alanine conformation adsorbed on Fe(111) substrate obtained by adsorption locator module[22, 28, 29]. The adsorption density of alanine on the Fe(111) substare has been presented in Fig. 3. As can be seen from Figs. 2 and 3 that alanine molecule shows ability to adsorb on Fe surface. Also, it has high binding energy to Fe surface as seen in Table 1.

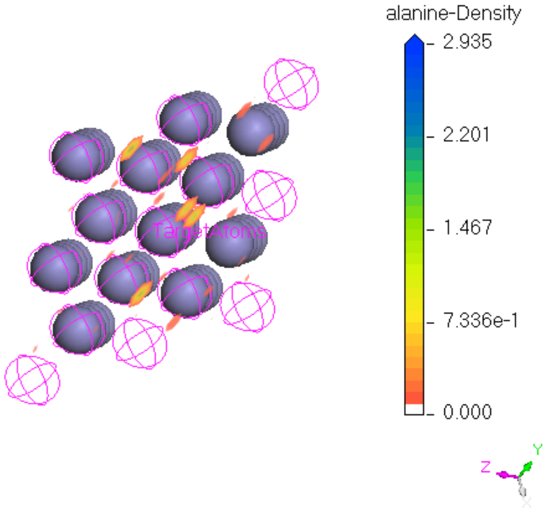

Figure 3. Adsorption density field of alanine on the Fe (1 1 1) substrate.

Table 1. The outputs and descriptors calculated by the Monte Carlo simulation of alanine conformations on iron (111) surface.

Structures	Total energy	Adsorption energy	Rigid adsorption energy	Deformation energy	alanine : dE_{ad}/dN_i	Calculated binding energy / kcal mol^{-1}
Fe (1 1 1) – 1	-30.788	-51.044	-51.584	0.539	-51.04	148.67
Fe (1 1 1) – 2	-28.612	-48.868	-49.202	0.334	-48.868	143.54
Fe (1 1 1) – 3	-28.3754	-48.631	-48.766	0.1346	-48.6314	140.91
Fe (1 1 1) – 4	-27.4801	-47.7361	-49.551	1.8158	-47.7361	138.34
Fe (1 1 1) – 5	-27.1520	-47.408	-48.377	0.9691	-47.408	126.56
Fe (1 1 1) – 6	-26.8982	-47.154	-47.4238	0.2695	-47.154	122.12
Fe (1 1 1) – 7	-26.427	-46.683	-47.1268	0.4431	-46.683	116.23
Fe (1 1 1) – 8	-26.150	-46.406	-47.120	0.71349	-46.4068	111.4
Fe (1 1 1) – 9	-25.1556	-45.411	-45.928	0.51654	-45.411	108.71

The outputs and descriptors calculated by the Monte Carlo simulation are presented in Table 1. The parameters presented in Table 1 include total energy, in kcal mol^{-1}, of the substrate–adsorbate configuration. The total energy is defined as the sum of the energies of the adsorbate components, the rigid adsorption energy and the deformation energy. In this study, the substrate energy (iron surface) is taken as zero. In addition, adsorption energy in kcal mol^{-1}, reports energy released (or required) when the relaxed adsorbate components (alanine in H_2O) are adsorbed on the substrate. The adsorption energy is defined as the sum of the rigid adsorption energy and the deformation energy for the adsorbate components. The rigid adsorption energy reports the energy, in kcal mol^{-1}, released (or required) when the unrelaxed adsorbate components (i.e., before the geometry optimization step) are adsorbed on the substrate. The deformation energy reports the energy, in kcal mol^{-1}, released when the adsorbed adsorbate components are relaxed on the substrate surface. Table1 shows also (dEads/dNi), which reports the energy, in kcal mol^{-1}, of substrate–adsorbate configurations where one of the adsorbate components has been removed. The binding energy introduced in Table 1 calculated from equation 5

$$E_{\text{binding}} = E_{\text{total}} - (E_{\text{surface}} + E_{\text{inhibitor}}) \qquad (5)$$

Where E_{total} is the total energy of the surface and inhibitor, E_{surface} is the energy of the Fe (111) surface without the inhibitor, and $E_{\text{inhibitor}}$ is the energy of the inhibitor without the surface.

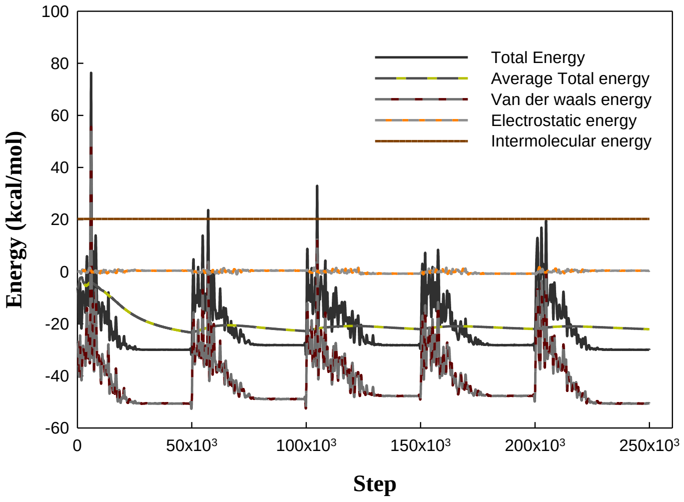

Figure 4. Total energy distribution of adsorbate (alanine)- adsorbent (iron) system.

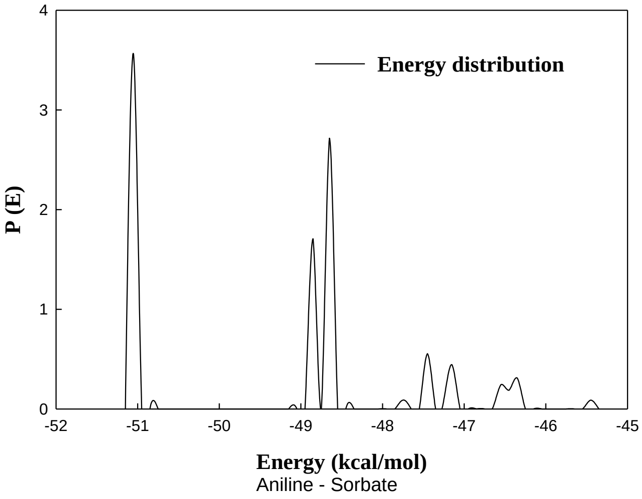

Figure 5. The adsorption energy distribution of the adsorbate (alanine molecules) on iron (111) surface.

Figure 4 and Fig. 5 show the total energy and adsorption energy distribution of the alanine molecules on Fe (1 1 1), respectively. As can be seen in Fig. 5, the adsorption energy of alanine reaches (-51.0 Kcal mole^{-1}) which shows the adsorption power for alanine molecules on iron (111) surface.

4.2 Experimental study

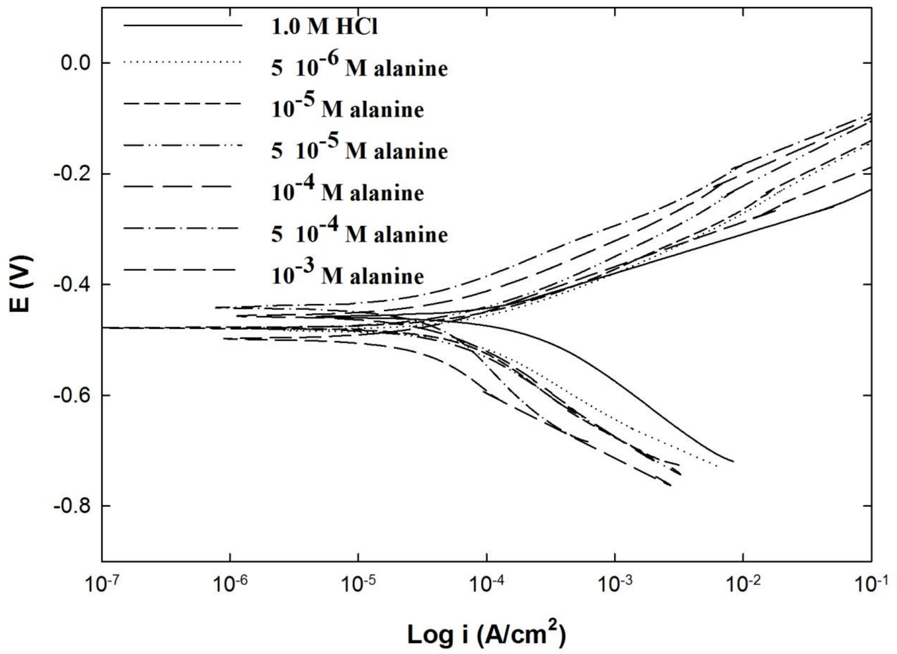

Figure 6. Anodic and cathodic polarization curves for iron in 1.0 M H Cl solutions in the absence and presence of various concentrations of alanine at 25 ± 1 °C.

Table 2. Electrochemical kinetic parameters, inhibition efficiencies (E_{pot}%) and rates of corrosion associated with Tafel polarization measurements recorded for iron in 1.0 M HCl solutions without and with various concentrations of alanine at 25 ± 1 °C.

Concentration /M	b_a V.dec^{-1}	$-b_c$ /V.dec^{-1}	i_{corr} /μA.cm^{-2}	$-E_{corr}$/mV	C.R / mpy	E_{pot}%
blank	81.8	139.6	119	458	54.59	----
$5 \cdot 10^{-6}$	101.6	147.3	84.8	483	38.73	**28.73**
10^{-5}	99.9	180.1	73.8	478	33.73	**37.98**
$5 \cdot 10^{-5}$	109.8	165.5	59.6	479	27.22	**49.96**
10^{-4}	105.6	167.7	46.6	459	21.28	**60.84**
$5 \cdot 10^{-4}$	101.5	217.5	34.3	441	15.68	**71.17**
10^{-3}	83.1	156.1	27.5	498	12.55	**76.89**

The potentiodynamic profiles of mild steel electrode in 1.0 M HCl, recorded in the absence and the presence of different concentration of alanine are shown in Fig. 6. Figure 6 shows that the addition of alanine to the acid solution shifts the anodic polarization to more positive and the cathodic polarization to more negative values. Values of the electrochemical parameters and the percentage inhibition efficiency E_{pot} % are given in Table 2.

The inhibition efficiency $E_{pot}\%$ are given from the equation 6[30]:

$$E_{pot}\% = 1 - \frac{i_{corr}}{i^{o}_{corr}} \times 100 \qquad (6)$$

Where $i_{corr} = i_{corr} / A$: A is the exposed surface area and i^{o}_{corr}, i_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of Tafel lines. The values of i_{corr} decreases with increasing concentration, the decrease in i_{corr} is associated with a shift in E_{corr} to more negative values. These results suggest that alanine behaves as a mixed-type inhibitor. The approximately constant values of the Tafel slopes (near 0.09 V.dec-1 for b_a and 0.13 V.dec-1 for b_c suggest that inhibition mechanism for alanine involves a single reaction site blocking [31, 32].

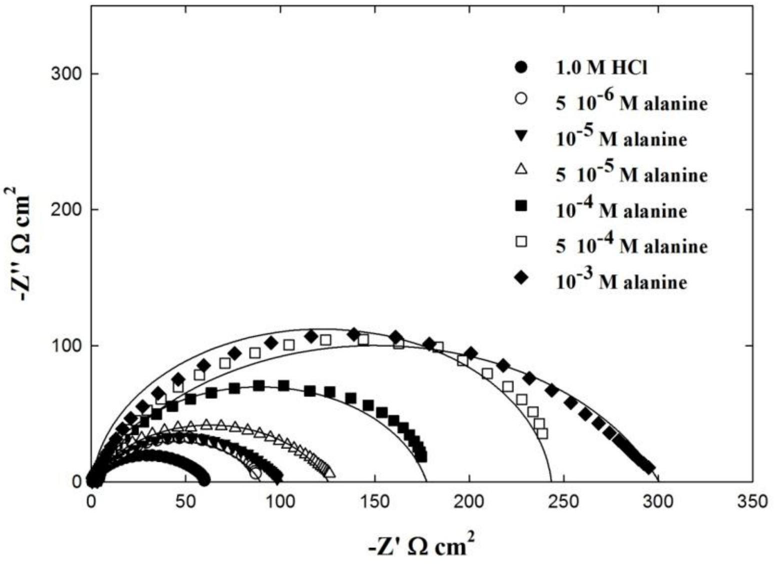

Figure 7. Nyquist plots for iron in 1.0 M HCl solutions in the absence and presence of various concentrations of alanine at 25 ± 1 °C, solid line represent fitted data obtained by equivalent circuit in Fig. 8.

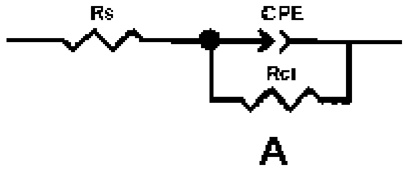

Figure 8. Equivalent circuit model for iron /1.0 M HCl interface.

Figure 7 shows the Nyquist plots of mild steel in 1 M HCl without and with various concentrations of alanine ($5\cdot10^{-6}$ M - 10^{-3} M) at 25± 1 °C. The impedance diagrams obtained are not perfect semicircles and this difference has been attributed to frequency dispersion [33]. The charge transfer resistance R_{ct} is calculated from the difference in impedance at lower and higher frequencies, as suggested by Harnyama and Tsuru [34]. From the charge transfer resistance we can calculate the inhibition efficiency of the corrosion of steel, as in equation 7[35].

$$E_{imp}\% = \frac{1/R_{ct}^{o} - 1/R_{ct}}{1/R_{ct}^{o}} \times 100 \qquad (7)$$

where R_{ct}^{o} and R_{ct} are the charge transfer resistance values without and with alanine, respectively. The impedance parameters derived from this investigation are given in Table 3. The equivalent circuit model used to fit the experimental results is suggested in Fig. 8, the suggested model is used to generate a simulated data, which is fitted well with experimental data as shown in Fig. 7.

Table 3. Electrochemical parameters calculated from EIS measurements for iron electrode in 1.0 M HCl solutions without and with various concentrations of alanine at 25 ± 1 °C using equivalent circuit in Fig. 8

Concentration /M	R_{ct} / Ω cm^2	R_s / Ω cm^2	$CPE \times 10^6$ / S s^n	n	E_{imp}%
blank	63	0.4	20	0.74	----
$5\cdot10^{-6}$	89	0.6	19	0.76	**29.21**
10^{-5}	100.8	0.56	16	0.78	**37.50**
$5\cdot10^{-5}$	125	0.46	15	0.81	**49.60**
10^{-4}	177	0.64	13	0.83	**64.41**
$5\cdot10^{-4}$	243	0.71	12	0.95	**74.07**
10^{-3}	300	0.82	10	0.81	**79.0**

4.3 Mechanism of adsorption

Two main types of interaction can describe the adsorption of alanine on iron surface in acid medium: physical adsorption and chemisorption. Physical adsorption is the result of electrostatic attractive forces between the cationic form of alanine and the electrically charged iron (negative charge due to the adsorption of chloride ion on iron) surface. Chemisorption process involves charge sharing or charge transfer from the lone pairs of electrons in the alanine to the vacant d-orbital in the iron surface to form a coordinate type of bond. This is possible in case of a positive as well as a negative charge of the surface. The presence of oxide layer on the iron surface encourage the adsorption of the alanine molecules on the iron surface via H-bonding. Adsorption in this case is assisted by hydrogen bond formation between alanine and oxidized surface species.

5. CONCLUSIONS

Computational studies help to find the most stable inhibitor conformation and adsorption sites for a broad range of materials. This information can help to gain further insight about corrosion system, such as the most likely point of attack for corrosion on a surface, the most stable site for inhibitor adsorption , adsorption density of the inhibitor and the binding energy of the adsorbed layer. Tafel polarization studies have shown that the alanine molecules suppresses both anodic and cathodic process and thus acts as mixed-type inhibitor. The results of impedance indicate that the value of both charge transfer resistance and inhibition efficiency tend to increase by increasing the alanine concentration.

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