Corrosion Inhibition of Carbon Steel by Cationic Surfactants in 0.5 M HCl Solution

A.S. Fouda^{*}, Y.A. Elewady, H.K. Abd El-Aziz

Chemistry Department, Faculty of Science, El -Mansoura University

El-Mansoura-35516, Egypt

asfouda@mans.edu.eg

Abstract-The corrosion inhibition effect of cationic surfactants, namely cetyl trimethyl ammonium bromide: CTAB and dodecyl trimethyl ammonium chloride: DTAC, have been used as corrosion inhibitors for 1037 C-steel in 0.5 M HCl. The inhibition efficiency has been determined by weight loss and electrochemical measurements. The results show that the order of inhibition efficiency is CTAB > DTAC. Polarization curves indicate that all investigated surfactants are mixed inhibitors. Adsorption of these surfactants was in agreement with the Langmuir adsorption isotherm. The density function theory (DFT) was used to study the structural properties of the surfactants. The inhibition efficiencies of cationic surfactants showed a certain relationship to Pearson HSAB principle and Fukui indices.

Keywords-Carbon Steel; Electrochemical Calculations; DFT; Acid Corrosion

I INTRODUCTION

In oil fields, hydrochloric acid solution is recommended as the cheapest way to dissolve calcium carbonate, CaCO₃, scale inside the pipelines under most conditions. Accordingly, corrosion inhibitors (usually surfactants) must be injected with the hydrochloric acid solution to avoid the destructive effect of acid on the surface of the pipe lines [1]. C-steel has been widely employed as a construction materials for pipe work in the oil and gas production such as down hole tubular, flow lines and transmission pipelines [2]. Surfactants are compounds that can be found in a multitude of domains, from industrial settings to research laboratories and are the part of our daily lives. The surfactant inhibitors have many advantages such as high inhibition efficiency, low price, low toxicity and easy production [3]. An increase in inhibitory action was observed when the concentration of the surfactant in the corrosive solution approaches the critical micelle concentration (CMC). Above this value, there was no further increase in the efficiency that remains constant for further increase in surfactant concentration. In the absence of a charged head group, the driving force of micellization is the hydrophobic force and van der Waals attractions. The strong interaction between water molecules repels the hydrocarbon chain from the water bulk phase. This drives the surfactants to form aggregates where the hydrophilic head groups conceal the hydrocarbon chains. It has been observed that the adsorption of these inhibitors depends on the physicochemical properties of the functional groups and the electron density at the donor atom. The adsorption occurs due to the interaction of the lone pair and/or π -orbitals of inhibitor with d-orbitals of the metal surface atoms, which evokes a greater adsorption of the inhibitor molecules onto the surface, leading to the formation of a corrosion protection film [4–6]. The adsorption is also influenced by the structure and the charge of metal surface, and the type of testing electrolyte [7–9]. Recently, quantum chemical methods have already proven to

be very useful in determining the molecular structure as well as elucidating the electronic structure and reactivity [10]. Thus, it has become a common practice to carry out quantum chemical calculations in corrosion inhibition studies. The concept of assessing the efficiency of a corrosion inhibitor with the help of computational chemistry is to search for compounds with desired properties using chemical intuition and experience into a mathematically quantified and computerized form. Once a correlation between the structure and activity or property is found, any number of compounds, including those not yet synthesized, can be readily screened employing computational methodology [11] and a set of mathematical equations which are capable of representing accurately the chemical phenomenon under study [12,13].

The aim of the present paper is to obtain information on the level of corrosion activity in a system, using the chemical and the electrochemical techniques. These data are used to evaluate the effectiveness of the investigated surfactants as corrosion inhibitors. Another objective in this work is to calculate the more relevant molecular properties on its action as corrosion inhibitors. The local reactivity has been analyzed by means of the Fukui indices, since they indicate the reactive regions, in the form of the nucleophilic and electrophilic behavior of each atom in the molecule.

II EXPERIMENTAL

A. Chemicals and Materials

Hydrochloric acid (37 %), ethyl alcohol and acetone were purchased from Algamhoria Co.(Egypt). Cetyl trimethyl ammonium bromide: CTAB ($C_{16}H_{33}N(CH_3)_3$ -Br) and dodecyl trimethyl ammonium chloride: DTAC ($C_{12}H_{25}N(CH_3)_3$ -Cl) were obtained from Aldrich Chemical Company. The molecular structures of CTAB and DTAC are shown in Table 1. Bidistilled water was used for preparing test solutions for all measurements.

Surfac tant	Mol. formula	Str. formula	Mol. Wt.
СТАВ	Br' -N'-	C ₁₆ H ₃₃ N(CH ₃) ₃ -Br	364.4 5
DTAC	Cr	C ₁₂ H ₂₅ N(CH ₃) ₃ -Cl	263.8 9

TableI MOLECULAR STRUCTURE OF CTAB AND DTAC

B. Methods

1) Weight loss Measurements:

Rectangular specimens of C-steel with dimensions 2.0 cm x 2.0 cm x 0.2 cm were mechanically abrading with 80, 220, 400, 600, 1000, 1200 grades of emery paper and degreased with acetone, rinsed with distilled water two times and finally dried between filter paper. After weighting accurately, the specimens were immersed in 100 ml of 0.5 M HCl with and without different concentration of surfactants at 30° C. After different immersion time (30, 60, 90, 120, 150 and 180 min), the C-steel samples were taken out, washed with distilled water then dried and weighted accurately.

The weight loss values are used to calculate the corrosion rate (R) in mm per year by the relation:

$$R = \frac{Wt \log \times 8.75 \times 10^4}{D \times A \times T}$$
(1)

where Wt loss is weight loss in g , D is alloy density in g/cm3 , A is exposed area in cm2, T is exposure time in hr.

The inhibition efficiency (YW %) and the degree of surface coverage (Θ) was calculated from:

$$Y_{\rm w}\% = \frac{R^* \cdot R}{R^*} \times 100 = \theta \ x \ 100$$
(2)

where R^* and R are the corrosion rates of carbon steel in the absence and in the presence of inhibitor, respectively.

2) Electrochemical Measurement:

Three electrochemical techniques, namely potentiodynamic polarization, electrochemical impedance spectroscopy (EIS), and electrochemical frequency modulation (EFM), were used to study the corrosion behavior. All experiments were conducted in a conventional three electrodes glass cell. Platinum sheet as counter electrode and saturated calomel as reference electrode were used in this study. The C-steel specimen was machined in to rectangular (1.0 cm x 1.0 cm x 0.3 cm) and sealed with epoxy resin leaving a working area of 1.0 cm^2 . The specimens were abraded, degreased and rinsed as described in weight loss measurements.

Potentiodynamic polarization experiments were carried out using a Volta Lab PGZ 100 system connected to personal computer with Volta Master 4 version7.08 software for calculation. Volta Master 4 calculates and displays Ecorr, icorr, βa , βc and the corrosion rate (R). All the experiments were carried out at temperature ($30 \pm 1 \circ C$). Equilibrium time leading to steady state of the specimens was 30 min and the open circuit potential (OCP) was noted. The potentiodynamic curves were recorded from - 900 to - 200 mV at a scan rate 2 mV S-1.

The corrosion rate is calculated from the following equation [14]:

$$R = \frac{i \operatorname{corr} \times A \times M}{D \times V} \times 3270$$
(3)

where icorr. is the corrosion current density, M is the atomic mass of Fe and V is the valence entered in the Tafel dialogue box.

The YP% was calculated from:

$$Y_{\rm P}\% = \frac{i_{\rm corr}^0 - i_{\rm corr}}{i_{\rm corr}^0} \times 100$$
(4)

where i_{corr}^{v} and i_{corr} are the corrosion current densities of uninhibited and inhibited solution, respectively.

Electrochemical impedance spectroscopy (EIS) and electrochemical frequency modulation (EFM) experiments were carried out using Gamry Instrument Series G 750^{TM} Potentiostat/Galvanostat/ZRA with a Gamry framework system based on ESA400. Gamry applications include software EIS300 for EIS measurements, and EFM140 to calculate the corrosion current density and the Tafel constants for EFM measurements. A computer was used for collecting data. Echem Analyst 5.5 Software was used for plotting, graphing and fitting data. EIS measurements were carried out in a frequency range of 100 kHz to 100 mHz with amplitude of 5 mV peak-to-peak using ac signals at respective corrosion potential. EFM carried out using two frequencies 0.2 and 0.5 Hz and a perturbation signal with amplitude of 10 mV.

3) Quantum Chemical Calculation:

Highest occupied molecular orbital energy (EHOMO), lowest unoccupied molecular orbital energy (ELUMO) and Fukui indices calculations were performed using Materials Studio DMol3 version 4.4.0 [15,16], a high quality quantum mechanics computer program (available from Accelrys Inc., San Diego, CA). These calculations employed an ab initio, gradient-corrected functional (GGA) method with a double numeric plus polarization (DNP) basis set and a Becke One Parameter (BOP) functional.

It is well-known that the phenomena of electrochemical corrosion appear in aqueous phase. For this reason, it is necessary to include, solvent effect in the computational calculations. In a similar way, it is important to take into account the effects that can appear as much in the geometric properties as in the electrical ones. DMol3 includes certain COSMO1 [17] controls, which allow for the treatment of solvation effects.

III RESULTS AND DISCUSSION

A. Weight loss Measurements

Fig. 1 shows the weight loss-time curves for the corrosion of C-steel in 0.5 M HCl in the absence and presence of different concentrations of CTAB (DTAC not shown). The data of Table 2 shows that, the dependence of YW% on varying concentration of surfactants (DTAC and CTAB) in the range from 0.04 m mol 1-1 to 0.8 m mol 1-1. It is clear that; at constant temperature the inhibition efficiency increases with increasing the concentration of the surfactant. The lowest corrosion rate is obtained by CTAB therefore YW% tends to decrease in the following order: CTAB > DTAC. The inhibition action of surfactants in HCl cannot be simply considered as an electrostatic adsorption [18] and covalent bonding chemisorption .This action was attributed to the effect of bromide ion of CTAB, chloride ion of DATC, chloride ion of acid solution and chemisorption of C16H33N+ (CH3)3 and C12H25N+ (CH3)3. In addition, other factors such as CMC and structure of surfactant might be affecting the inhibition efficiency.

B. Electrochemical measurements

1) Potentiodynamic polarization measurements:

JCST Vol.1 Iss.2 2012 PP.45-53 www.sjcst.org (C) World Academic Publishing



Fig.1 Weight loss-time curves of C-steel in 0.5 M HCl in the absence and presence of different concentrations of CTAB at 30 °C.

TableII	DAT A OF WEIGHT LOSS MEASUREMENTS FOR C-STEEL IN
	0.5 M HCL SOLUTION IN THE ABSENCE AND PRESENCE OF
	DIFFERENT CONCENTRATIONS OF SURFACT ANTS AT 30°C.

Compou nd	Conc., M	R (mmy ⁻ 1)	θ	Yw%
Blank	0.00	2.68	0.000	00.0
	4.0x10 ⁻⁵	0.80	0.700	70.0
	8.0x10 ⁻⁵	0.56	0.791	79.1
AC	2.0x10 ⁻⁴	0.39	0.854	85.4
DT/	4.0x10 ⁻⁴	0.35	0.869	86.9
	6.0x10 ⁻⁴	0.22	0.918	91.8
	8.0x10 ⁻⁴	0.19	0.929	92.9
	4.0x10 ⁻⁵	0.54	0.799	79.9
	8.0x10 ⁻⁵	0.29	0.892	89.2
AB	2.0x10 ⁻⁴	0.20	0.925	92.5
Ċ	4.0x10 ⁻⁴	0.14	0.948	94.8
	6.0x10 ⁻⁴	0.12	0.955	95.5
	0 0 1 0 1	0.00	0.0.11	



Fig. 2 Potentiodynamic polarization for corrosion of C-steel in 0.5 M HCl in the absence and presence of different concentrations of CTAB at 30°C.

The otentiodynamic curves for C-steel in 0.5 M HCl in the absence and presence of CTAB are shown in Fig. 2. Similar curves were obtained for DTAC (not shown). It is clear that;

the selected surfactants act as mixed type inhibitors; i.e., promoting retardation of both anodic dissolution of C-steel and cathodic hydrogen discharge reaction. The icorr values decrease with increasing inhibitor concentration for all inhibitor (Table 3). Both cathodic Tafel slopes (β c) and anodic Tafel slopes (β a) do not change remarkably. This indicates that the mechanism of the corrosion reaction does not change and the corrosion reaction is inhibited by simple adsorption mode [19] and the irregular trends of β a and β c values indicate the involvement of more than one type of species adsorbed on the metal surface. The IE values decrease as follows (Table 3): CTAB > DTAC. Generally, the increase of the inhibitor concentration shifts corrosion potential into a less negative direction, what can be explained by a small domination of the anodic reaction inhibition.

FableIII P	POTENTIOD YNAMIC DATA OF C-STEEL IN 0.5 M HCL	AND
]	IN THE PRESENCE OF DIFFERENT CONCENTRATIONS	SOF
	SURFACT ANT S AT 30 °C.	

Co mp	Con c., M	E _{corr} , mV vs.S CE,	i _{ωrr} μAc m²	-βc, mV dec ⁻	β _a , mV dec ⁻	θ	Ү _Р %	R, mm y ⁻¹
Bla nk	0	529	515.6	69	54	0.000	00.0	5.976
	4.0x 10 ⁵	518	213.3	75	42	0.586	58.6	2.472
	8.0x 10 ⁵	502	130.9	78	39	0.746	74.6	1.517
DTAC	$\frac{2.0 \mathrm{x}}{10^4}$	477	87.2	82	39	0.831	83.1	1.010
	4.0x 10^4	472	85.1	79	46	0.835	83.5	0.994
	6.0x 10^4	452	82.3	89	45	0.840	84.0	0.954
	8.0x 10^4	446	69.8	80	45	0.865	86.5	0.809
	4.0x 10 ⁵	501	135.1	79	55	0.738	73.8	1566
	8.0x 10 ⁵	489	126.7	88	53	0.754	75.4	1468
AB	$\frac{2.0 \mathrm{x}}{10^4}$	478	86.4	67	44	0.833	83.3	1001
CT.	4.0x 10^4	472	79.2	65	43	0.846	84.6	918.5
	6.0x 10^4	470	71.5	64	42	0.861	86.1	828.4
	8.0x 10 ⁴	470	66.8	59	40	0.871	87.1	774.0

2) Electrochemical impedance spectroscopy:

The EIS provides important mechanistic and kinetic information for an electrochemical system under investigation. Nyquist impedance plots obtained for the C-steel electrode at respective corrosion potentials after 30 min immersion in 0.5 M HCl in presence and absence of various concentrations of CTAB is shown in Fig.3 (DTAC curves not shown). This diagram exhibits a single semi-circle shifted along the real impedance (Zr). The Nyquist plots of CTAB do not yield perfect semicircles as expected from the theory of EIS, the impedance loops measured are depressed semi-circles with their centers below the real axis, where the kind of phenomenon is known as the "dispersing effect" as a result of frequency dispersion [20] and mass transport resistant [21] as well as electrode surface heterogeneity resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous layers [22-26], etc. So one constant phase element (CPE) is substituted for the



Fig. 3 Nyquist plots for C-steel steel in 0.5 M HCl in the different concentrations of CTAB

TABLEIV EIS DATA OF C-STEEL IN 0.5 M HCL AND IN THE PRESENCE OF DIFFERENT CONCENTRATIONS OF SURFACTANTS AT 30 °C.

Compound	C _{inh} , M	R_{S} Ω cm ²	$\mu \Omega^{-1} \operatorname{s}^{n} \operatorname{cm}^{-2}$	n	R_{CT} $\Omega \text{ cm}^2$	C _{dl} µFcm ^{−2}	θ	%Y1
Blank	0.00	1.946	542.8	0.909	32.1	437	0.00	0.00
	4x10 ⁻⁵	1.711	113.1	0.864	187.5	79.4	0.829	829
	8x10 ⁻⁵	1.835	73.5	0.849	382.0	489	0.916	91.6
AC	2x10 ⁻⁴	1.794	57.7	0.840	535.3	40.2	0.940	94.0
DT	$4x10^{-4}$	1.826	55.3	0.824	637.0	37.2	0.949	94.9
	6x10 ⁻⁴	1.726	53.3	0.757	867.5	36.7	0.963	96.3
	8x10 ⁻⁴	1.473	52.7	0.738	1135.0	36.7	0.972	972
	4x10 ⁻⁵	1.902	80.8	0.871	424.4	61.7	0.924	92.4
	8x10 ⁻⁵	1.982	60.5	0.848	475.2	45.7	0.932	93.2
AF	2x10 ⁻⁴	2.234	55.5	0.820	559.9	41.8	0.943	94.3
CI	$4x10^{-4}$	1.935	38.3	0.781	664.0	27.7	0.952	95.2
	6x10 ⁻⁴	1.989	33.7	0.723	877.7	24.0	0.963	96.3
	8x10 ⁻⁴	1.556	30.4	0.693	1302.0	20.9	0.975	97.5

capacitive element, to explain the depression of the capacitance semi-circle, and give a more accurate fit. Impedance data are analyzed using the circuit in Fig.4; in which Rs represents the electrolyte resistance, Rct represents the charge-transfer resistance and the constant phase element (CPE). According to Hsu and Mansfeld [27], the correction of capacity to its real values is calculated from:

$$Cdl = Yo (\omega max)n 1$$
⁽⁵⁾

where Yo is the CPE coefficient, ω max is the frequency at which the imaginary part of impedance-(Zi) has a maximum [27] and n is the CPE exponent (phase shift).



Fig.4 Equivalent circuit model used to fit the impedance spectra

The data obtained from fitted spectra are listed in Table 4. The degree of surface coverage (θ) and inhibition efficiency

YI% were calculated from the EIS data by using following equation:

$$Y_{1}\% = \frac{R_{ct} - R_{ct}^{*}}{R_{ct}} \times 100 = \theta \times 100$$
(6)

where Rct and Rct*are the charge-transfer resistances with and without the inhibitors, respectively.

Data in Table 4 show that the Rs values are very small compared to the Rct values. Also, the Rct values increase and

the calculated Cdl values decrease by increasing the inhibitor concentrations, which causes an increase of θ and YI. The high Rct values are generally associated with slower corroding system [21]. The decrease in the Cdl suggests that surfactants molecules function by adsorption at the metal/solution interface [28].

The inhibition efficiencies, calculated from EIS results, show the same trend as those obtained from polarization measurements. The difference of inhibition efficiency from two methods may be attributed to the different surface status of the electrode in two measurements. EIS was performed at the rest potential, while in polarization measurements the electrode potential was polarized to high over potential, non-



Fig.5 Intermodulation spectra for C-steel in 0.5 M HCl in absence and presence of 8 x10⁴ M concentrations of DTAC and CTAB respectively

uniform current distributions, resulted from cell geometry, solution conductivity, counter and reference electrode placement, etc., will lead to the difference between the electrode area actually undergoing polarization and the total area [29].

3) Electrochemical Frequency modulation (EFM):

EFM is a nondestructive corrosion measurement like EIS; it is a small signal ac technique. Unlike EIS, however, two sine waves (at different frequencies) are applied to the cell simultaneously. The great strength of the EFM is the causality factors which serve as an internal check on the validity of the EFM measurement [30].With the causality factors, the experimental EFM data can be verified.

The results of EFM experiments are a spectrum of current response as a function of frequency. The spectrum is called the intermodulation spectrum. The spectra contain current responses assigned for harmonical and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (icorr), the Tafel slopes (β c and β a) and the causality factors (CF-2 and CF-3). Intermodulation

spectra obtained from EFM measurements are presented in Fig. 5 for 0.5 M HCl in absence and presence of 8x10-4 M of CTAB and DTAC respectively. Similar curves were obtained for other concentrations of inhibitors (not shown). Table 5 indicated that; the corrosion current densities decrease by increasing the concentrations of the studied inhibitors. The inhibition efficiencies, YEFM% calculated from Eq. (7) increase by increasing the studied inhibitor concentrations.

$$Y_{EFM} \% = \frac{i_{corr}^{0} - i_{corr}}{i_{corr}^{0}} \times 100$$
(7)

where: i0corr and icorr are corrosion current densities in the absence and presence of inhibitors, respectively.

The causality factors in Table 5 are very close to theoretical values which according to the EFM theory [31] should guarantee the validity of Tafel slopes and corrosion current densities.

4) Adsorption of surfactants:

JCST Vol.1 Iss.2 2012 PP.45-53 www.sjcst.org C World Academic Publishing

Table V ELECTROCHEMICAL KINETIC PARAMETERS OBTAINED BY EFM TECHNIQUE FOR C- STEEL THE ABSENCE AND IN PRESENCE OF VARIOUS CONCENTRATIONS OF SURFACTANTS IN 0.5 M HCL AT 30 °C

Compound	Conc., M	$i_{\rm orr}$ $\mu A \ \rm cm^{-2}$	β_c mVdec ⁻¹	$\beta_a \ m V dec^{-1}$	CF-2	CF-3	CR µmy ⁻¹	%Y _{EF} м
Blank	0.00	488.9	126	107	1.86	2.95	5763	0.00
	4x10 ⁻⁵	79.10	114	105	1.67	3.01	691	83.8
	8x10 ⁻⁵	42.46	114	106	1.55	3.13	493	91.3
AC	$2x10^{-4}$	41.03	132	113	1.91	2.69	476	91.61
DT	$4x10^{-4}$	30.79	130	115	2.01	2.77	357	93.7
	6x10 ⁻⁴	28.67	118	113	1.63	2.67	333	94.1
	8x10 ⁻⁴	27.85	150	134	1.91	2.60	323	94.3
	4x10 ⁻⁵	50.19	121	116	2.10	3.31	0.897	89.7
	8x10 ⁻⁵	41.46	121	112	2.2	3.20	0.915	91.5
AB	$2x10^{-4}$	32.34	139	104	1.91	2.80	0.934	93.4
CI	$4x10^{-4}$	29.65	127	109	2.09	2.71	0.939	93.9
	6x10 ⁻⁴	21.53	121	115	2.11	2.78	0.956	95.6
	8x10 ⁻⁴	18.66	1240	119	1.80	2.73	0.962	962

Adsorption of surfactants on solid surfaces can modify their hydrophobicity, surface charge, and other key properties that govern interfacial processes such as corrosion inhibition [32]. In general, adsorption is governed by a number of forces such as covalent bonding, electrostatic attraction, hydrogen bonding or non-polar interactions between the adsorbed species, lateral associative interaction, solvation, and desolvation [33]. The total adsorption is usually the cumulative result of some or all of the above forces [34].

Standard free energy of adsorption (- $\Delta G^{\circ}ads$) can be written as [33]:

$$\Delta G^{\circ}ads = \Delta G^{\circ}elec + \Delta G^{\circ}chem + \Delta G^{\circ}C - C + \Delta G^{\circ}C - S + \Delta G^{\circ}H + \Delta G^{\circ}H_2O + \dots$$
(8)

Where ΔG° elec is the electrostatic interaction term, ΔG° chem the chemical term due to covalent bonding, ΔG° C-C the free energy gained upon association of methyl groups in the hydrocarbon chain ΔG° C-S the free energy due to interactions between the hydrocarbon chains and hydrophobic sites on the solid ΔG° H the hydrogen bonding term and ΔG° H₂O is the term owing to dissolution or solvation of the adsorbate species or any species displaced from the interface due to adsorption.

5) Mechanism of Adsorption [35]:

The adsorption of ionic surfactants on oppositely charged surface could be taking the following path:

- At low surfactant concentrations, the adsorption is due to electrostatic interaction between individual isolated charged monomeric species and the oppositely charged solid surface.
- Surfactant species begin to form surface aggregates, colloids (surface colloids), including hemi-micelles, admicelles, etc., due to lateral interactions between hydrocarbon chains. Due to this additional driving force resulting from the lateral association with the electrostatic interaction still active
- When the solid surface is electrically neutralized by the adsorbed surfactant ions, the electrostatic attraction is no longer operative and adsorption takes place due to lateral attraction alone with a reduced slope.
- When the surfactant concentration reaches critical micelle concentration, the surfactant monomer activity

becomes constant and any further increase in concentration contributes only to the micellization in solution and it does not change the adsorption density. The adsorption in this region is mainly through lateral hydrophobic interaction between the hydrocarbon chains.

In steps 3 and 4, surfactant molecules adsorb with a reversed orientation (head groups facing the bulk solution) resulting in a decrease in the hydrophobicity of the particles in this region.

PH plays a very significant role in controlling adsorption of ionic surfactants. Thus the adsorption of anionic surfactants is higher on positively charged surfaces (pH below isoelectric point (IEP)) than on negatively charged surfaces while the cationic surfactants adsorb more on negatively charged surfaces [36,37]. Molecular structure of surfactant does influence its adsorption behavior markedly.

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm was found to be the best description of the adsorption behavior of the investigated surfactants which obeys the following equations:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh}$$
(9)

$$K = \frac{1}{C_{\text{solvent}}} \exp\left(\frac{\Delta G_{\text{ads}}}{RT}\right)$$
(10)

where C_{inh} is the inhibitor concentration, Θ is the fraction of the surface coverage, K is the modified adsorption equilibrium constant which can be related to the free energy of adsorption ΔG

 ΔG_{ads} and C solvent is the molar concentration of solvent which in the case of the water is 55.5 mol L-1.

Fig. 6 shows that the dependence of the fraction of the surface coverage (C/ θ) as a function of the concentration (C) of CTAB and DTAC. Therefore, Δ Gads can be calculated according to equation (12). The degrees of surface coverage (θ) were evaluated from weight loss measurements using equation 3 and are given in table 2. The regression coefficient R2 = 0.999 suggest a good relation between C/ θ and C. The values of Δ Gads recorded in table 6 are negative, suggesting the spontaneity of the adsorption process. It is well known that values of Δ Gads order of 20 kJ mol-1 or lower indicate a physisorption, while those of order of 40 kJ mol-1 or higher

involve charge sharing or charge transfer from the inhibitor molecules to the metal surface to form a coordinate type of bond (chemisorption) [38, 39]. The calculated values of ΔG

 ΔG_{ads} for CTAB are around -39.9 KJ mol-1, and for DTAC approximately -39.8 KJ mol-1. It suggests a comprehensive adsorption (physical and chemical adsorption) might be occur [40].



Fig.6 Langmuir's adsorption plots for C-steel in 0.5M HCl containing various concentrations of surfactants

TableVI PARAMETERS OF LANGMUIR ADSORPTION ISOTHERM

Inhibi tor	Temp. , K	Adsorpti o n isotherm	K X10 ⁻ M ⁻¹	slope	- ∆G _{ads,} kJ mol ⁻¹	R ²
DTAC	303	Langmuir	4.88	1.02	37.3	0.99 9
СТАВ	303		10.30	1.00	39.2	0.99 9

IV DEVICES

A. Computational Study

Lower values of ionization potential "IP" (-EHOMO) are likely to indicate a tendency of the molecule to donate electrons to appropriate acceptor molecules with low energy or empty electron orbital. The higher the values of electron affinity "EA" (-ELUMO) are, the stronger the electron accepting abilities of the molecules. On the other hand, the hydrophobic properties of the long hydrocarbon tail could be associated with the formation of a protective film that reduces drastically the corrosion process [41]. Pearson introduced the quantities of electronic hardness (η) and softness (σ) in his hard-soft-acid-base principle [42] (HSAB) in the early stage of the reactivity theory. The species are classified as soft (hard) if their valence electrons are easy (hard) to polarize or to remove and the relationship between hardness or softness and the chemical reactivity was given through the HSAB principle. A soft base will interact favorably with a soft acid, sharing electrons, to form bonds of covalent character. Hard acids prefer hard bases and form bonds dominated by electrostatic forces, or ionic character. The concepts of electronegativity (χ) [43] and global hardness (η) [44, 45] are given by:

$$\chi = -\mu = -\left(\frac{\partial E}{\partial N}\right)_{\nu(\vec{r})} \tag{11}$$

$$\eta = \frac{1}{2} \left(\frac{\partial^2 E}{\partial N^2} \right)_{\nu(i)} = \frac{1}{2} \left(\frac{\partial \Box}{\partial N} \right)_{\nu(i)}$$
(12)

Where μ is the chemical potential, E is the total energy, N is the number of electrons, and $\dot{\mathfrak{b}}(\)$ is the external potential of the system.

The global hardness (η), softness (σ), and chemical potential (μ) were calculated in terms of IP and EA [46] from the following equations:

$$\eta = \frac{\mathbf{I}_{\mathbf{P}} - \mathbf{E}_{\mathbf{A}}}{2} \tag{13}$$

$$\sigma = \frac{1}{\eta} = \frac{2}{I_{\rm P} \cdot E_{\rm A}}$$
(14)
$$I_{\rm P} + E_{\rm A}$$

$$\mu = -\frac{\nu - x}{2} \tag{15}$$

Table 7 shows the quantum chemical calculation parameters obtained by DFT method. The results for the above calculations in gaseous phase as well as in liquid phase are presented. These parameters are mainly ionization potential (IP), electron affinity (EA), energy gap (ΔE), global hardness (η), softness (σ), chemical potential (μ) and total energy (Etot). From these results, CTAB exhibits the lowest value of global hardness. It is means that this one has a higher reactivity than DTAC, and it is expected to have the highest corrosion inhibition than DTAC. This expectation is in a good agreement with the experimental results.

From Fig. 7 we can observe that:

The HOMO location in cationic part of CTAB and DTAC surfactant is mostly distributed on hydrophobic part. The LUMO location in cationic part of CTAB and DTAC is mostly distributed on the head group ions that the preferred sites for the nucleophilic attack through metallic negative centers. The position of the surfactant (lying vertically) could be the reason for the high inhibitor efficiency.

TableVII QUANTUM-CHEMICAL DESCRIPTORS FOR CATIONIC SURFACT ANTS OBTAINED WITH DFT METED

		Quantum-chemical descriptors											
				I _P , eV	E_A, eV	$\Delta E, eV$	η, <i>eV</i>	μ, <i>eV</i>	σ, eV	X,eV	-EtobeV		
		Cationic nant	Gas phase	8.158	2.934	5.224	2.612	0.383	-5.546	5.546	646.3		
Surfactant	C I	Canonic pari	Liquid phase	6.700	-0.795	7.495	3.748	0.267	-2.952	2.952	646.4		
	DTA	Cl-	Gas phase	-2.33	-19.08	16.75	8.375	0.119	10.705	-5.35	460.23		
		counter	Liquid phase	4.53	-12.22	16.75	8.375	0.119	3.85	-3.85	460.35		
		Cationic nart	Gas phase	7.761	3.424	4.337	2.169	0.461	-5.593	5.593	803.6		
	AB	cunona pun	Liquid phase	6.569	-0.747	7.316	3.658	0.273	-2.911	2.911	803.69		
	СT	Br ⁻ counter	Gas phase	-1.78	-15.04	13.26	6.63	0.151	8.41	-8.41	343.94		
			Liquid phase	4.70	-8.54	13.24	6.62	0.151	1.92	-1.92	344.06		

JCST Vol.1 Iss.2 2012 PP.45-53 www.sjcst.org (C) World Academic Publishing

51



Fig.7 Molecular orbital plots as well as the active sites for electrophilic and nucleophilic attack for DTAC and CTAB respectively.

Among the theoretical models proposed to compute local reactivity indices is Fukui functions that makes possible to rationalize the reactivity of individual molecular orbital contributions thus to account for the response of the whole molecular spectrum and not only of the frontier orbitals. Frontier orbital electron densities on atoms provide a useful means for the detailed characterization of donor–acceptor interactions. In the case of a donor molecule, $f^{-}(r)$ electrophilic electron density corresponds to reactivity with respect to electrophilic attack or when the molecule loss electrons and in the case of an acceptor molecule, $f^{+}(r)$ nucleophilic electron density corresponds to reactivity with respect to nucleophilic attack. However, frontier electron densities can strictly be used only to describe the reactivity of different atoms in the same molecule.

The highest FI values are presented in Table 8. The most susceptible sites for electrophilic attack located on C(13), C(14) and C(15) atoms in the case of CTAB, C(10), C(11), C(12)and C(13) atoms in the case of DTAC. In addition, susceptible sites are observed to be attacked by anions or nucleophilic attack, positioned on C(2), C(3), C(4), C(5) and N(1) of CTAB and DTAC.

B. Mechanism of Corrosion Inhibition

The role of the counter ions on the adsorption of ionic surfactants is an important factor. The feasible adsorption of organic cations in the presence of the halide ions is due to the formation of intermediate bridge, the negative ends of the halide metal dipoles being oriented towards the solution, whereby setting up an additional potential difference between the metal and the solution. This will shift the zero charge potential positively. This shift will make the charge on the metal surface more negative and facilitates the adsorption of positively charged quaternary ammonium compound by formation of ionic bonds. High hardness of Br- ions and Cl- ions (counter ion effect) and cationic part of CTAB and DTAC suggested higher tendency of an electrostatic adsorption of CTAB and DTAC to occur (Cooperative effect) leads to a high inhibition percentage. Brand CI ions act as an adsorption mediator for bonding the two positive partners, the metal surface and the positively charged ammonium compound. This gives rise to the formation of an adsorption composite film in which the anions are sandwiched between the metal and positively charged part of the inhibitor [47]. This film acts as a barrier facing the corrosion process as shown in Fig.8.

	DTAC		СТАВ			
	Liquia	l phase		Liquia	phase [
	f(r)	$f^{+}(r)$		f(r)	$f^{+}(r)$	
N1	0.000	0.034	N1	-0.003	0.036	
C2	0.001	0.077	C2	-0.001	0.061	
C3	0.000	0.054	C3	0.001	0.077	
C4	0.001	0.062	C4	0.002	0.053	
C5	0.007	0.059	C5	0.004	0.058	
C6	0.012	0.018	C6	0.006	0.018	
C7	0.020	0.009	C7	0.011	0.008	
C8	0.032	0.005	C8	0.017	0.006	
C9	0.041	0.002	C9	0.024	0.002	
C10	0.052	0.001	C10	0.032	0.001	
C11	0.054	0.000	C11	0.038	0.000	
C12	0.057	0.000	C12	0.044	0.000	
C13	0.051	0.000	C13	0.046	0.000	
C14	0.046	0.000	C14	0.047	0.000	
C15	0.035	0.000	C15	0.045	0.000	
C16	0.029	0.000	C16	0.042	-0.001	
			C17	0.034	0.000	
			C18	0.029	-0.001	

TableVIII THE HIGHEST FUKUI INDICES VALUES FOR THE SURFACT ANT S BY HIRSHFELD MET HODS IN LIQUID PHASE CALCULATED WITH BOP/DNP BASIS SET



Fig.8 The expected scheme of adsorption of CTAB and DATC inhibitor on C-steel surface

From above, it is mentioned that a hydrophilic metal surface attracts a large hydrophilic head group of chosen surfactants

Inhibition efficiency of CTAB is larger than DTAC may be due to:

- Br is a borderline base attached with a borderline acid (Fe+2 surfaces) and soft acid (bulk Fe metal surfaces) more than the harder according to Pearson classification of acids and bases.
- The alkyl chain of CTAB is longer than DTAC. The greater will be the forces of attraction between the alkyl chains of adjacently adsorbed head group ions [48].
- Br ions are more hydrophobic, large ionic radius and low electronegativity, compared to Cl [49, 50]. Thus, it adsorbed more tightly on carbon steel surfaces than Cl ions.

V CONCLUSIONS

• The surfactants inhibit the corrosion of C-steel in 0.5 M HCl.

• The inhibition is due to adsorption of the surfactant molecules on the C-steel surface and blocking its active sites.

• Adsorption of the inhibitor fits a Langmuir isotherm model.

• Results obtained from weight loss, dc polarization, ac impedance and EFM techniques are in reasonably good agreement and show increased inhibitor efficiency with increasing inhibitor concentration.

• Polarization data show that the used surfactants act as mixed-type inhibitor in 0.5 M HCl.

•The theoretical study of molecules indicated the differences between CTAB and DTAC according to HSAB principle.

REFERENCES

- [1] J.E. Oddo, M.B. Tomson, J. Pet. Tech. (1982) 1583.
- [2] B. Ridd, T.J. Blakset, D. Queen, Corrosion, NACE, Paper No (78), Houston, Texas, 1998.
- [3] G. Banerjee, S.N. Malhotra, Corrosion, 48 (1992)10.
- [4] O. Olivares, N.V. Likhanova, B. Gomez, J. Navarrete, M.E. Llanos-Serrano, E. Arce, J.M. Hallen, Appl. Surf. Sci., 252 (2006) 2894.
- [5] S. Trasatti, Electrochim. Acta, 37 (1992) 2137.
- [6] A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corros. Sci., 45 (2003) 33.
- [7] M. Lagrenee, B. Memari, M. Bouanis, M. Traisnel, F. Bentiss, Corros. Sci. 44 (2002) 573.
- [8] S. Tamil Selvi, V. Raman, N. Rajendran, J. Appl. Electrochem., 33 (2003) 1175.
- [9] M. Kissi, M. Bouklah, B. Hammouti, M. Benkaddour, Appl. Surf. Sci., 252 (2006) 4190.
- [10] E. Kraka, D. Cremer, J. Am. Chem. Soc., 122 (2000) 8245.
- [11] M. Karelson, V. Lobanov, Quantum chemical descriptors in QSAR/QSPR studies, Chem. Rev. 96 (1996) 1027.

- [12] A. Hinchliffe, Modelling Molecular Structures, John Wiley & Sons, New York, 1994.
- [13] A. Hinchliffe, Chemical Modelling From Atoms to Liquids, John Wiley & Sons, New York, 1999 VoltMaster 4 Manual, 2000.
- [14] B. Delley, J. Chem. Phys., 92 (1990) 508.
- [15] B. Delley, J. Chem. Phys., 113 (2000) 7756.
- [16] R.S. Mulliken, J. Chem. Phys., 23 (1995) 1833.
- [17] H. Ma, S. Chen, B. Yin, S. Zhao, X. Liu, Corros. Sci., 45 (2003)867-882.
- [18] C.N. Cao, Corrosion Electrochemistery Mechanism, Chemical Industrial Engineering Press, Beijing, (in Chinese), (2004) 325.
- [19] M. El Achouri, S. Kertit, H.M. Gouttaya, B. Nciri, Y. Bensouda, L. Perez, M.R. Infante, K. Elkacemi, Prog. Org. Coat., 43 (2001) 267.
- [20] K.F. Khaled, Electrochim. Acta, 48 (2003) 2493.
- [21] A. Popova, E. Sokolova, S. Raicheva, M. Christov, Corros. Sci. 45 (2003) 33.
- [22] F.B. Growcock, J.H. Jasinski, J. Electrochem. Soc., 136 (1989) 2310.
- [23] U. Rammet, G. Reinhart, Corros Sci., 27 (1987) 373.
- [24] A.H. Mehaute, G. Grepy, Solid State Ionics 9-10 (1983) 17.
- [25] E. Machnikova, M. Pazderova, M. Bazzaoui, N. Hackerman, Surf. Coat. Technol., 202 (2008) 1543.
- [26] C.H. Hsu, F. Mansfeld, Corrosion 57 (2001) 747.
- [27] M. Lebrini, M. Lagrenée, M. Traisnel, L. Gengembre, H. Vezin, F. Bentiss, Appl. Surf. Sci., 253 (2007) 9267
- [28] R.G. Kelly, J.R. Scully, D.W. Shoesmith, R.G. Buchheit, Electrochemical Techniques in Corrosion Science and Engineering. Marcel Dekker, Inc., New York, 2002. p. 148.
- [29] Gamry Echem Analyst Manual, 2003.
- [30] R.W. Bosch, J. Hubrecht, W.F. Bogaerts, B.C. Syrett, Corrosion, 57 (2001) 60.
- [31] Wasan DT, Ginn M, Shah DO, editors. Surfactants in process engineering. New York: Marcel Dekker; 1988.
- [32] Somasundaran P, Grieves RB, editors. Advances in interfacial phenomena of particulate/solution/gas systems. AIChE Symposium Series, 1975; 71 AIChE Symp. Ser. 71 (1975) 124.
- [33] Fuerstenau DW. The adsorption of surfactants at solid/water interfaces. In: Hair ML, editor. The chemistry of biosurfaces, vol. New York: Marcel Dekker; 1971. p. 143.
- [34] Rui Zhang, P. Somasundaran Advances in Colloid and Interface Science 123–126 (2006) 215.
- [35] L. Koopal, E. Lee, M. Böhmer. J Colloid Interface Sci., 170 (1995) 85.
- [36] A.X.Fan, P. Somasundaran, and N.J. Turro, Langmuir, 13 (1997) 506.
- [37] F.M. Donahue, K. Nobe, J. Electrochem. Soc. 112 (1965) 886.
- [38] E. Khamis, F. Belluci, R.M. Latanision, E.S.H. El-Ashry, Corrosion 47 (1991) 677.
- [39] A.K.Singh, M.A.Quraishi, Corros.Sci., 52 (2010)1378.
- [40] D.A. Lo´ pez, S.N. Simison, S.R. de Sa´nchez, Corros. Sci., 47 (2005) 735.
- [41] R.G. Pearson, J. Am. Chem. Soc., 85 (1963) 3533.
- [42] R.G. Parr, D.A. Donnelly, M. Levy, M. Palke, J. Chem. Phys., 68 (1978) 3801.
- [43] R.G. Parr, R.G. Pearson, J. Am. Chem. Soc., 105 (1983) 7512.
- [44] R.G. Pearson, Inorg. Chem., 27 (1988) 734.
- [45] V.S. Sastri, J.R. Perumareddi, Corros. Sci.,53 (1997) 617
- [46] T.Y. Soror, M.A. El-Ziady, Mater. Chem. Phys., 77 (2002) 702.
- [47] V. Branzoi, F. Branzoi, M. Biabarac, Mater. Chem. Phys., 65(2000)294.
- [48] E.E. Oguzie, G.N. Onuoha, A.I. Onuchukwu, Mater. Chem. Phys. 89 (2004) 305.
- [49] Y.I. Kuznetsov, N.N. Andreev, Corrosion 96, NACE International, Houston, paper No. 214.