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SOME SURFACTANTS AS CORROSION INHIBITORS FOR C-STEEL IN ACIDIC SOLUTIONS

Y.A. Elewady, A.S. Fouda and H.K. Abd El-Aziz
Chemistry Department, Faculty of Science, El-Mansoura University, El Mansoura-35516, Egypt E-mail: yehiaelewady@yahoo.com

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ABSTRACT

The corrosion inhibition effect of three different types of surfactant, namely, dodecyl trimethyl ammonium chloride (DTAC), octyl phenol poly(ethylene glycol ether)$_x$ (TX-100) and dioctyl sodium sulfosuccinate (AOT) have been used as corrosion inhibitors for 1037 C-steel in 0.5 M HCl. The inhibition properties of the inhibitors were studied by means of weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) measurements. The results show that the order of inhibition efficiency is DTAC > TX-100 > AOT. Polarization curves indicate that investigated surfactants are mixed-type inhibitors, affecting both cathodic and anodic corrosion processes. Adsorption of these surfactants on C-steel surface was found to obey Langmuir's isotherm. The calculated free energies from Langmuir adsorption isotherm indicate that the investigated surfactants adsorb on C-steel by mixed mode of adsorption (physisorption and chemisorption) in 0.5 M HCl. The results obtained from the different techniques are in good agreement.

Keywords: C-steel; HCl; corrosion inhibition; surfactants; EIS; EFM

INTRODUCTION

In oil fields HCl solution is recommended as the cheapest way to dissolve calcium carbonate, $CaCO_3$, scale inside the pipelines under most conditions. Accordingly, corrosion inhibitors must be injected with the HCl solution to avoid the destructive effect of acid on the surface of the pipe lines **[Oddo *et al.*, (1982)]** . 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 **[Ridd *et al.*, (1989)]**.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 .Mixture of surfactants have found many application in technology .these mixtures often show synergetic effects ,which are evidence of non ideal behavior and are the reason of their extensive use in industry. The surfactants inhibitor has many advantages such as high inhibition efficiency, low price, low toxicity and easy production **[Banerjee *et al.*, (1992)]**. 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 physico-chemical 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 **[Olivares *et al.*, (2006) and Popova *et al.*, (2003)]**.The adsorption is also influenced by the structure and the charge of metal surface, and the type of testing electrolyte**[Lagrenee *et al.*, (2002), Tamil Selvi *et al.*, (2003) and Kissi *et al.*, (2006)]**.

The aim of the present paper was to determine the effectiveness of the investigated surfactants as corrosion inhibitors, using the chemical and the electrochemical techniques. These data were used to determine the inhibition efficiency of these compounds.

EXPERMINTAL

1. Chemicals and Materials

Hydrochloric acid(37%wt) ,ethyl alcohol and acetone was purchased from Algamhoria Co.(Egypt).Surfactants(Dodecyl Trimethyl Ammonium Chloride:DTAC ($C_{12}H_{25}N(CH_3)_3$ -Cl), Octyl phenol poly(ethylene glycol ether)$_x$: TX-100 ($C_{34}H_{62}O_{11}$ for x=10) and Dioctyl sodium sulfosuccinate: AOT ($C_{20}H_{37}O_7NaS$) were obtained from Aldrich Chemical Company. The molecular structure of DTAC, TX-100 and AOT are shown in **Fig.(1)**. Distilled water was used for preparing test solutions for all measurements .The corrosion tests were performed on 1037 carbon steel. Rectangular specimens with dimensions 2.00 cm x 2.00 cm x 0.20 cm were used for weight loss measurements. For electro- chemical tests, the exposed surface area of carbon steel was1.00 cm^2.

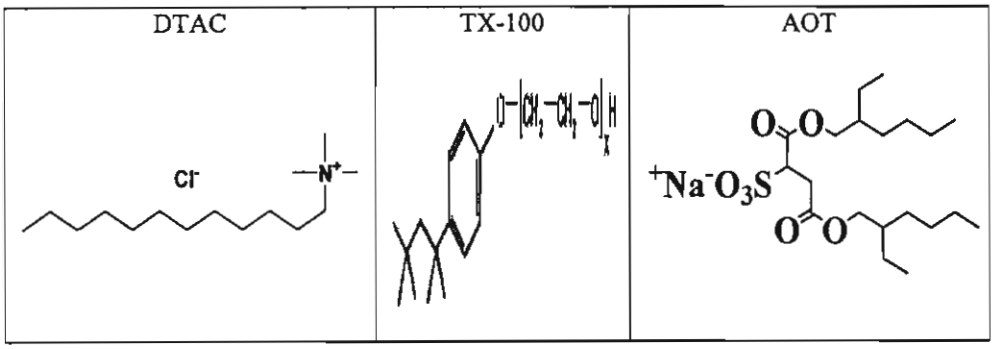

Fig. (1): Molecular structure of DTAC, TX-100 and AOT

2. METHOS

2.1. Weight loss measurements

Medium C-steel specimens were mechanically polished 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 papers. After weighting accurately, the specimens were immersed in 100 ml of 0.5 M HCl with and without different concentrations of surfactants at 30 °C. After different immersion times (30, 60, 90, 120, 150 and180 min), the C-steel samples were taken out, washed with distilled water, dried and weighed accurately. The experiments were done in triplicate and the average value of the weight loss was taken. The weight loss values are used to calculate the corrosion rate (CR) in millimeter per year (mmy^{-1}) by the relation:

$$CR = \frac{\text{Weight loss } (g) * K}{\text{Alloy Density } (g/cm^3) * \text{Exposed Area}(cm^2) * \text{Exposure Time}(hr)} \quad (1)$$

where K is the constant and equals to $8.75X10^4$, when the exposed surface area calculated by cm^2.

The inhibition efficiency (IE %) and the degrees of surface coverage (Θ) were calculated from the following equations:

$$IE\ \% = \frac{CR^{\bullet} - CR}{CR^{\bullet}} X100 \quad (2)$$

$$\theta = \frac{CR^{\bullet} - CR}{CR^{\bullet}} \quad (3)$$

where $CR^{\bullet}$ and CR are the corrosion rates of C- steel in the absence and in the presence of inhibitor ,respectively.

2.2. Electrochemical measurements

Three electrochemical techniques, namely potentiodynamic polarization, ac 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. A Pt electrode as counter electrode and a saturated calomel electrode as reference electrode were used in this study. The C-steel specimen was machined in to rectangular (1 cm x1 cm x 0.3 cm) and sealed with epoxy resin leaving a working area of 1 cm^2. The specimens were polished , degreased and rinsed as described before.

Potentiodynamic polarization experiments were carried out using a VoltaLab PGZ 100 system connected to personal computer with VoltaMaster 4 version7.08 software for calculation. All the experiments were carried out at temperature (30 °C ±1 °C). Equilibrium time leading to steady state of the specimens was 20 min and the open circuits potential (OCP) was noted. The potentiodynamic curves were recorded from -900 to -200 mV at a scan rate 2 mV s^{-1}.

The calculation is performed as follows:

$$CR.(mm/year)=\frac{I\ corr.\ (A/cm^2)\ x\ M\ (g)}{D\ (g/cm^3)\ x\ V}\ x\ 3270 \qquad (4)$$

with: 3270 = 10 x [1 year (in seconds) / 96497.8] and 96497.8 =1Faraday in Coulombs. The inhibition efficiency was (IE %) calculated from:

$$IE_p\% = \frac{I^0_{corr} - I_{corr}}{I^0_{corr}} X\,100 \quad , \quad IE_p\% = \frac{R_p^* - R_p}{R_p^*} X\,100 \qquad (5)$$

where i^0_{corr} and i_{corr} are the corrosion current densities of uninhibited and inhibited solution, respectively. R_p and R_p^* are the polarization resistance 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™ 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 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. The base frequency was 0.1 Hz. In this study, we use a perturbation signal with amplitude of 10 mV for both perturbation frequencies (0.2 and 0.5 Hz).

RESULTS AND DISSCUSION

1. Weight loss measurements

Table(1) shows the dependence of inhibition efficiency (IE %) on varying concentration of surfactants (AOT, TX-100, DTAC) in the range from $4.0x10^{-5}$ mol l^{-1} to $8.0x10^{-4}$ mol l^{-1}. The data of **Table (1)** show that, at constant temperature the inhibition efficiency increases with increasing the concentration of the surfactant and the IE% tends to decrease in the following order: DTAC > TX-100 > AOT. The inhibition action of surfactants in HCl cannot be simply considered as an electrostatic adsorption **[Ma *et al.*, (2003)]**. This action was attributed to the effect of chloride ion of the surfactant and of acid solution and chemisorption of these surfactants on C-steel surface. In addition, other factors such as CMC and structure of surfactant might be affecting the inhibition efficiency. The length of the hydrocarbon chain shows that by increasing the length of the hydrophobic parts of the molecule, more inhibition efficiency was obtained. This effect can be attributed to CMC of the investigated surfactant **[Menger *et al.*, (2000)]**.

Table (1): Data of weight loss measurements for carbon steel in 0.5 M HCl solution in the absence and presence of different concentrations of surfactants at 30 °C.

Comp.	Conc., M	CR (mm y^{-1})	θ	IE%
Blank	٠,٠٠	2.68	0.000	00.00
AOT	$4x10^{-5}$	2.13	٠,٢٠5	20.5
	$8x10^{-5}$	1.94	٠,٢76	27.6
	$2x10^{-4}$	1.27	٠,٥26	52.6
	$4x10^{-4}$	1.17	٠,٥٦3	56.3
	$6x10^{-4}$	1.16	٠,٥٦٥	56.7
	$8x10^{-4}$	1.08	0.597	59.7
TX-100	$4x10^{-5}$	1.10	0.590	59.0
	$8x10^{-5}$	0.82	0.694	69.4
	$2x10^{-4}$	0.48	0.820	82.0
	$4x10^{-4}$	0.46	0.828	82.8
	$6x10^{-4}$	0.36	0.866	86.6
	$8x10^{-4}$	0.341	0.873	87.3
DTAC	$4x10^{-5}$	0.80	0.700	70.0
	$8x10^{-5}$	0.56	0.791	79.1
	$2x10^{-4}$	0.39	0.854	85.4
	$4x10^{-4}$	0.35	0.869	86.9
	$6x10^{-4}$	0.22	0.918	91.8
	$8x10^{-4}$	0.19	0.929	92.9

2. Electrochemical measurements

2.1. Potentiodynamic polarization measurements

The potentiodynamic curves of C-steel in 0.5 M HCl in the absence and presence of DTAC is shown in **Fig(.2).** Similar curves were obtained for other surfactants (not shown). Corrosion parameters for C-steel in 0.5 M HCl without and with the addition of investigated inhibitors are shown in **Table(2).** 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. This may be due to the small shift of E_{corr} (less than 40 mV) due to addition of inhibitors. The effectiveness of organic inhibitors is related to the extent to which they adsorb and cover the metal surface. The adsorption depends on the structure of inhibitors, on the surface charge of the metal, and on the type of the electrolyte. The IE % of the investigated surfactants decreases as follows (Table.2): DTAC > TX-100 > AOT.

The i_{corr} values decrease with increasing inhibitor concentration, while R_p values increase for all inhibitors **Table(2).** Both cathodic (β_c) and anodic (β_a) Tafel slopes do not change remarkably, which indicates that the mechanism of the corrosion reaction does not change and the corrosion reaction is inhibited by simple adsorption mode [Cao., (2004)]. 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. Small changes in potentials can be a result of the competition of the anodic and the cathodic inhibiting reactions, and of the metal surface condition. 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. The results of weight loss measurements confirm the ones obtained by potentiodynamic investigation.

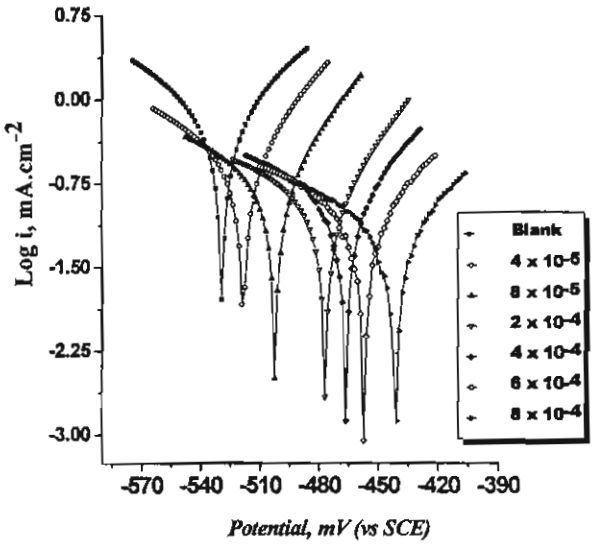

Fig. (2): potentiodynamic polarization for corrosion of C-steel in 0.5 M HCl in the absence and presence of different concentrations of DTAC at 30°C.

Table (2): Potenitiodynamic data of carbon steel in 0.5 M HCl and in the presence of different concentrations of surfactants at 30°C.

Comp.	Conc., M	$-E_{corr}$ vs. SCE, mv	I_{corr} μAcm^{-2}	Rp Ωcm2	$-\beta c$, mV dec^{-1}	βa, mV dec^{-1}	Θ_I	IE_I %	θ_R	IE_R %	C.R $\mu m\ y^{-1}$
Blank	0	529	516	19.9	69	54	0.000	00.0	0.000	00.0	5976
AOT	$4x10^{-5}$	528	405	25.5	72	51	0.215	21.5	0.219	21.9	4641
	$8x10^{-5}$	528	388	26.9	72	50	0.248	24.8	0.261	26.1	4495
	$2x10^{-4}$	.516	284	36.2	68	52	0.449	44.9	0.450	45.1	2427
	$4x10^{-4}$	515	202	43.4	64	46	0.608	60.8	0.541	54.1	2338
	$6x10^{-4}$	511	191	48.6	67	48	0629	62.9	0.590	59.0	2212
	$8x10^{-4}$	489	182	57.8	67	50	0.647	64.7	0.655	65.5	2103
TX-100	$4x10^{-5}$	507	225	44.58	69	49	0.564	56.4	0.553	55.3	2604
	$8x10^{-5}$	496	179	58.55	71	51	0.653	65.3	0.660	66.0	2051
	$2x10^{-4}$	487	161	64.32	70	53	0.688	68.8	0.690	69.0	1860
	$4x10^{-4}$	484	140	68.64	72	49	0.728	72.8	0.710	71.0	1622
	$6x10^{-4}$	483	115	94.11	79	52	0.777	77.7	0.788	78.8	1332
	$8x10^{-4}$	479	102	97.98	81	49	0.802	80.2	0.797	79.7	1179
DTAC	$4x10^{-5}$	518	213	42.96	74	41	0.587	58.7	0.536	53.6	2472
	$8x10^{-5}$	502	131	69.32	77	38	0.746	74.6	0.713	71.3	1517
	$2x10^{-4}$	477	87	108	82	39	0.831	83.1	0.815	81.5	1010
	$4x10^{-4}$	471	85	111	78	45	0.835	83.5	0.820	82.0	993.6
	$6x10^{-4}$	452	82	120	89	45	0.841	84.1	0.834	83.4	954.0
	$8x10^{-4}$	445	70	137	80	45	0.864	86.4	0.855	85.5	809.3

2.2. 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 15 min immersion in 0.5 M HCl in the presence and absence of various concentrations of DTAC is shown in **Fig(.3).** Similar curves were obtained for other inhibitors (not shown).This diagram exhibit a single semi-circle shifted along the real impedance (Z_r) axis. This diagram shows single capacitive loop, which is attributed to charge transfer of the corrosion process, and the diameters of the loops increase with the increase of inhibitor concentration. The R_{ct} values increased with inhibitors concentrations may suggest the formation of a protective layer on the C-steel electrode surface. This layer makes a barrier for mass and charge-transfer. The Nyquist plots (Fig. 3) 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 **[El Achouri *et al.*, (2001)]**and mass transport resistant **[K.F. Khaled., (2003)]** as well as the heterogeneity of electrode surface resulting from surface roughness, impurities, dislocations, grain boundaries, adsorption of inhibitors, formation of porous **layers [Popova *et al.*, (2003), Growcock *et al.*, (1989), Rammet *et al.*, (1987), Mehaute *et al.*, (1983) and Machnikova *et al.*, (2008)].** So, constant phase element (CPE) is substituted for the capacitive element, to explain the depression of the capacitance semi-circle, to give a more accurate fit. Impedance data are analyzed using the circuit in **Fig.(4),** in which R_s represents the electrolyte resistance, R_{ct} represents the charge-transfer resistance and the constant phase element (CPE). The CPE impedance is obtained by:

$$Z_{CPE} = Y_o^{-1}(j\omega)^{n-1} \quad (6)$$

Where: Y_o is the CPE coefficient, n the CPE exponent (phase shift), ω the angular frequency ($\omega = 2\pi f$, where f is the AC frequency), and j here is the imaginary unit.
When the value of n is 1, the CPE behaves like an ideal double-layer capacitance (C_{dl}) [Machnikova et al., (2008), Gohr et al., (1993), Kliskic et al., (2000) and Babic et al., (2006)].According to Hsu and Mansfeld, The correction of capacity to its real values is calculated from:

$$C_{dl} = Y_o(\omega_{max})^{n-1} \quad (7)$$

where ω_{max} is the frequency at which the imaginary part of impedance ($-Z_i$) has a maximum.
The data obtained from fitted spectra are listed in **Table(4).**The degree of surface coverage (θ) is calculated from the EIS data by using following equation:

$$\theta = \frac{R_{ct} - R^{\bullet}_{ct}}{R_{ct}} \quad (8)$$

The IE % is calculated from:

$$IE\,\% = \frac{R_{ct} - R^{\bullet}_{ct}}{R_{ct}} x\,100 \quad (9)$$

where R_{ct} and $R_{ct}^{\bullet}$ are the charge-transfer resistances with and without the inhibitors, respectively.

Charge transfer resistance values (R_{ct}) and double layer capacitance values (C_{dl}) were obtained and shown in **Table(3).** It can be seen from **Table(3)** that the values of charge transfer resistance increase and the values of C_{dl} decrease, with the inhibitor concentration, which is related to the corrosion inhibition effect of the inhibitor molecules. The decrease in the C_{dl} values which can result from a decrease in local dielectric constant and/or an increase in the thickness of the electrical double layer, suggests that surfactant molecules function by adsorption at the metal/solution interface **[Lebrini *et al.*, (2007)].**

The inhibition efficiencies, calculated from EIS results, show the same trend as those obtained from polarization measurements. The difference of inhibition efficiency from the two methods may be attributed to the different surface status of the electrode in two measurements. EIS were performed at the rest potential, while in polarization measurements the electrode potential was polarized to high overpotentials, also, due to non-uniform current distributions which resulted from cell geometry, solution conductivity, the position of counter and reference electrodes with respect to working electrode, these will lead to the difference between the two methods **[Kelly *et al.*, (2002)].**

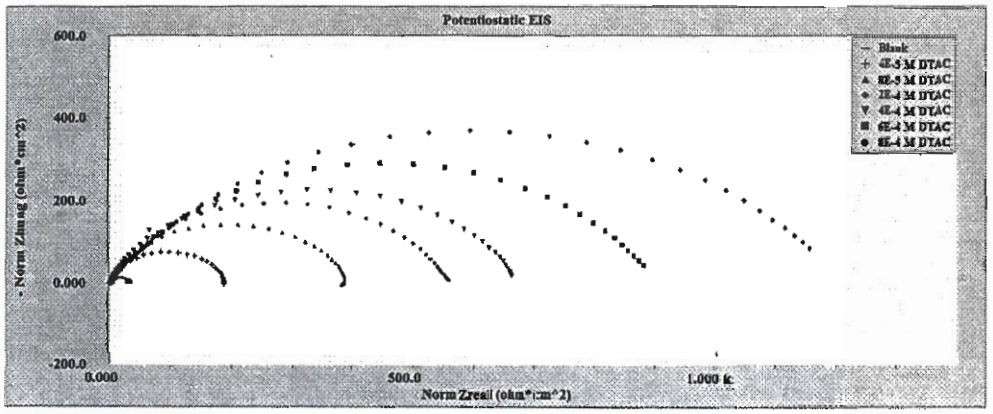

Fig. (3): Nyquist plots for mild steel in 0.5 M HCl in the absence and presence of DTAC.

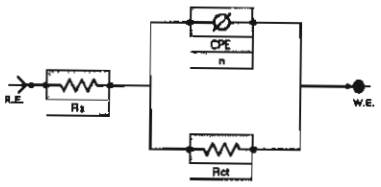

Fig. (4): Equivalent circuit model used to fit the impedance spectra

Table (3): EIS data of carbon steel in 0.5 M HCl and in the presence of different concentrations of surfactants at 30 °C.

Comp.	Conc., M	R_s (Ωcm^2)	Y ($\mu\Omega^{-1} s^n cm^{-2}$)	n	R_{CT} (Ωcm^2)	C_{dl} (μFcm^{-2})	θ	%IE
Blank	٠,٠٠	١,٩٤٦	٥٤٢,٨	٠,٩٠٩	٣٢,١٠	٤٣٧	٠,٠٠	٠,٠٠
AOT	$4.0x10^{-5}$	٢,١٩٥	٣٨١,٥	٠,٨٦٧	٤٧,٠٩	٢٣٦,٥	0.3183	٣١,٨٣
	$8.0x10^{-5}$	٢,٠٦٤	٣٣١,٨	٠,٨٨٦	٥٦,٤٣	٢٠٢,٦	0.4315	٤٣,١٥
	$2.0x10^{-4}$	١,٨١٤	٢٥٩,٠	٠,٨٧٢	٧٤,١١	١٨٣,١	0.5669	٥٦,٦٩
	$4.0x10^{-4}$	٢,٣٤٤	١٦٥,٧	٠,٨٩٠	٨٤,٩١	١٢٠,٦٧	0.6220	٦٢,٢٠
	$6.0x10^{-4}$	٣,٢٨٤	١٣٧,٨	٠,٨٨٩	١١٠,٠	٩٩,٢٢	0.7082	٧٠,٨٢
	$8.0x10^{-4}$	٢,١٠٣	١٢٩,٥	٠,٨٨٥	١١٩,٩	٩٣,٣٧	٠,٧323	٧٣,٢٣
TX-100	$4.0x10^{-5}$	٢,١٠٢	١٣٣,٦	٠,٨٥٦	١٧٥,٠	٩٢,٩٨	0.8166	٨١,٦٦
	$8.0x10^{-5}$	١,٧٥٧	٧٨,٧	٠,٨٩٩	١٩٠,٢	٥٨,٩٣	0.8312	٨٣,١٢
	$2.0x10^{-4}$	١,٨٣٥	٧٣,٦	٠,٨٩٧	٢١٧,٩	٥٥,٤٦	0.8527	٨٥,٢٧
	$4.0x10^{-4}$	٢,٤٣٣	٦٣,٢	٠,٧٩٨	٢٦٨,٢	٤٢,٥	0.8803	٨٨,٠٣
	$6.0x10^{-4}$	١,٩٢٧	٥٩,٨	٠,٨٢٩	٣٠٣,٢	٣٨,٩	0.8941	٨٩,٤١
	$8.0x10^{-4}$	٢,٠٠٦	٥٦,١	٠,٨٤٦	٣١٦,٨	٣٨,٧	0.8987	٨٩,٨٧
DTAC	$4.0x10^{-5}$	١,٧١١	١١٣,١	٠,٨٦٤	١٨٧,٥	٧٩,٣٥	٠.8288	٨٢,٨٨
	$8.0x10^{-5}$	١,٨٣٥	٧٣,٤٨	٠,٨٤٩	٣٨٢,٠	٤٨,٨٧	٠,9160	٩١,٦٠
	$2.0x10^{-4}$	١,٧٩٤	٥٧,٧	٠,٨٤٠	٥٣٥,٣	٤٠,٢	٠,٩400	٩٤,٠٠
	$4.0x10^{-4}$	١,٨٢٦	٥٥,٢٦	٠,٨٢٤	٦٣٧,٠	٣٧,٢٣	٠,٩496	٩٤,٩٦
	$6.0x10^{-4}$	١,٧٢٦	٥٣,٢٥	٠,٧٥٧	٨٦٧,٥	٣٦,٧٣	٠,٩630	٩٦,٣٠
	$8.0x10^{-4}$	١,٤٧٣	٥٢,٧٠	٠,٧٣٨	١١٣٥,٠	٣٦,١٥	٠,٩717	٩٧,١٧

2.3. 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. 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 harmonically and intermodulation current peaks. The larger peaks were used to calculate the corrosion current density (i_{corr}), 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 AOT, TX-100 and DTAC, respectively. Similar curves were obtained for other inhibitors concentration (not shown). As can be seen from **Table(4)** the corrosion current density decreases by increasing the concentration of the inhibitor. The inhibition efficiency, IE_{EFM} (%) calculated from equation **(10)** increases by increasing the inhibitor concentration.

$$IE_{EFM}\,\% = \frac{I^{0}_{corr} - I_{corr}}{I^{0}_{corr}} X\,100 \qquad (10)$$

where: I°_{corr} and I_{corr} are corrosion current densities in the absence and presence of inhibitors, respectively.

The causality factors in **Table(4)** are very close to theoretical values which according to the EFM theory **[Bosch *et al.*, (2001)]** should guarantee the validity of Tafel slopes and corrosion current densities. . Here again, the values of i_{corr} recorded by the EFM technique were converted into the corrosion rate (in mmy^{-1}) using equation **(4).**

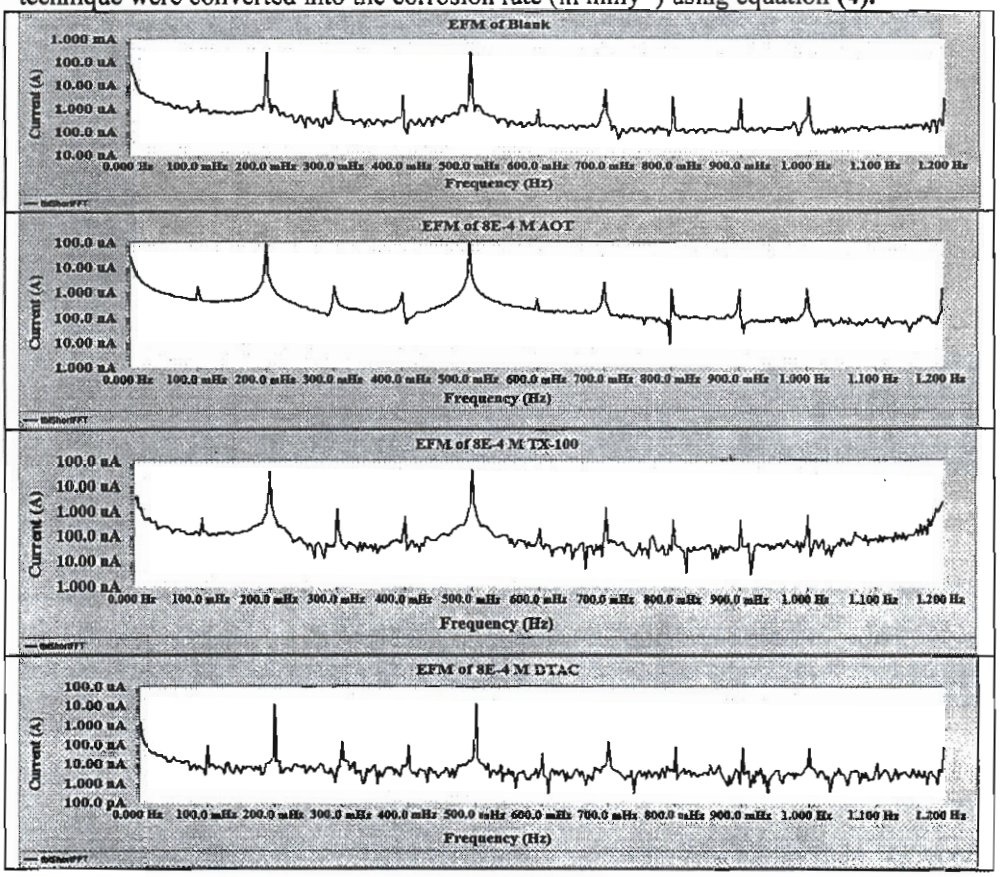

Fig. (5): Intermodulation spectra for C-steel in 0.5M HCl in absence and presence of 8 $x10^{-4}$ M concentrations of AOT, TX-100 and DTAC, respectively.

Table (4): Electrochemical kinetic parameters obtained by EFM technique for carbon steel in absence and presence of various concentrations of surfactants in 0.5 M HCl at 30±1°C.

Comp.	Conc., M	I_{corr} ($\mu A\ cm^{-2}$)	βc ($mV\ dec^{-1}$)	βa ($mVdec^{-1}$)	CF-2	CF-3	CR μmy^{-1}	%IE
Blank	٠,٠٠	٤٨٨,٩	١٢٦,٠	١٠٦,٧	١,٨٦	٢,٩٥	5763	٠,٠٠
AOT	$4x10^{-5}$	٣٩٤,٣	٩٥,٨٣	٨٨,٢٩	١,٦٧	٢,٩٨	4575	١٩,٣٤
	$8x10^{-5}$	٣٢١,٩	١٠٦,٩	٨٨,٣٢	١,٨٤	٢,٩٢	3735	٣٤,١٦
	$2x10^{-4}$	٢٧٢,٨	١٠٢,٠	٨٧,٥٠	١,٨٠	٣,٢٠	3165	٤٤,٢٠
	$4x10^{-4}$	٢٣٨,٦	٩١,٧٣	٨٦,٢٦	١,٣٣	٢,٨٢	2768	٥١,٢٠
	$6x10^{-4}$	٢٠٨,٧	٩٧,٢٨	٨٧,٥٤	١,٧٤	٢,٧٣	2422	٥٧,٣٢
	$8x10^{-4}$	١١٧,٤	٩٤,٨٩	٨٢,٣٧	١,٨٧	٢,٨٧	1362	٧٥,٩٨
TX-100	$4x10^{-5}$	٨٨,٣٢	٩٨,٣٣	٩٢,٥٤	١,٤٤	٢,٧٧	١٠٢٥	٨١,٩٣
	$8x10^{-5}$	٨٧,١٣	٩٤,٦٦	٨٩,٢٢	١,٤٦	٣,٠١	١٠١١	٨٢,١٨
	$2x10^{-4}$	٨٣,١٩	٩٦,٩٧	٩١,١٢	١,٥٦	٢,٧٧	٩٦٥	٨٢,٩٨
	$4x10^{-4}$	٧٠,٠٠	١٠٧,٢	٩٢,٨٤	١,٧٢	٢,٦٤	٨١٢	85.68
	$6x10^{-4}$	٥٦,٢٠	٩٨,٠٤	٨٤,٦٦	١,٨٦	٣,٣٢	٦٥٢	٨٨,٤٦
	$8x10^{-4}$	٥٠,٨٨	٨٤,٨٧	٧٢,٨٥	١,٩٩	٥,٦٨٤	٥٩٠	٨٩,٥٩
DTAC	$4x10^{-5}$	٧٩,١٠	١١٤,٣	١٠٤,٥	١,٦٧	٣,٠١	٦٩١	٨٣,٨٢
	$8x10^{-5}$	٤٢,٤٦	١١٣,٨	١٠٦,٣	١,٥٥	٣,١٣	٤٩٣	٩١,٣٢
	$2x10^{-4}$	٤١,٠٣	١٣١,٥	١١٣,٤	١,٩١	٢,٦٩	٤٧٦	٩١,٦١
	$4x10^{-4}$	٣٠,٧٩	١٣٠,٢	١١٤,٥	٢,٠١	٢,٧٧	٣٥٧	٩٣,٧٠
	$6x10^{-4}$	٢٨,٦٧	١١٨,٢	١١٢,٦	١,٦٣	٢,٦٧	٣٣٣	٩٤,١٤
	$8x10^{-4}$	٢٧,٨٥	١٤٩,٧	١٣٤,٠	١,٩١	٢,٦٠	٣٢٣	٩٤,٣٠

Fig. (6): shows the inhibition efficiency that recorded for DTAC, TX-100 and AOT at a concentration of 8 x 10^{-4} M using the four different techniques, namely weight loss, Tafel polarization, EIS and EFM. The calculated inhibition efficiencies obtained are in good agreement as shown in **Fig(.6).**

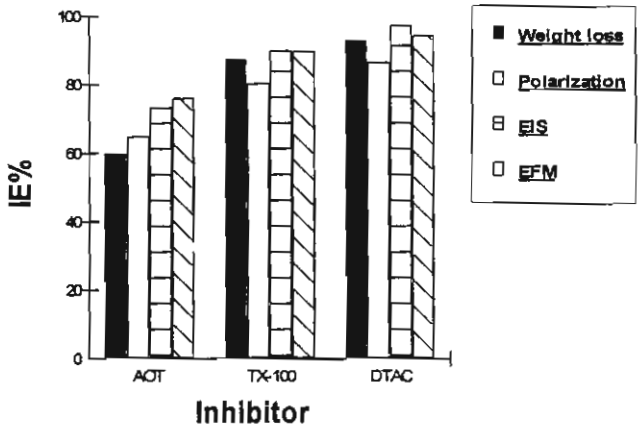

Fig. (6): Comparison of inhibition efficiencies (recorded using EFM, EIS, Tafel polarization and weight loss measurements) obtained for the three surfactants during carbon steel corrosion in 0.5 M HCl solutions containing 8x 10^{-4} M of these three surfactants at 30 °C respectively.

2.4. Adsorption of surfactants

The adsorption of ionic surfactants on oppositely charged surface could be taking the following paths **[Zhang *et al.*, (2006)]:**

1. At low surfactant concentration, 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.

2. 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.

3. 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 2 and 3, 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 **[Koopal *et al.*, (1995) and Fan *et al.*, (1997)].** Molecular structure of surfactant does influence its adsorption behavior markedly.

Most nonionic surfactants contain polar groups that form hydrogen bonds with the hydroxyl groups on the solid surface. Since the hydrogen bonding is weaker than the electrostatic interaction, the adsorption of the nonionic surfactant to most solids is less than that of ionic surfactant. Nonionic surfactants exhibit adsorption similar to those of cationic surfactants, except for a sharp increase in step 3 of the adsorption mechanism because of the absence of electrostatic interactions. The adsorption of the nonionic surfactants also depends on the pH and number of the hydrophilic groups and the hydrocarbon chain length.

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 in 0.5 M HCl:

$$\frac{C_{inh}}{\theta} = \frac{1}{K} + C_{inh} \qquad (11)$$

$$K = \frac{1}{55.5}\exp\left(\frac{-\Delta G_{ads}}{RT}\right) \qquad (12)$$

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_{ads} and 55.5 is the concentration of water in mol l^{-1}.

Fig (7) shows the plot of C/Θ against C_{inh} for AOT, TX-100 and DTAC give straight lines with almost unit slope, indicating that the tested surfactants obey the Langmuir adsorption isotherm on the C-steel in 0.5 M HCl. The values of ΔG_{ads} recorded in Table 6 are negative, suggesting the spontaneity of the adsorption process. It is well known that values of ΔG_{ads} of the order of 20 kJ mol^{-1} or lower indicate a physisorption, while those of the 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 **[Donahue *et al.*, (1965), Khamis *et al.*, (1991)]**. The calculated values of ΔG_{ads} for DTAC are around -39.8 kJ mol^{-1}, for TX-100 approximately -39.4 kJ mol^{-1} and for AOT approximately -33.5 kJ mol^{-1}, so physisorption and some of chemisorption are purposed.

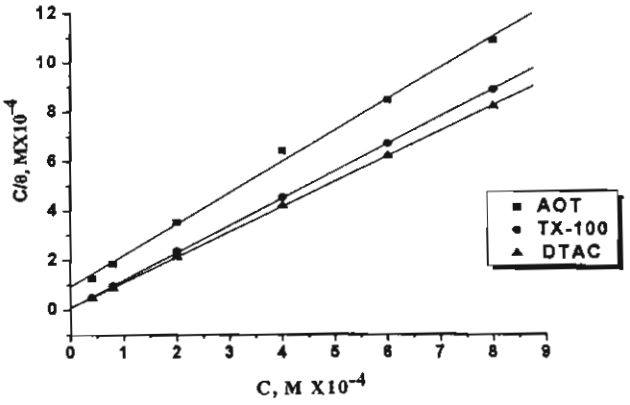

Fig. (7): Langmuir's adsorption plots for C-steel in 0.5M HCl containing various concentrations of surfactants.

Table (6): Values of adsorption isotherms parameters

Inhibitor	Temp (K)	Adsorption isotherm	K x10^{-4}	slope	$-\Delta G_{ads}$ KJ mol^{-1}	R^2
AOT	303	Langmuir	1.08	1.27	33.51	0.998
TX-100			10.95	1.10	39.36	0.999
DTAC			12.92	1.02	39.77	0.999

CONCLUSIONS

The main conclusions drawn from this study are:

- The surfactants inhibit the corrosion of. C-steel in 0.5 M HCl
- The inhibition is due to adsorption of the inhibitor 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 shows that the used surfactants act as mixed-type inhibitor in 0.5 M HCl.

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الملخص العربى

استخدام بعض المركبات ذات النشاط السطحى لتاكل الصلب الكربونى فى المحاليل الحامضية

يحيي عبد اللطيف العواضى –عبد العزيز فودة–حسن كمال عبد العزيز

تم استخدام بعض المركبات ذات النشاط السطحى كمثبطات لتاكل الصلب الكربونى فى ٠,٥ مولر حمض الهيدروكلوريك بطرق كيميائية(فقد الوزن) وكهروكيميائية(الاستقطاب البوتنشوديناميكى، المعاوقةالكهروكيميائية و التردد الكهروكيميائي المعدل).وجد من النتائج ان كفاءة التثبيط تعتمد على تركيز هذه المركبات والتركيب الكيميائى لها. وقد دلت طريقة الاستقطاب البوتنشوديناميكى على ان هذه المركبات تعمل كمثبطات مختلطة (انودية و كاثودية) وان ادمصاص هذه المركبات على سطح الصلب الكربونى تتبع ايزوثيرم لانجمير.