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The Inhibitive Action Of Mono And Bis- Quats Ammonium Surfactants On The Corrosion Of Iron In Hydrochloric Acid Medium

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ABSTRACT

In this work, the (mono-quat) ammonium surfactant: N, N-dimethyl dodecyl ammonio-2-ethanol and the bis-quat ammonium surfactant:1,2-ethanediyl bis-(dimethyl dodecyl ammonium bromide), were synthesised. These compounds have been purified and characterised by the usual methods. Their associative properties have been investigated by conductimetric and surface tension measurements. The critical micelle concentration (cmc) of the bis-quat is lower than that of the mono-quat by one order of magnitude. The inhibitive effect of these surfactants on the corrosion of iron in hydrochloric acid was studied by weight-loss, electrochemical polarisation methods and electrochemical impedance spectroscopy. The inhibition mefficiency increase with the increase of concentration and reach a maximum value near their critical micellar concentrations. These surfactants act on the cathodic hydrogen reaction without modifying its mechanism. Nyquist plots of iron/1M HCl systems obtained by electrochemical impedance spectroscopy(EIS) indicate that the corrosion of iron is mainly controlled by charge transfer process. This study has shown that the gemini surfactant is better than its corresponding mono- quat counterpart in the inhibition due its lower critical micelle concentration. So, the application of this gemini surfactant in corrosion industrial process could lead to a dramatic reduction in the concentration of surface active compound for the same level of performance.

KEYWORDS

(Mono-quat ammonium) surfactant;
Gemini-surfactant;
Critical micellar concentration;
Surface tension;
Corrosion Inhibitor.

INTRODUCTION

Acid media used in various industries generally can be inhibited by the addition of small amounts of chemicals substances called "corrosion inhibitors" in order to decrease corrosive attack on metals[1]. Acid cleaning is one of the numerous applications of the corrosion inhibitors, this operation requires often several hours of contact of acid solutions with the metallic surface in order to remove scales and deposits, in these conditions, efficient corrosion inhibitors must be present to limit the severe corrosion attack that would otherwise occur[2].

The most commonly tested inhibitors for the prevention of corrosion of iron and steel in various acidic media were amines, amides, nitriles, imidazolines, triazoles, pyrolines, quinoline derivatives and quaternary ammonium compounds[2-12].

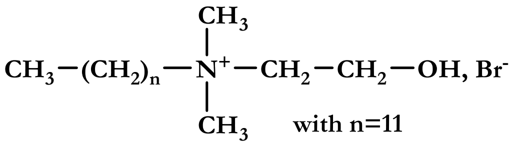
The application of surfactants as corrosion inhibitors has been studied[13-18]. Effective use of surfactants for corrosion inhibition requires appropriate information about the application environment as well as the ability of the surfactant to adsorb onto the desired metal surface and reduce the rate of corrosion. The ability of a surfactant to physically adsorb onto a metal surface is dependent on the properties of the surfactants as well as the properties of the solution. Corrosion inhibition using surfactant inhibitors is influenced by the metal, surfactant functional group, hydrocarbon chain length and the solution environment[19-20].

In this work, a comparative study of the inhibitive effect of a conventional surfactant {mono-quat} in the series of 2-(dodecyl dimethyl ammonio) ethanol bromide and a gemini surfactant {bis-quat} in the series of alkanediyl-α,ω-bis-(dimethyl dodecyl ammonium bromide) on the corrosion inhibition of iron in hydrochloric acid medium was undertaken. Weight-loss, resistance and polarisation electrochemical and electrochemical impedance spectroscopy methods were used.

EXPERIMENTAL

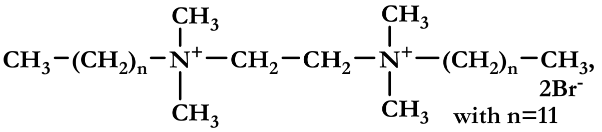
Synthesis

The mono-quat ammonium surfactant in the series of 2-(dodecyl dimethyl ammonio) ethanol bromide was synthesised using N, N-dimethyl ethanolamine(Aldrich)and 2-amino-1-butanol (Aldrich) after dimethylation. The amines were treated by dodecyl bromide under reflux for 15hours in the absolute ethanol. Bromides were extracted and then purified by recrystallisation. The compound structure is as follow :



$$CH_3-(CH_2)_n-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_2-CH_2-OH,\ Br^- \quad \text{with } n=11$$

The bis-quat ammonium surfactant(Ethanediyl 1,2-bis(dimethyl dodecyl ammonium) bromide) referred as(12-2-12) was prepared from N, N, N', N'-tetraethylene diamine and the corresponding dodecyl bromide in large excess as described in[17]. The excess of dodecyl bromide was removed by extraction with a mixture of ether-toluene and finally by an extraction with hexane. The product was recrystallised in pure acetone and acetone- ethanol mixtures. The compound structure is as follow :



$$CH_3-(CH_2)_n-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-CH_2-CH_2-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{N^+}}-(CH_2)_n-CH_3,\ 2Br^- \quad \text{with } n=11$$

The structures of the mono and bis-quats ammonium surfactants were confirmed by elemental analysis, ^{1}H-NMR and mass spectra.

Electrical conductivity measurements

Electrical conductivity of aqueous solutions of mono and bis-quats ammonium surfactants was measured using a conductimeter WTW LF 90 and a WTW KLE 1 cell. Aqueous surfactant solutions were prepared by serial dilution of a concentrated solution. Water used was deionised, its conductivity was less than 4μS cm^{-1}. Critical micellar concentrations(cmc) were derived from the break points in the specific conductivity (χ) versus concentration curves. The solutions of the surfactants were performed by weight in bidistilled water.

Measurements of surface tension

Surface tension measurements were performed with a Lauda tensiometer model equipped with a platinium-irridium ring. The solutions were placed in a beaker at a constant temperature. The ring was washed and heated with a Bunsen burner to an orange color to remove contamination between tests. Surface tension was determined from the measured force exerted on the ring by the solution. All sample solutions were aged(at least 10mn before measurement) before taking measurements in order to reach equilibrium. Bidistilled water was used for preparing solutions. Surfactants solutions were progressively diluted with bidistilled water; the surface tension of water was measured regularly in order to check the experimental technique. The critical micellar concentration(cmc) value is determined by the intersection of the two straight lines of the plot(surface tension against the logarithm of the concentration).

Weight-loss measurements

The weight-loss of square iron specimens of size of($1.5\times1.5cm^2$)in 1M HCl with and without addition of different concentrations of mono and bis-quats ammonium surfactant was determined after six hours of immersion period at temperature of 297K in air without bubbling. The volume of the solution was 50ml. Weight-loss tests were performed at least twice.

Electrochemical measurements

Electrochemical experiments were carried out in a conventional three electrodes cylindrical Pyrex glass cell at room temperature with a platinum counter electrode and a saturated calomel electrode(SCE) as reference. The working electrode in the form of disc was cut from iron and was embedded in poly tetra fluoroethylene(PTFE) holder; the working electrode has a geometric area of $1cm^2$.

The polarisation curves were recorded with an EG&C Princeton applied research potentiostat/ galvanostat model 263A. The potentiostat was monitored by a computer equipped with an IEEE-488 (GPIB) interface and computer program. The potential scan rate was 0.5mV/s. In order to work under well-defined experimental conditions, the working electrode was polarised at -800mV/SCE for 10min before recording the cathodic potentiokinetic curves up the corrosion potential. Solutions were de-aerated with nitrogen. Before recording the anodic polarisation curves, the iron electrode was maintained at its corrosion potential for 30min. The subsequent polarisation measurements were performed between this potential and more positive value.

Polarisation resistance was performed by scanning through a potential range very close to the corrosion potential. The potential range was ±5mV around E_{corr}. The resulting current was plotted versus potential. Polarisation resistance values were obtained from the current potential plots.

Electrochemical impedance spectroscopy measurements

Electrochemical impedance measurements were performed at room temperature in unstirred and deaerated 1M HCl, by using an electochemical impedance analyser(EGG Instruments Model 6310) and a computer. The frequency range was 64KHz to 10MHz with applied potential signal amplitude of 10 mV around the rest potential. Tests were performed at the free corrosion potential of the iron electrode at room temperature. The impedance diagrams are given in Nyquist representation. Measurements at rest potentials after 30 mn of exposure were automatically controlled by computer programs.

The iron specimens used were cut from an iron(99, 5% purity) 'Ref LS 99376 J.Fe.000405/14' from good fellow cambridge science park. UK.

The aggressive solutions 1M HCl were prepared by dilution of analytical grade 37% HCl with double distilled water.

Prior to the weight-loss, electrochemical and impedance measurements, the iron samples were polished with a series of emery papers of variable grade starting with the most coarse and proceeding in steps to the finest (1200 grade). The samples were subsequently washed thoroughly with double distilled water followed by acetone and finally with distilled water just before insertion in the cell.

RESULTS

Conductivity measurements

The results of specific conductivity measurements of aqueous solutions of mono-quat ammonium surfactant are illustrated as example in figure 1. The plot of specific conductivity versus concentration of bis-quat ammonium surfactant shows the same trend. The values of the critical micellar concentration(cmc) were estimated from the breaks on specific conduc

TABLE 1: Surface properties of surfactants studied at T=295K: critical micellar concentration(cmc), degree of ionisation β, surface excess concentration $T_{max,}$ minimum area per molecule A_0, free energies of micellization ΔG^0_{m1} and ΔG^0_{m2}

	Mono-quat ammonium surfactant	Bis-quat ammonium surfactant
Cmc(mol/l)(conductivity)	$8, 5.10^{-3}$	$5,7.10^{-4}$
Cmc(mol/l)(surface tension)	8.10^{-3}	$4.\ 10^{-4}$
Degree of ionisation β	0,76	0,74
Surface excess concentration T_{max} (mol/cm^2)	$2, 37.10^{-10}$	$1, 5.10^{-10}$
Minimum area per moleculeA_0(Å^2)	70	110
Free enegy of micellization ΔG^0_{m1} (Kj/mol)	-24	-36
Free enegy of micellization ΔG^0_{m2} (Kj/mol)	-27	-45

tivity against concentration plots. The values are collected in TABLE 1. The degree of ionisation β was estimated from the ratio of the slopes of the plots in pre and post micellar respectively. The experimental values are reported in TABLE 1 together with the standard free energies of micellization estimated from the relation(1)[21]:

$$\Delta G^0_{ml} = (2-\beta)RTLnX_{cmc} = (2-\beta)RTLn\frac{C_{cmc}}{\varphi} \qquad (1)$$

X_{cmc} is expressed in mole fraction units.

φ=55, 6mol H_2O/ l, cmc: critical micellar concentration

C: concentration

Measurements of surface tension

Figure 2 shows the relationship between surface tension and the logarithm of the concentration of bis-quat ammonium surfactant. The plot of surface tension versus the logarithm of concentration of mono-quat ammonium surfactant shows the same trend. The cmc was taken as the concentration at the point of intersection of the two linear portions of the plots. Experimental cmc values determined from surface tension measurements are reported in TABLE 1.

The surface excess concentration(T_{max}) at the air/water interface and the minimum area per molecule (A_0) were calculated according to the following equations derived from the Gibbs adsorption isotherms

$$\Gamma = -\frac{\frac{\delta\gamma}{\delta \log C}}{2,303\times nRT} \qquad (2)$$

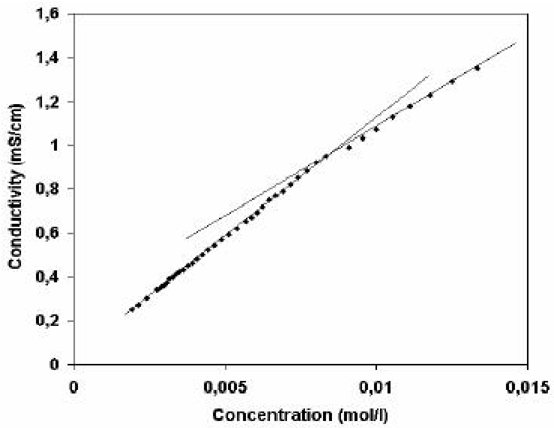


Figure 1: Plot of specific conductivity versus concentration of mono-quat ammonium surfactant C_{12}

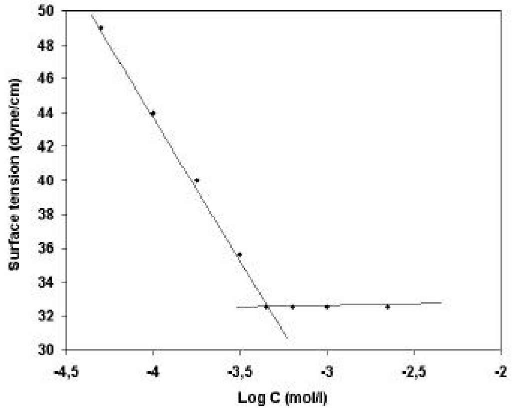


Figure 2: Surface tension versus Log C of bis- quat ammonium surfactant

$$A_0 = \frac{10^{16}}{N\times\Gamma} \qquad (3)$$

where R=8.3110^7 ergs/(mol. K), N=Avogadro's number, n is a constant that depends on the species constituting the surfactant and which adsorbed at the interface.

The relationship between the critical micellar concentration(cmc) of a surfactant and its free energy of micellization was calculated from the equation(4) proposed by Blandamer[22]:

$$\Delta G^0_{m2} = \left(\nu^+ + \nu^-\right)RTLn\left(\frac{Q\times cmm}{m_0}\right) \qquad (4)$$

ν+ and ν-are respectively the number of moles of cations and anions produced on complete dissociation of one molecule of surfactant.

Q is defined as:

$Q = (\nu+)^{\nu^+} \times (\nu-)^{\nu^-}$

cmm is the critical molality and m_0 is 1mol/kg.

Values of cmc, T_{max} , A_0 and ΔG^0_m are reported in TABLE 1.

Weight-loss measurements

TABLE 2 gives values of the corrosion rate and the inhibition efficiency obtained from the weight loss measurements of iron in 1M-HCl in the absence and in the presence of different concentrations of mono and bis-quats ammonium surfactants determined after six hours of immersion at 297K. The inhibition efficiency is defined as follow:

$$E(\%)\left(1-\frac{W}{W_0}\right)\times 100 \qquad (5)$$

Where W and W_0 are the corrosion rates of iron after immersion in solutions with and without inhibitor respectively.

From this table, the inhibition efficiency increases with increasing inhibitors concentrations, The maximum values were reached around the critical micellar concentration(cmc) values of the mono and bis-quats ammonium surfactants.

Electrochemical measurements

Polarisation resistance method

Polarisation resistance values were obtained from the current potential plots.

The corresponding inhibition efficiency was calculated as follow:

$$E\% = \left(1-\frac{R_p}{R'_p}\right) \qquad (6)$$

where R_p and R'_p are the polarisation resistance in the absence and in the presence of inhibitor, respectively.

Values of R_p and R'p and the corresponding inhibition efficiency for various concentrations of each surfactant in 1M-HCl studied are summarised in TABLE 4. It is found from this table that the polarisation resistance values increase with increase in the concentration of surfactants studied.

Tafel method

Figure 3 shows the potentiodynamic polarization curves for iron in 1M-HCl in the absence and in the presence of various concentrations of mono-quat ammonium surfactant. The curve obtained in the case of the bis-quat ammonium surfactant shows the same trend.

TABLE 2 : Weight-loss results of the iron in 1M-HCl with and without addition of mono and bis-quat ammonium surfactants studied

Inhibitor	C(mol/l)	W(mg/cm².h)	E%
Blank	0	2,48	-
Mono-quat ammonium surfactant "C12"	10^{-6}	1.93	22
	10^{-5}	1.88	24
	5.10^{-5}	1.59	36
	10^{-4}	0.39	84
	5.10^{-4}	0.22	91
	10^{-3}	0.15	94
	2.10^{-3}	0.1	96
	4.10^{-3}	0.1	96
Bis-quat ammonium surfactant "12-2-12"	10^{-8}	2.08	16
	10^{-7}	1.98	20
	10^{-6}	1.41	43
	5.10^{-6}	0.92	63
	10^{-5}	0.50	80
	5.10^{-5}	0.25	90
	10^{-4}	0.17	93
	5.10^{-4}	0.10	96
	6.10^{-4}	0.10	96

TABLE 3: Electrochemical parameters of iron in 1M-HCl with and without addition of different concentrations of surfactant studied and the corresponding inhibition efficiency values determined by polarisation resistance and Tafel methods

		Polarisation resistance method		Tafel method			
	C(M)	Rp(Ω)	E%	Ecorr (mV/SCE)	Icorr (μA/cm²)	-bc (mV/dec)	E%
Blank	0	80	-	-470	362	170	-
Mono-quat ammonium surfactant " "C12"	10^{-6}	97	18	-465	290	175	20
	10^{-5}	104	23	-501	271	169	25
	510^{-5}	114	30	-462	246	162	32
	10^{-4}	333	76	-488	72	173	80
	510^{-4}	533	85	-498	36	180	90
	10^{-3}	727	89	-431	29	167	92
	$2.\ 10^{-3}$	1333	94	-445	14	165	96
	8.10^{-3}	1333	94	-469	14	170	96
Bis-quat ammonium surfactant "12-2-12"	10^{-7}	117	32	-430	295	180	30
	10^{-6}	123	35	-449	278	181	34
	10^{-5}	216	63	-467	160	176	62
	510^{-5}	307	74	-481	92	171	78
	10^{-4}	400	80	-469	42	185	90
	510^{-4}	1000	92	-450	26	175	94
	10^{-3}	1143	93	-445	21	175	95

In the case of electrochemical method, E% was defined as:

$$E\% = \left(1-\frac{I'_{corr}}{I_{corr}}\right) \qquad (7)$$

Where I_{corr} and I'_{corr} are uninhibited and inhibited corrosion current densities determined by extrapolation of cathodic Tafel lines to corrosion

TABLE 4 : Electrochemical impedance parameters for iron in 1M-HCl in the absence and presence of different concentrations of surfactants studied

Surfactant	C(mol/l)	R_T(Ω.cm²)	C(μF/cm²)	E%
1M HCl	0	71	112	-
Mono-quat	10^{-4}	100	105	29
ammonium	10^{-3}	210	98	66
surfactant	10^{-2}	700	56	90

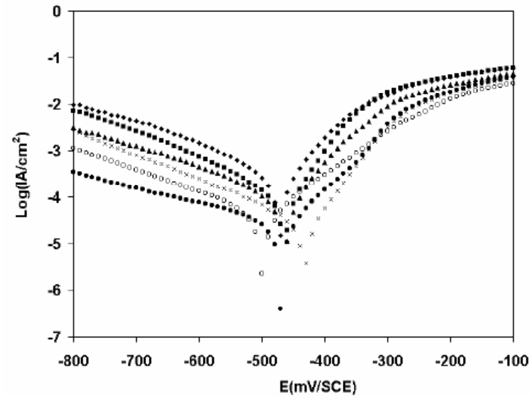


Figure 3 : Polarisation curves of iron in 1M-HCl in the absence and in the presence of different concentrations of mono -quat ammonium surfactant.

(♦) 0 M; (■) 10^{-6}M;(▲)10^{-5}M; (x) 5.10^{-4}M; (?) 10^{-3} M; (●) 6.10^{-3}M

potential.

TABLE 3 gives corrosion kinetic parameters derived from electochemical polarisation curves such as a current density(I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope(b_c) and corrosion inhibition efficiency (E%) as function of inhibitors concentrations in 1M-HCl.

A decrease of a cathodic current densities was noticed. From these results, we can conclude that:

- The corrosion current density decreases with increasing inhibitor concentration.
- The high inhibition efficiency is observed when the inhibitor concentration reaches values close to the cmc, and then the inhibiting effect remains stable with increasing concentration.
- There was a relationship between inhibiting effect and micelle formation.
- Values of Tafel slopes obtained for iron in 1M HCl with and without addition of differrent concentrations of mono and bis-quats ammonium surfactants are almost the same.

Electrochemical impedance spectroscopy measurements

Nyquist plot for iron in 1M HCl for various concentrations of bis-quat ammonium surfactants is shown in as example in figure 5.

The main parameters deduced from the analysis of Nyquist diagram are

- The resistance of charge transfer R_T (R_T is the diameter of high frequency loop)
- The capacity of double layer which is defined as:

$$C = \frac{1}{2\Pi R_T f_c} \tag{8}$$

Where R_T and f_c are, respectively, the resistance of charge transfer of the capacitive loop and the associated characteristic frequency corresponding to the maximum of capacitive arc. The inhibition efficiencies of the surfactant were evaluated by impedance spectroscopy measurements using the following relation:

$$E\% = \left(1 - \frac{R_T}{R_{T'}}\right) \times 100 \tag{9}$$

where R_T and $R_{T'}$ are , respectively, the resistance of charge transfer in 1M-HCl with and without different concentrations of surfactants studied.

TABLE 4 gives values of charge transfer resistance(R_T), double layer capacitance(C) and inhibition efficiency obtained from the Nyquist plots. For each surfactant studied, the resistance of charge transfer increase with increasing inhibitors concentration whereas the double layer capacitance decreases with the increase of the inhibitors concentrations.

DISCUSSION

From conductivity and surface tension measurements, it is clear that the bis-quat ammonium surfactant has the lower critical micellar concen tration [cmc(bis-quat)/cmc(mono-quat)=0.071]. The observed cmc of the bis-quat (12-2-12) is smaller than the cmc of mono-quat by up one order. This result would be explained by the fact that the electrostatic repulsion between the cationic hydrophilic group of the mono-ammonium salt would hinder the aggregation to form micelles, so, the aggregation of molecules of mono- quat ammonium salts occurs at high concentration by the action of London dispersion forces which are the main attractive forces in the formation of micelles[23]. In the case of bis-quat ammonium salt, this repulsion would be minimised by the linkage of the covalent bonds between the hydrophilic parts. Otherwise, the bis- ammonium salt(12-2-12) is formally a dimmer, which is a premicelle of the ammonium salt, an aggregation prior to the formation of the micelles. So the(12-2-12) would be assembled much readily compared with the mono-ammonium salts. Moreover, The free energies of micellization ΔG^0m were negatives for the both ammonium surfactant studied which indicate that the formation of micelles was spontaneous. The value of ΔG^0_m of the bis-quat ammonium surfactant was more negative than that of the mono-quat, so the formation of micelles was more spontaneous.

The inhibitive action of mono and bis-quats ammonium surfactants on the corrosion of iron in 1M-HCl was studied. From weight-loss measurements, it was found that the inhibition efficiency increases with an increase of inhibitors concentrations, the maximum values were obtained around the critical micellar concentrations.

Cathodic and anodic polarisation curves obtained from electrochemical measurements at various concentrations of mono and bis-quats ammonium surfactants showed that the cathodic reaction was inhibited and the inhibition efficiency increases with an increase of inhibitors concentrations reaching maximum value around the cmc of each surfactant tested. The polarisation resistance also increases with increasing the concentration of the inhibitors. Tafel lines with approximately equal slope were obtained. The constancy of the cathodic slopes indicates that the hydrogen evolution reaction was activation controlled and the addition of the both inhibitors did not modify the mechanism of this process. This result suggests that the inhibition mode was by simple blockage of the surface by adsorption.

From the electrochemical impedance spectro scopy measurements, it was found that the inhibition efficiency of surfactants studied is characterised by an increase in the diameter of the capacitive loop and a decrease in the values of associated capacities. In addition to the high frequency loop, a low inductive frequency loop was also observed(Figure 4) indicating that a faradic process is taking place on the free electrodes sites. This inductive loop is generally attributed to the adsorption of species resulting from the iron dissolution and the adsorption of hydrogen [24-26]. The capacity of double layer decreases with the increase of concentration of each inhibitor. This means that when the mono or the bis-quat ammonium surfactants adsorb on the surface of electrode, they influence the double layer (Helmotz layer). The double layer between the charged metal surface and the solution is considered as an electrical capacitor. The adsorption of ammonium surfactants on the metal electrode decreases its electrical capacity because they displace the water molecules and others ions originally adsorbed on the surface. The decrease of this capacity with increasing surfactants concentrations may be attributed to the formation of a protective layer at the surface of electrode[27-28].

As we have shown from electrochemical polarisation and electrochemical impedance spectro scopy, the inhibitive mode of these surfactants was by simple blockage of the surface by adsorption. This adsorption can occur via electrostatic(i)and hydrophobic effects(ii):

(i) Electrostatic effect

The adsorption occur via electrostatic interaction between ammonium groups and cathodic sites on the metallic surface. The molecules of surfactants form an adsorbed film on the metal surface; this film forms a barrier that prevents the diffusion of corrosive agents to the metallic surface. The film of adsorbed quaternary ammonium is formed at low concentration

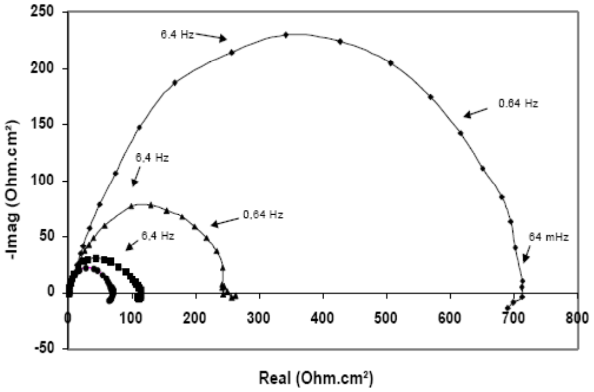


Figure 4: Nyquist plots of the iron at Ecorr in the case of 1M-HCl and in 1M-HCl added of various concentrations of the gemini surfactants(12-2-12)
(•) 1M HCl (■) 10^{-5} M (▲) 10^{-4} M and (♦) 10^{-3} M

in the case of bis- quat ammonium surfactant because each molecule of surfactant had two polar heads bonded strongly; the film is formed at high concentration in the case of mono-quat ammonium surfactant because the electrostatic repulsion between the quaternary ammonium heads are more strong comparatively to that of the bis-quat ammonium salt. The effectiveness of adsorption can be also explained by the difference in the interfacial area,A_0, occupied by the surfactant molecules. The interfacial area of the bis- quat was greater than that of the mono- quat ammonium surfactant, so the surface of the metal was completely covered by the molecules of the of bis-quat ammonium surfactant at low concentration, whereas, the interfacial area of the mono-quat ammonium surfactant was small so the total coverage of the metallic surface occurs at high concentration.

(ii) Hydrophobic effect

The hydrophobic interaction is mainly influenced by the structure and particularly the size of the hydrophobic part. From surfactant studied, the hydrophobic group is the alkyl chain and lyophilic group was the quaternary ammonium ions, the hydrophobic groups were oriented away from the metallic surface. In the case of bis-ammonium salt, the presence of two hydrophobic groups in each molecule leads to a higher degree of association of alkyl chains which would form a dense packing arrangement which hindered the mobility of corrosive agents. The marked difference between hydrophobic effect of the mono and bis- quats ammonium surfactants may account for the less compact arrangement of alkyl chains of the mono-ammonium salt.

Figure 5 shows exemplary experimental adsorption isotherms of the mono-quat ammonium surfactant, it was found that experimental data fit Frumkin adsorption isotherm. The Frumkin adsorption isotherm is given by:

$$\left(\frac{\Theta}{1-\Theta}\right)\exp(-f\Theta)=KC \qquad (10)$$

Where C is the inhibitor concentration, f, the parameter related to the variation in adsorption energy with surface coverage and K is defined as

$$\mathrm{Ln}\left(K_{ads}\times 55.5\right)=-\left(\frac{-\Delta G^{0}_{ads}}{R\times T}\right) \qquad (11)$$

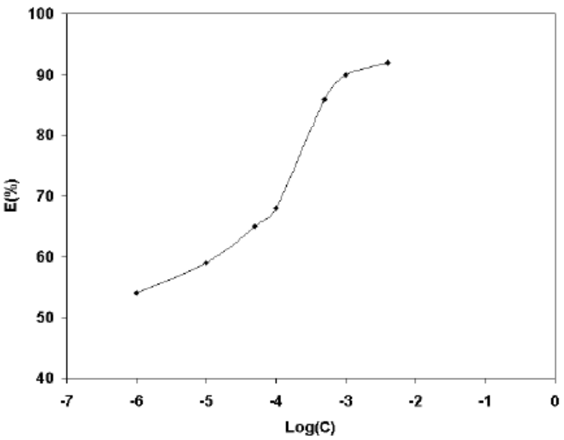


Figure 5 : The variation of the inhibition efficiency obtained by electrochemical method versus concentration of mono-quat ammonium surfactant in 1M-HCl

TABLE 5: Thermodynamic data obtained in 1M-HCl in the presence of surfactants studied determined from experimental adsorption isotherm

	$K_{(T1)}$	ΔG^0_{ads}(Kj/mol)
1M-HCl+mono-quat ammonium surfactant	$6, 8.10^5$	-48
1M HCl bis-quat ammonium surfactant	$5, 6.10^6$	-53

Two values of concentrations permit to determine f and K. The thermodynamic parameters for adsorption shown in TABLE 5 were calculated using the values of K according to the following equations :

$$\Delta G_{ads}° = RTL_n(K\times 55.5)$$

The value of ΔG_{ads}^{0} is negative. This means that the adsorption process takes place easily and the adsorbed layer on iron is stable.

CONCLUSIONS

- The following conclusions can be drawn:
- The critical micellar concentration (cmc) of the bis-quat ammonium surfactant is lower than the CMC of the mono-quat ammonium surfactant.
- Mono and bis-quat ammonium surfactants are good cathodic inhibitors for iron in 1M HCl media.
- The steady-state measurements have shown that added surfactants studied do not change the proton reduction mechanism.
- High inhibition efficiencies are observed around

the critical micellar concentration for mono and bis-quats ammonium surfactants in the corrosive media.

- The bis-quat surfactant is better than mono-quat, this is due to its lower critical micellar concentration witch lead to the reduction in the concentration of the surface active compound.
- The impedance measurement shows that the increase of the inhibition efficiency with the increase in concentrations is interpreted by a strong adsorption of surfactants molecules on the iron surface. The maximum of the inhibition efficiency is attributed to a formation of a protective layer on the iron surface.

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