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Adsorption and inhibitive properties of fatty imidazoline surfactants on mild steel

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ABSTRACT

Nine selected fatty imidazoline surfactants with alkyl chain length of 11,15 and 17 carbon atoms were synthesized and evaluated for their surface active characteristics and corrosion inhibition of mild steel in boiling 15% hydrochloric acid solution at 110 ± 2^0C for 0.5 1,1.5 and 3.0 h by the weight loss method. The surface and adsorption characteristics showed that all the investigated compounds have significant surface activity and distinguished inhibition efficiency and followed Temkin's adsorption isotherm.

Keywords : imidazoline surfactants , surface activity, inhibition efficiency.

INTRODUCTION

Corrosion causes the destruction or deterioration of metals by chemical means in environments to which they are exposed and results in enormous economic losses[1]. Thus, the impetus for the intense interest in studying inhibition efficiency for many chemicals is due to economic importance. Corrosion inhibitors are chemical compounds whose presence in small quantities can retard corrosion of metal in aggressive environments. They are adsorbed onto the metal surface and act by forming a barrier to oxygen and moisture, by complexing with metal ions or by removing corodants from the environment. Amines and their derivatives are well known as corrosion inhibitors for iron and alloys, their relatively high water solubility is an advantage for their use as inhibitors [2-4]. It has been found that most of the organic inhibitors act by adsorption on the metal surface . [5]

The presence of heteroatoms in an organic compound causes an adsorption process on the metal surface which reduces metal dissolution [6]. In spite of the widespread use of amines as corrosion inhibitors, the inhibition mechanism remains so far unexplained. However, generally, in the case of physisorption an increase in temperature reduces an inhibitor efficiency due to its desorption from the metal surface[7,8]. Thus, finding an inhibitor with high efficiency at low and high temperatures is of substantial economic significance. On the other hand, recently, Quraishi et al [9] have attracted interest not only to an open chain fatty acid derivatives but also in heterocyclic corrosion inhibitors. The increasing interest in using fatty acid derivatives as corrosion inhibitors is due to their environmentally benign and low toxicity [10,11].

The aim of this paper was to synthesize some fatty imidazoline derivatives and the study of their surface properties and inhibition efficiency. The influence of inhibitor concentration on the corrosion rate of the prepared fatty imidazoline derivatives containing between 11 and 17 carbon atoms was studied using aqueous 15% hydrochloric acid solution and mild steel at a temperature of 110 ± 2 ^{0}C. The surface properties of the investigated compounds were also examined through surface tension, critical micelle concentration, molecular surface area, efficiency, effectiveness, surface tension reduction, free energy of micellization and critical micelle concentration/surface tension reduction. The relation between the surface and adsorption properties and inhibition efficiency was also investigated.

MATERIALS AND METHODS

Materials:

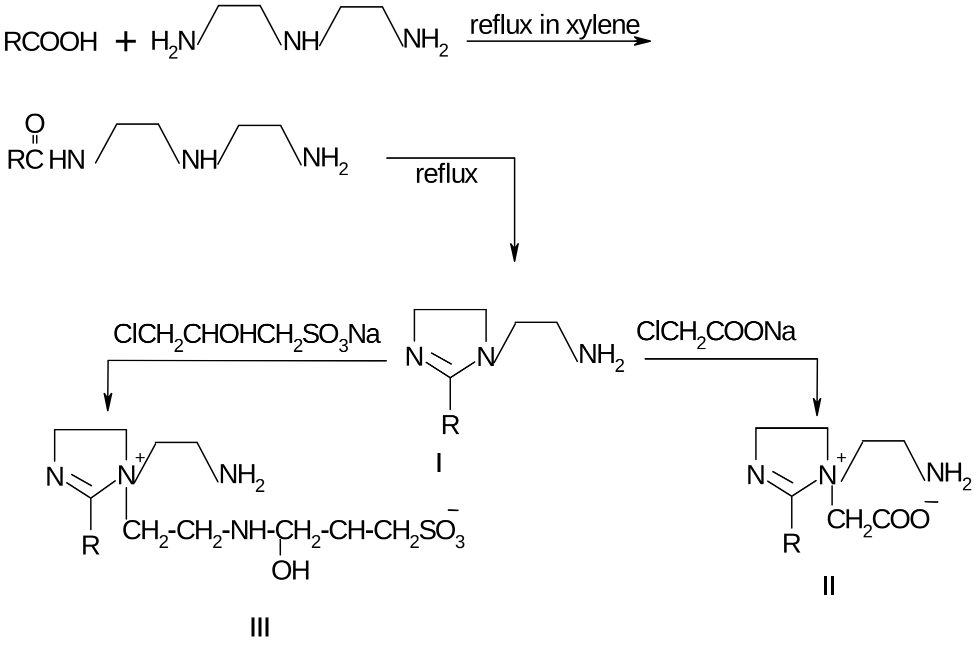
The fatty acids, lauric, palmitic and stearic acids were purchased from Prolabo laboratory chemicals analytical grade, purity 99%. Diethylenetriamine, epichlorohydrin and monochloroacetic acid were Merck chemically pure grade. All solvents used throughout this study were of the chemically pure grade and were fractionally distilled just before use.

Apparatus:

Melting points were determined with an Electrothermal IA9100 apparatus and were uncorrected. IR spectra were obtained on a Vector 22 Burker spectrometer. ^{1}H nuclear magnetic resonance ^{1}HNMR spectra were obtained using a 200 MHz signal Varian Jemini spectrometer and mass spectra was determined in a Model 5988 HB diode- array spectrometer.

Synthesis:

The structure of the compounds synthesized is shown in Scheme (1) (compounds I-III).



Scheme (1)

Compounds (I_{a-c}) were prepared by reacting the appropriate fatty acids with diethylenetriamine in xylene, followed by purification. The products obtained were converted into compounds (II_{a-c}) by reaction with sodium monochloroacetate in presence of Na_2CO_3. Compounds (III_{a-c}) were prepared by condensation of the corresponding I_{a-c} with sodium 1- chloro - 2-hydroxypropane sulfonate, the products were recrystalized from absolute ethanol.

2-Alkyl-N-(2-aminoethyl) imidazoline I_{a-c}. A solution of lauric acid (4g, 0.02mol) in xylene (50ml) was added dropwise by a syringe to a solution of diethylenetriamine (2.06g,0.02mol) in xylene (25ml). After addition was complete (1h), the reaction mixture was refluxed for 4h. The solvent was removed and the residue was recrystallized from ethyl acetate to give the imidazoline derivatives (I_{a-c}). The same procedure was followed for the preparation of palmitic and stearic acid derivatives.

The following results were obtained for compound I_a: yellowish white crystals, yield 83%, m.p 80^0C. The infrared spectra of 2-lauryl-N-(2-aminoethyl) imidazoline showed the characteristic absorption band at 1604cm^{-1} of C=N, at 2862 cm^{-1} 2926 cm^{-1} for CH-aliphatic and at 3284 cm^{-1} for $-NH_2$.^{1}HNMR revealed δH ($CDCl_3$) 0.8 (3H, t, CH_3), 1.25 (20H, s, $(CH_2)_{10}$), 1.6 (2H, s, NH_2), 2.15 (2H, t, $CH_2–NH_2$), 2.75 (2H, t, $N–CH_2$), 3.3 (2H, t, $CH_2–N$), 3.6 (2H, t, $CH_2N=C$). The mass spectra showed a molecular ion peak at m/z 267 (1.76%) with a base peak at m/z 85 (100%).

2-Alkyl-N-(2-aminoethyl)N-carboxymethyl imidazoline II_{a-c}. Sodium monochloroacetate (1.17g,0.01mol) was added to (2.67g,0.01mol) 2-lauryl-N-(2-aminoethyl) imidazoline solution in100 ml acetone in 250 ml Erlenmeyer flask. The mixture was heated under reflux for about 5h, left to stand for 2h and the solvent was distilled off under reduced pressure where a solid product was obtained (yield 77%; m.p130 °C). The infrared spectra of 2-lauryl –N-(2-aminoethyl) N-carboxy methyl imidazoline showed the absorption bands for C=N at 1602 cm^{-1}; at 1650 cm^{-1} for C=O; at 2856 cm^{-1}, 2924 cm^{-1} for CH aliphatic and at 3288 cm^{-1} for NH.

2-Alkyl-N-(2-aminoethyl) N-(2-hydroxypropanesulfonate) III_{a-c}. 3-chloro, 2-hydroxy propane sulfonate (1.7 g , 0.01 mol) was heated under reflux for 1 h with lauryl imidazoline (2.67g , 0.01 mol) in 100 ml ethyl alcohol. The reaction mixture was cooled to room temperature. After removal of inorganic salts and crystallization from ethyl alcohol, a solid product was obtained (yield : 81.2 %; m.p 120 °C). IR spectra: showed expected absorption bands of $SO_2–O$ at 1422 cm^{-1}; at 2974 cm^{-1} and 2924 cm^{-1} for CH aliphatic; at 3356cm^{-1} for –OH stretch, and at 1048 cm^{-1} for N^+ .

Surface Active Properties

Surface tension measurements were carried out using Du Nouy mobile digital surface tensiometer K9. The surface tension was plotted against the logarithm of the concentration of the solution, the critical micelle concentration (*cmc*) values were obtained at points on these curves where inclination started to change. Molecular surface area (A_{min}), efficiency (pC_{20}) effectiveness π_{cmc} free energy of micellization (ΔG_{mic}), were carried out as described elsewhere[12-15].

Corrosion weight loss test:

Weight loss measurements were carried out as described previously [16]. The mild steel used had the following composition (wt %): 0.045C, 0.011P, 0.360Mn, 0.015S, 0.010Si, the remainder Fe. The specimens were polished with different grades of emery paper down to 600, degreased with acetone and dried. Hydrochloric acid (15%) was used as blank corrosion test solution. Triplicate mild steel strips were immersed in 200 ml of inhibited and uninhibited solutions and boiled for 0.5,1.5 and 3.0 hr at 110 ±2 °C. Inhibition efficiencies for 125, 250, 500 and 1000 ppm concentrations of the tested compounds were calculated from the difference in weight loss values in the absence and presence of the surfactants in the 15% hydrochloric acid solution.

RESULTS AND DISCUSSION

Diethylenetriamine reacted with fatty acids (lauric, palmitic and stearic acids) to form fatty acid monoamides, which were cyclized to 2-Alkyl-N-(2-aminoethyl) imidazoline that contain a free amine group (I_{a-c}). The purity of the products was checked by determination of the acid number which showed analytical figures in agreement with the theoretical calculated values (Table 1).

2-Alkyl-N-(2-aminoethyl) imidazolines (I_{a-c}) were further carboxymethylated with sodium monochloroacetate to give 2-Alkyl-N-(2-aminoethyl) N-carboxymethyl imidazoline (II_{a-c}). These derivatives were completely soluble in water as the krafft points were all below 0 ^{0}C.

2-Alkyl-N-(2-aminoethyl) imidazolines (I_{a-c}) were also treated with 3-chloro-2-hydroxypropane sulfonate to produce derivatives containing strong ionic solubilizing sulfonate and hydroxyl groups (III_{a-c}).

Surface characteristics

The coupled hydrophobic and hydrophilic groups within the same molecule impart them evident surface activities. Thus, plots of the surface tension versus logarithm molar concentration of aqueous solution of the surfactants (Fig. 1 and 2) showed that for each chain length, there was a gradual decrease in the surface tension with increase in concentration of solution up to a certain point above which a nearly constant value was obtained.

The surface tension at the cmc (γ_{cmc}), the critical micelle concentration(*cmc*), maximum excess concentrations (Γ) and the minimum surface molecular area (A_{min}) indicated that all members of these derivatives possessed evident surface behavior (Table 2 and 3). It was widely known that the decrease of the surface tension in the region below the (*cmc*) indicated the absorption of the surfactant molecule at the air/water interface and that, in the region above the cmc the surfactant molecules were closely packed at the surface of the solution. Accordingly, the slope of the straight portion near the cmc suggested saturation adsorption of the surfactant molecules at the air/water interface. The amount of adsorption of surfactants at the air/water interface may be calculated by applying the Gibbs adsorption equation [12] .

The data of standard free energy of micellization (ΔG_{mic}) surface tension reduction (C_{20}) , efficiency (pC_{20}), (cmc /C_{20}) and effectiveness (Πcmc) at the liquid / air interface at 25^{0}C was illustrated in (Tables 4 and 5). It was found that both efficiency pC_{20} and the ratio cmc /C_{20} increased with the increase in the number of carbon atoms in the alkyl chain of the hydrophobic portion of the surfactants which means an increase in the tendency of absorption relative to the tendency of micellization as the chain length of the hydrophobe increased.

Weight loss measurements

The values of percentage inhibition efficiency (% IE) and corrosion rate obtained by the weight loss method at different concentration of fatty imidazoline derivatives in 15 % HCl under boiling condition are summarized in (Tables 6-8).

Corrosion inhibition of metal in acidic media by organic inhibitors is commonly attributed to the adsorption of organic molecules on metal surface, and the inhibition efficiency is directly proportional to surfactant coverage . [17]

The % IE and surface coverage (ϴ) were calculated using the following equations:

$$\% IE = \{(W^0 – W) / W^0\} X\ 100$$
$$\Theta = (W^0 – W) / W^0$$

Where W° and W are the weight loss in the absence and presence of inhibitors, respectively. The data showed that the % IE increased with increasing concentration of inhibitor and maximal % IE was obtained at 1000 ppm of inhibitor for all the derivatives. The % IE of alkyl imidazolines at maximal concentration (1000 ppm) follows the order of increasing alkyl chain length = $C_{17}H_{35} > C_{15}H_{31} > C_{11}H_{23}$.

Corrosion inhibition tests at different immersion times were also carried out on mild steel using concentrations of 125, 250, 500 and 1000 ppm,respectivily. The % IE of all inhibitors decreased with increasing test duration from 0.5 to 3.0 h. The decrease in inhibitor effectiveness at longer immersion times (3 h) can be caused by various factors such as increase in hydrogen evolution kinetics or increase in concentration of ferrous ions [18].

One plausible mechanism for the corrosion inhibition exhibited by the fatty imidazoline derivatives used in this study is that through adsorption. Thus, imidazoline derivatives can adsorb onto metal surface through the lone pair of electrons present on nitrogen and/or sulfur atoms and through π electrons present in the imidazoline ring. To test this hypothesis, we plotted the surface coverage (ϴ) and logarithm concentration values where straight lines were obtained (Fig4-6).These observations suggest that adsorption of fatty imidazoline derivatives to the mild steel surface /acidic solution interface occurs according to Temkins adsorption isotherm [19].

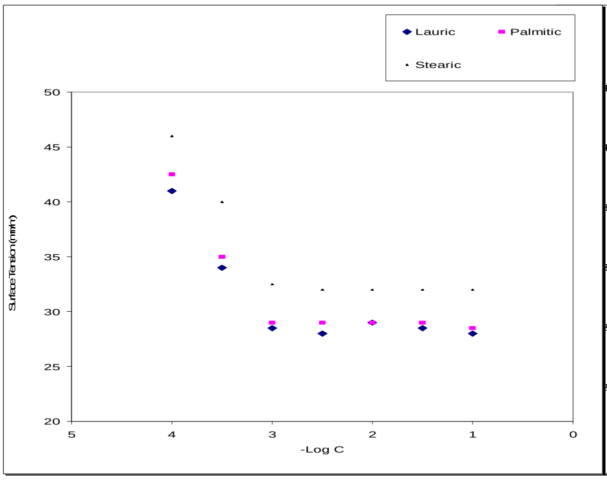


Fig.(1)Plots of surface tension vs.Log C for imidazoline derivatives IIa-c in aqueous solution

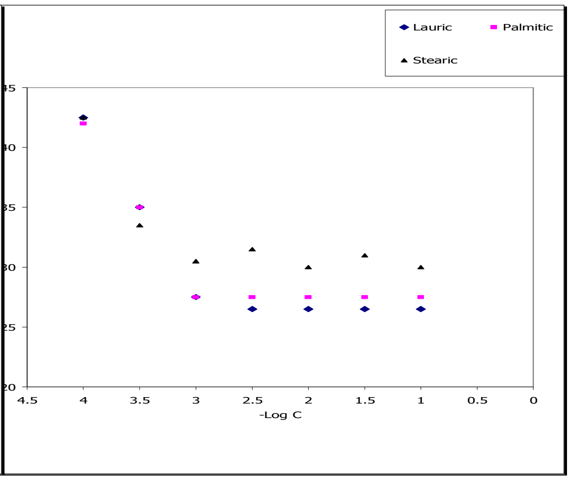
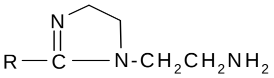


Fig.(2) Plots of surface tension vs.Log C for imidazoline derivatives IIIa-c in aqueous solution

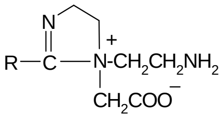
Moreover fatty imidazoline derivatives may exist in acid solution as neutral molecules or in the form of cations. Thus, they can adsorb on the metal either surface in the form of neutral molecules via chemisorption mechanism involving the sharing of electrons between the atoms of nitrogen and / or sulfur with iron [20] or they can also adsorb on the metal surface in the form of a positively charged protonated species which can interact electrostatically with negatively charged metal surfaces [21]. Since the corrosion inhibition mechanism of surfactants depends on their ability to adsorb on the corroding surface, forming a protective layer, so, the critical micelle concentration (cmc) considers a key factor in determining the effectiveness of surfactants as corrosion inhibitors[22]

Table (1) : Physicochemical Characteristics of Alkyl Imidazoline Type I_{a-c} Surfactants.



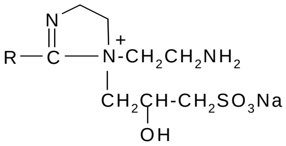
R	*M.P C*	*Yield %*	*Acid number*
$C_{11}H_{23}$	80	83	1.88
$C_{15}H_{31}$	60	85	0.90
$C_{17}H_{35}$	72	90	1.50

Table (2) : Surface Tension at CMC (γ_{cmc}) Critical Micelle Concentration (cmc), Maximum Surface Excess Concentration ($\tau_{max.}$) and Minimum Area/Molecule (A^2) at Liquid air Interface at 25°C of Alkyl Imidazoline Type III_{a-c} Surfactants.



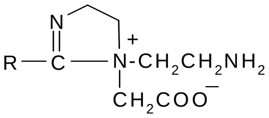
R	*Krafft pt. °C*	*γ_{cmc} mN/m*	*cmc mol/L*	*τx 10^{10} mol/cm^2*	*Area/mol C^{-1} A^2*
$C_{11}H_{23}$	< 0	28.5	8.91×10^{-4}	2.03	81
$C_{15}H_{31}$	< 0	29.1	7.58×10^{-4}	2.28	72
$C_{17}H_{35}$	< 0	32.4	4.46×10^{-4}	2.67	62

Table (3) : Surface Tension at CMC (γ_{cmc}) Critical Micelle Concentration (cmc), Maximum Surface Excess Concentration ($\tau_{max.}$) and Minimum Area/Molecule (A^2) at Liquid air Interface at 25°C of Alkyl Imidazoline Type II_d Surfactants.



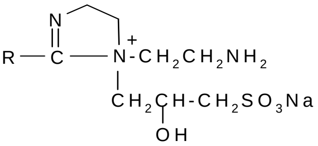
R	*Krafft pt. °C*	*γ_{cmc} mN/m*	*cmc mol/L*	*τx 10^{10} mol/cm^2*	*Area/mol C^{-1} A^2*
$C_{11}H_{23}$	<0	26.8	2.9×10^{-3}	2.28	72
$C_{15}H_{31}$	<0	28.0	2.9×10^{-4}	2.46	67
$C_{17}H_{35}$	<0	30.7	3.4×10^{-4}	2.80	59

Table (4) : Standard free Energy of Micelleization (ΔG_{mic}), Surface Tension Reduction (C_{20}), Efficiency (PC_{20}), cmc/c_{20} Ratio and Effectiveness (π_{cmc}) at the Liquid air Interface at 25°C of Alkyl Imidazoline Type II_{a-c} Surfactants.



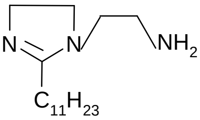
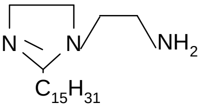
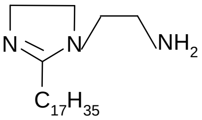
R	*ΔG_{mic}* *KJ/mol*	*C_{20}*	*PC_{20}*	*cmc/C_{20}*	*π_{cmc}* *mN/m*
$C_{11}H_{23}$	-17.10	5.98 x 10^{-4}	3.22	1.48	21.94
$C_{15}H_{31}$	-17.50	4.89 x 10^{-4}	3.30	1.55	22.44
$C_{17}H_{35}$	-18.79	2.51 x 10^{-4}	3.60	1.77	23.71

Table (5) : Standard Free Energy of Micelleization (ΔG_{mic}), Surface Tension Reduction (C_{20}), Efficiency (PC_{20}), cmc/c_{20} Ratio and Effectiveness (π_{cmc}) at the Liquid air Interface at 25°C of Alkyl Imidazoline Type III_d Surfactants.



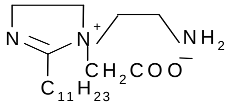
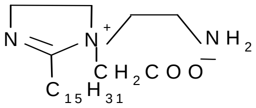
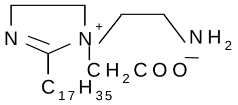
R	*ΔG_{mic}* *KJ/mol*	*C_{20}*	*PC_{20}*	*cmc/C_{20}*	*π_{cmc}* *mN/m*
$C_{11}H_{23}$	-17.38	5.55 x 10^{-4}	3.25	1.43	21.65
$C_{15}H_{31}$	-18.51	3.29 x 10^{-4}	3.48	1.53	22.16
$C_{17}H_{35}$	-19.07	1.07 x 10^{-4}	3.97	1.66	23.20

Table (6): Corrosion parameters[a] for mild steel in boiling 15% HCl (105 ±2) in the absence and presence of four concentrations of three inhibitors for 0.5 , 1.5 and 3 hours.

Concentration (ppm)	*Weight Loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*
0.5 h									
	1.030	-	0.504	1.030	-	0.504	1.030	-	0.504
125	0.423	58.93	0.208	0.385	62.62	0.504	0.379	63.20	0.186
250	0.201	80.48	0.099	0.197	80.87	0.189	0.189	81.65	0.093
500	0.117	88.54	0.057	0.111	89.22	0.097	0.105	89.80	0.051
1000	0.020	98.05	0.009	0.017	98.34	0.008	0.014	98.64	0.007
1.5 h									
	1.850	-	0.304	1.850	-	0.304	1.850	-	0.304
125	1.220	33.56	0.200	1.163	37.13	0.191	1.143	38.20	0.187
250	0.911	50.57	0.149	0.796	56.97	0.130	0.739	60.05	0.121
500	0.425	77.02	0.069	0.397	78.54	0.065	0.373	79.83	0.061
1000	0.113	93.89	0.018	0.093	94.97	0.015	0.085	95.40	0.014
3 h									
	2.146	-	0.176	2.146	-	0.176	0.176	-	0.176
125	1.660	22.64	0.136	1.530	28.70	0.125	1.490	30.56	0.122
250	1.320	38.49	0.108	1.280	40.35	0.105	1.190	44.54	0.097
500	0.980	54.33	0.080	0.923	56.90	0.075	0.918	57.22	0.075
1000	0.701	71.99	0.049	0.570	73.43	0.046	0.490	77.16	0.040

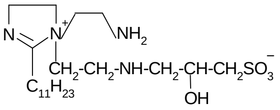
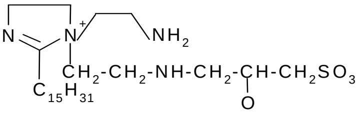
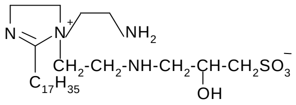
[a] Determined from weight loss measurements , [b] inhibition efficiency and [c] corrosion rate in millimeters per year

Table (7): Corrosion parameters [a] for mild steel in boiling 15% HCl (105 ±2) in the absence and presence of four concentrations of three inhibitors for 0.5 , 1.5 and 3 hours.

Concentration (ppm)	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*
0.5 h									
	1.020	-	0.503	1.020	-	0.503	1.020	-	0.503
125	0.396	61.17	0.195	0.372	63.52	0.183	0.369	63.82	0.182
250	0.195	80.88	0.096	0.188	81.56	0.093	0.182	82.15	0.089
500	0.105	89.70	0.051	0.094	90.78	0.046	0.090	91.17	0.044
1000	0.013	98.72	0.006	0.011	98.92	0.005	0.010	99.02	0.009
1.5 h									
	1.880	-	0.309	1.880	-	0.309	1.880	-	0.309
125	1.020	45.74	0.167	0.980	47.87	0.161	0.950	49.46	0.156
250	0.751	60.05	0.123	0.711	62.1	0.116	0.696	62.97	0.114
500	0.396	78.93	0.065	0.323	82.81	0.053	0.301	83.98	0.049
1000	0.109	94.20	0.017	0.081	95.69	0.013	0.076	95.95	0.012
3 h									
	2.149	-	0.176	2.149	-	0.176	2.149	-	0.176
125	1.250	41.83	0.103	1.223	43.08	0.101	1.197	44.29	0.098
250	1.020	52.53	0.084	0.980	54.39	0.081	0.971	54.81	0.079
500	0.683	68.21	0.056	0.655	69.52	0.054	0.635	70.45	0.052
1000	0.318	85.20	0.026	0.305	85.80	0.025	0.289	86.55	0.024

[a] Determined from weight loss measurements , [b] inhibition efficiency and [c] corrosion rate in millimeters per year

Table (8): Corrosion parameters [a] for mild steel in boiling 15% HCl (105 ±2) in the absence and presence of four concentrations of three inhibitors for 0.5 , 1.5 and 3 hours.

Concentration (ppm)	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*	*Weight loss (g)*	*I.E.[b] (%)*	*C.R.[c] (mmpy)*
0.5 h									
	1.080	-	0.532	1.080	-	0.532	1.080	-	0.532
125	0.369	65.83	0.181	0.355	67.13	0.175	0.333	69.17	0.164
250	0.197	81.76	0.097	0.189	82.50	0.093	0.182	83.15	0.090
500	0.099	90.83	0.048	0.094	91.29	0.046	0.089	91.75	0.043
1000	0.015	98.61	0.007	0.013	98.79	0.006	0.011	98.98	0.005
1.5 h									
	1.900	-	0.321	1.900	-	0.312	1.900	-	0.312
125	1.180	37.89	0.193	1.119	41.12	0.184	1.115	41.32	0.183
250	0.890	53.12	0.146	0.879	53.70	0.144	0.871	54.16	0.113
500	0.398	79.05	0.065	0.395	79.21	0.064	0.391	79.42	0.064
1000	0.096	94.94	0.015	0.084	95.31	0.013	0.079	95.84	0.012
3 h									
	2.160	-	0.177	2.160	-	0.177	2.160	-	0.177
125	1.600	25.93	0.131	1.560	27.78	0.128	1.530	29.17	0.125
250	1.180	45.37	0.096	1.114	48.43	0.091	1.105	48.84	0.091
500	0.913	57.73	0.075	0.903	58.19	0.074	0.900	58.33	0.073
1000	0.511	76.34	0.042	0.452	79.07	0.037	0.405	81.25	0.033

[a] Determined from weight loss measurements , [b] inhibition efficiency and [c] corrosion rate in millimeters per year

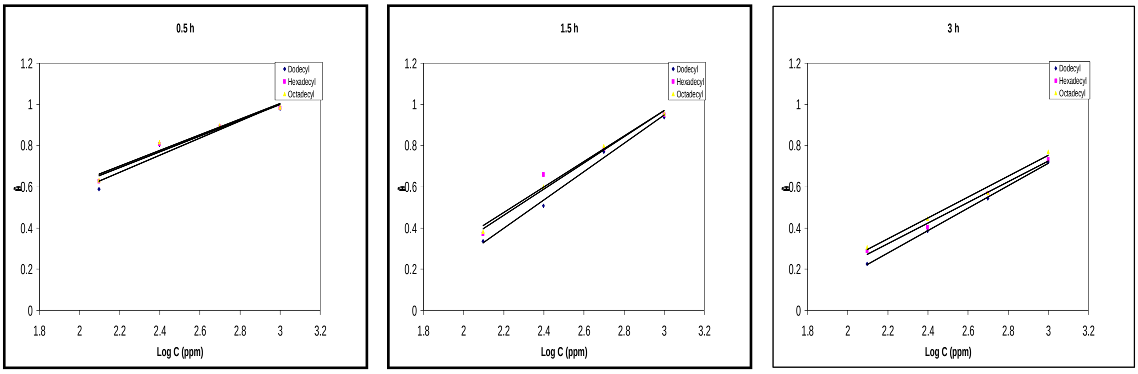


Fig.(3): Temkin's adsorption isotherm plots for the adsorption of 2-Alkyl, N-(2-aminoethyl) imidazoline in 15% boiling HCl on the surface of mild steel

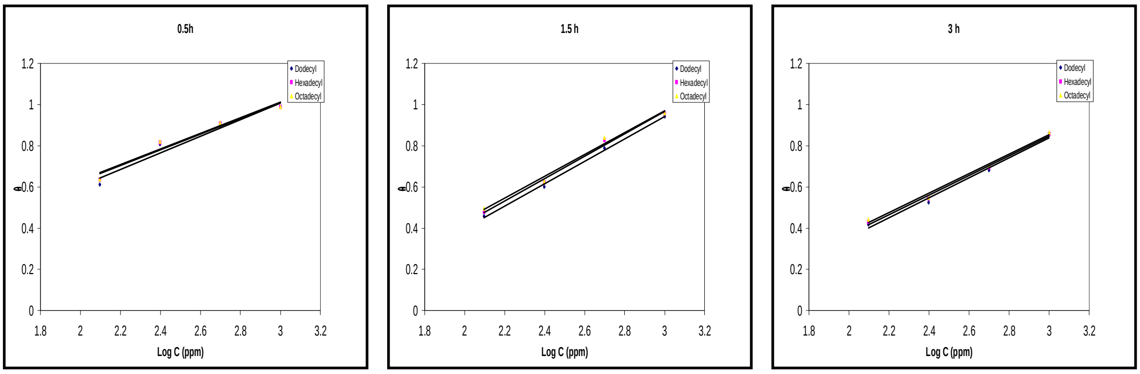


Fig.(4): Temkin's adsorption isotherm plots for the adsorption of 2-Alkyl,N-(2-aminoethyl)N-carboxymethyl imidazoline in 15% boiling HCl on the surface of mild steel

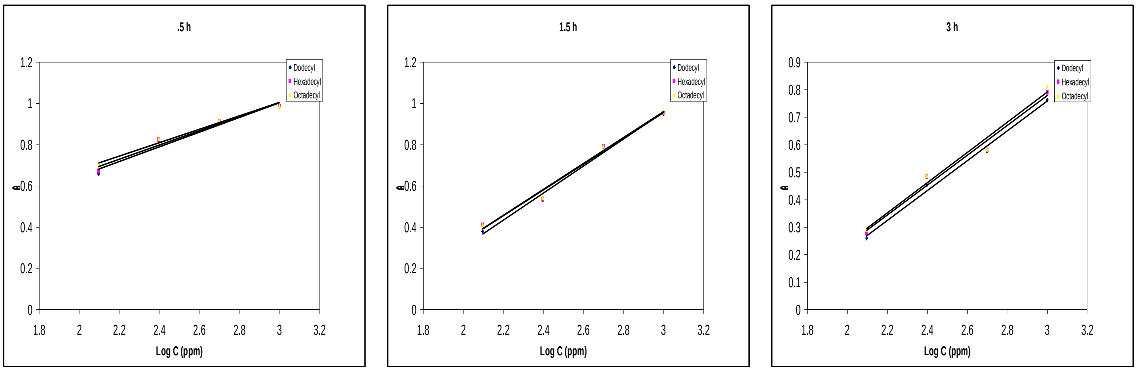


Fig.(5) Temkin's adsorption isotherm plots for the adsorption of 2-Alkyl, N-(2-aminoethyl) N-(2-hydroxypropanesulfonate) in 15% boiling HCl on the surface of mild steel

CONCLUSION

(i) All the fatty imidazoline derivatives are surface active molecules as they have the ability to reduce the surface tension and to adsorb at the liquid / air interface as well as micellization .
(ii) They show good inhibition efficiency in boiling 15% HCl .
(iii)The inhibition efficiency of all derivatives increases with increase inhibitor concentration.
(iv) The inhibition efficiency of all compounds decreases with increase immersion time .
(v) The inhibition efficiency of alkyl imidazoline derivatives follows the order of increasing alkyl chain length: $C_{17}H_{35} > C_{15}H_{31} > C_{11}H_{23}$.

(vi) The adsorption of all derivatives on mild steel from acidic solution obeys a Temkin's adsorption isotherm.

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