Preparation, Characterization of Surfactants and study of Their corrosion Inhibitors for Carbon-Steel in acidic media

Hawraa .K. Dhaef &Ala' a. A. Hussain & Kawkab .A. Hussain

Chemistry department , Collage of Education for pure Sciences

Basrah university

Mh19112006@yahoo.com

Abstract

Tow Compounds of Gemini Surfactants Cationic were prepared the hydrophilic (4,4'- Sulfonyl bis (N-hexadecyl benzenaminium) di bromide H_{22}) and (N,N- di hexadecyl-4-(4-(hexadecyl ammonio)phenyl sulfonyl) benzenaminium) di bromide H_{33}) , these surfactants were characterized by (IR,^{1}H.NMR,) and as corrosion inhibitor for Carbon-Steel in 0.5 M HCl solution, two methods were used for this study weight loss and galvanostatic polarization techniques. The result show that the inhibition efficiency of inhibitors increases with concentration to attain (80.60%,82.27%) of H_{33} and H_{22} at 1×10^{-4} M HCL, time 240 min and temperature 25°C.. Polarization curves revealed that the studied inhibitors represent a mixed – type inhibitors .

Keyword : Acid inhibition , Gemini Surfactants ,Adsorption

Introduction

The c-steel is used as essential part in the manufacturing of installations used in the petroleum and other industries. The use of inhibitors is one of the most practical methods for protection against metallic corrosion, especially in acidic media(Clubby *et al*., 1990 ; Sputnik *et al*., 1995). Inhibitors are chemical substances added to liquid to prevent corrosion or to control it at an acceptably low rate. They are used mainly in closed or circulating systems(Craddock *et al*., 2004; Ajmal *et al*., 1999) . And are selected for their effectiveness in protecting the specific metal or combination of metals in a given system(Walker., 2003; Yu and Garosshen., 2004). Most commercial acid inhibitors are organic compounds containing heteroatom such as nitrogen, oxygen, sulpher, phosphor atoms, by which the inhibitor molecules are adsorbed on the metal surface in acidic media(Obi-Egbedi and Obot., 2011), thus resulting adsorption film acts as a barrier separating the metal form the active sites(Lgmri et al., 2003; Popova *et al*., 2004; Elayyach *et al*., 2006). As a representative type of these organic inhibitors, quaternary ammonium salts have been demonstrated to be highly cost-effective and used widely in various industrial processing for preventing corrosion of iron and steel in acidic media(Saleh et al., 2006; Niu *et al*., 2005; Mohanan et al., 2005) . This study is concerned with the evaluation of two synthesized cationic surfactants (H_{22}, H_{33}) as corrosion inhibitors for c-steel in an acidic medium (0.5 M HCl) using weight loss and galvanostatic polarization techniques.

Practical

Preparation of Cetyl bromide

Cetyl bromide was prepared by the reaction of (48.48 gm , 1 mole) of cetyl alcohol with (54.4 gm, 0.67 mole) of Hydrobromic acid in round bottom flask, then the reactant was refluxed for 6 hrs. after completion of reaction. The mixture was cooled and separation the oil layer from aqueous layer in separation funnel, after separation, added methanol to extract the unreacted cetyl alcohol. The oil layer was drying by added magnesium sulfate, filtered off, evaporating of solvent to obtained the product with yield 75% (Ac.,1916).

Preparation of H_{22}

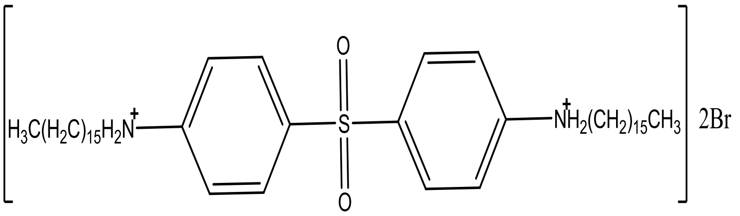
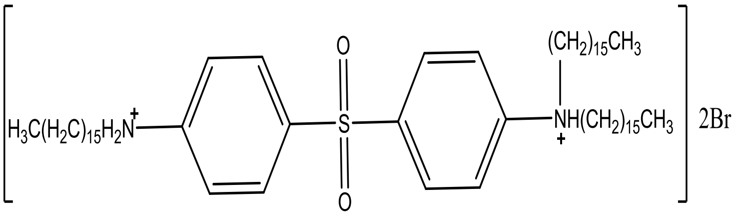
Compound H_{22} was prepared through the react of (6.2 gm , 1 mole) of 4,4'-Sulfonyl di aniline dissolve in 15 ml of ethanol with (5.25 gm , 0.017 mole) (Esumi *et al*., 1996; Esumi *et al*., 1998) of cetyl bromide, the mixture was reflux for 48 hrs, then the reaction content was cooled to obtained a solid product filtered off and recrystallized from methanol to give final product with yield 75%.

Preparation of H_{33}

Compound H_{33} was prepared from solving (6.2 gm , 1 mole) of 4,4'-Sulfonyl di aniline in 15 ml of ethanol with adding (22.92 ml , 3 mole) (Esumi *et al*., 1996; Esumi *et al*., 1998) of cetyl Bromide with stirring and refluxed for 48 hs . after completion of reaction , the reaction mixture was cooled , the solid thus obtained was filtered off , recrystallized from methanol , yield 70%.

The structure and some physical properties of Surfactants compounds were given in Table 1.

Table 1: Some Physical Properties of Surfactants Compounds.

Compound	Chemical structure	Physical Stat	Color	Melting Point
H_{22}		Powder	Whit	158-160°C
H_{33}		Powder	Whit	195-200°C

Experimentalmethod

The C-steel sample used (N-80) had the composition (wt%) 0.3C, 1.2Mn, 0.05P, 0.06S and the remainder Fe .coupons of C-steel with dimension of 3 *1.9 *0.4 cm were used for weight loss measurements . For galvanostatic studies a cylinder rod embedded in araldite with an expose surface area of ($1cm^2$) was used .The electrode surface was polished with different grades of emery paper ,degreased with acetone , and rinsed with distilled water . (0.5 M) A.R grade hydrochloric acidwas used for preparing the corrosive solution . For weight loss experiments , the cleaned C-steel coupons were weighed before and after immersion in 25 ml of the test solution for a period of time 4hrs . The weight loss for experiments was expressed in (gm) .Galvanostatic polarization studies were carried out using Bank EIEIKTRONKIK INTELLGENT CONTROLS Model M Lab 200-Chemistry Department-College of Education for pure Sciences – Basrah University ,for calculation of electrochemical parametersThree compartment cell with a saturated calomel electrode (Reference electrode), platinum for auxiliary electrode and working electrode was used.

Results and Discussion

Identification of Prepared Surfactants

The chemical structure of the prepared Surfactants were confirmed by the FTIR, and H^1NMR.

FTIR Spectra

FTIR Spectra of the synthesized compounds were carried out using (FT- IR- 8400S. Fourier Transform Infrared Spectrophotometer) Shimadzu (Japan)- Chemistry Department-College of Education for pure Science-Basrah University. The Spectra were shown in Figs 1 and 2 and the characterized bands were given in Table 2. (Selverstein and Clayton., 2000; Ponchert., 1983; Selverstein and Wbster., 1998).

Table 2: Characterized Bands in FTIR Spectra for Prepared Surfactants.

Compound H_{22}	
C-N^+ stretch	1145
N-H stretch	3466-3369
Aliphatic C-H stretch	2918-2850
Aromatic –C=C- stretch	1598
C-H bend	1471
Aromatic C-N bend	1348
O=S=Osym., and assym.,	1159-1222
Aromatic C-H bend	727
Compound H_{33}	
C-N^+ stretch	1139
N-H stretch	3452-3385
Aliphatic C-H stretch	2920-2848
Aromatic –C=C- stretch	1597
C-H bend	1467
Aromatic C-N bend	1380
O=S=Osym., and assym.,	1109-1139
Aromatic C-H bend	720

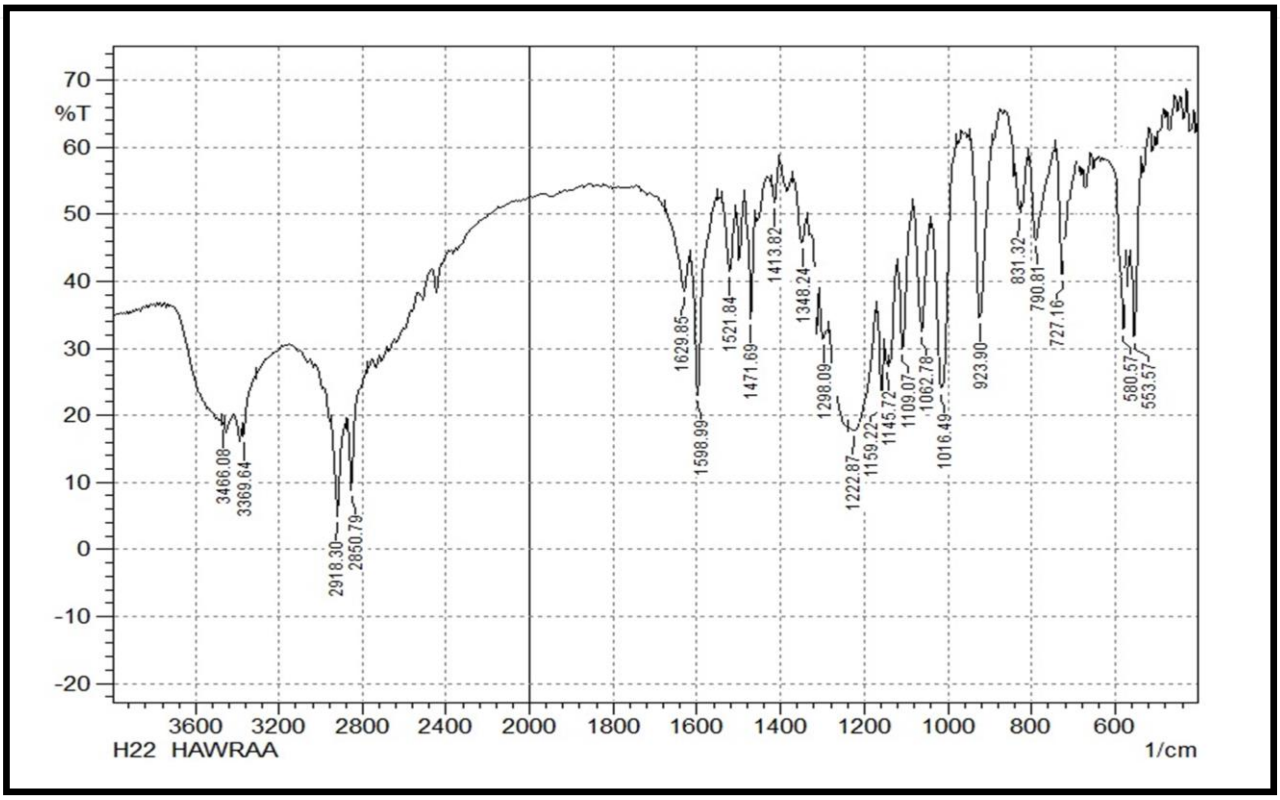


Fig1: FTIR Spectrum of H_{22}

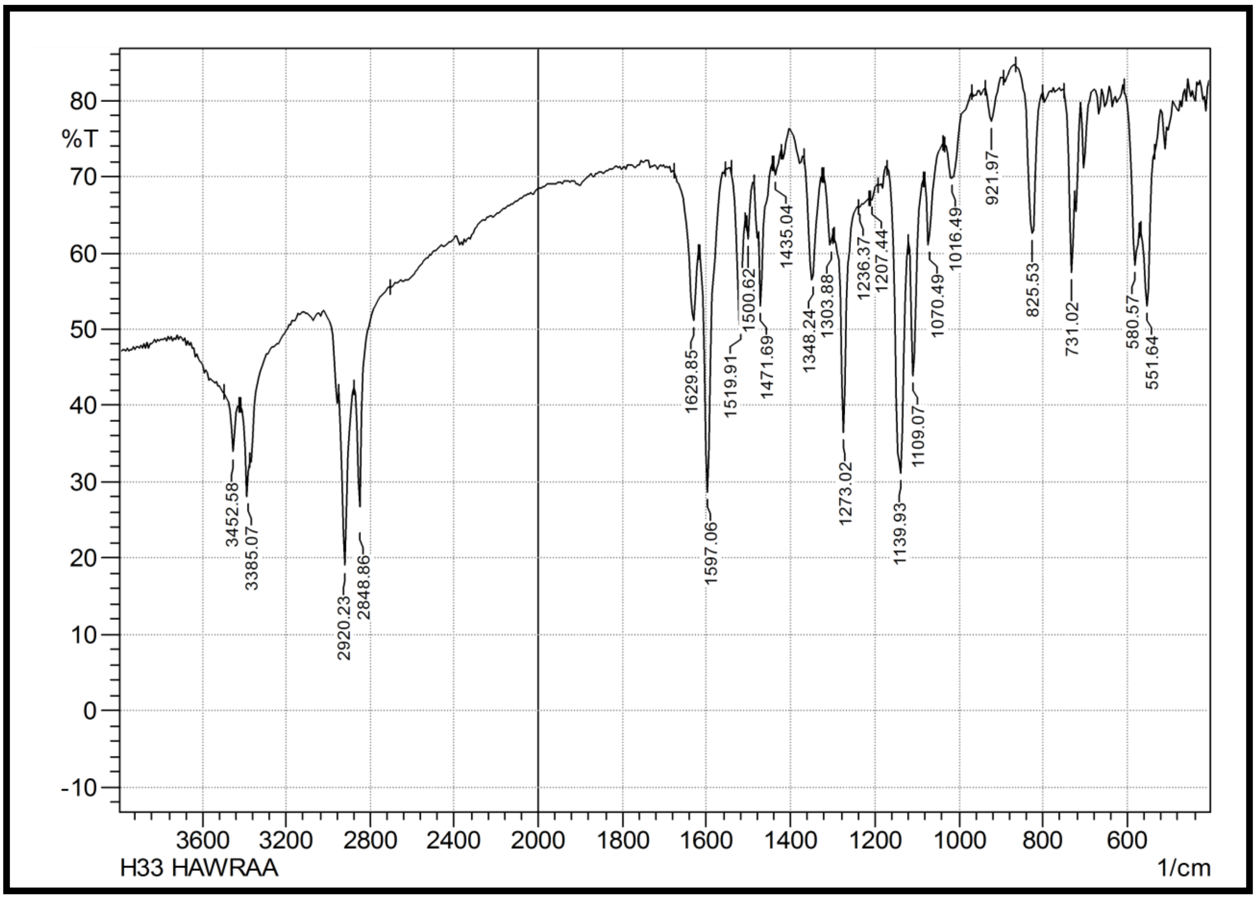
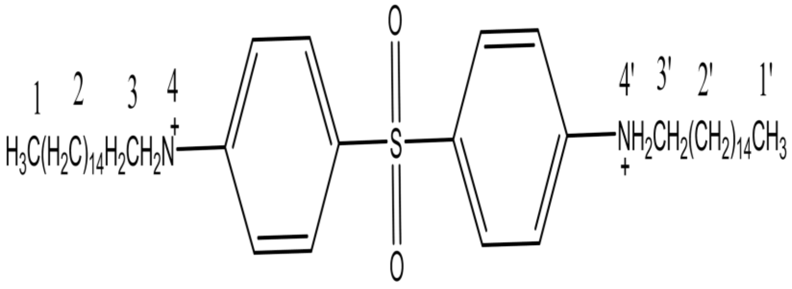
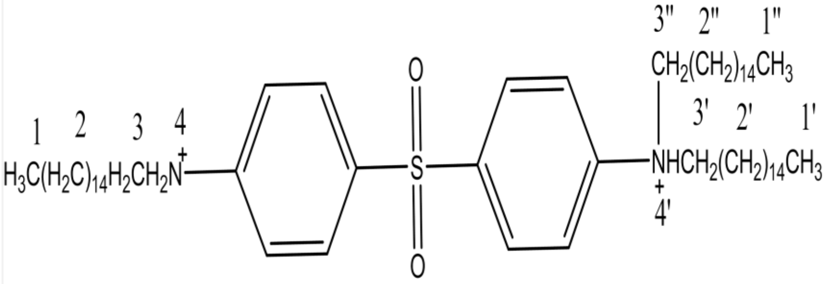


Fig2: FTIR Spectrum of H_{33}

H^1NMRSpectra

H^1NMR Spectra of the synthesized compounds were carried out using BRUKER, Germany-400 MHZ– Iran – Central Laboratory of Isfahan University. Chemical shifts of H^1NMR for the prepared Surfactants in d DMSO are given in Table 3 and the spectra was shown in Figs (3 and 4).(Selverstein and Clayton., 2000; Ponchert., 1983)

Table 3: Chemical Shifts of H^1NMR for Prepared Surfactants in DMSO.

Data of H^1NMR for Compound H_{22}	
Compound	**Data of chemical shifts in ppm**
	$H_{1,1'}$, 6H, σ = 0.83-0.87 ppm $H_{2,2'}$, 56H, σ = 1.23-1.50 ppm $H_{3,3'}$, 4H, σ = 3.00-3.01 ppm $H_{4,4'}$, 4H, σ = 7.43-7.45 ppm Ar-H , 8H, σ = 6.56-7.48 ppm
Data of H^1NMR for Compound H_{33}	
Compound	**Data of chemical shifts in ppm**
	$H_{1,1',1''}$, 9H, σ = 0.85 ppm $H_{2,2',2''}$, 84H, σ= 1.23 ppm $H_{3,3',3''}$, 6H, σ= 3.00-3.02 ppm $H_{4,4',4''}$, 3H, σ = 7.43-7.45 ppm Ar-H , 8H, σ = 6.56-7.48 ppm

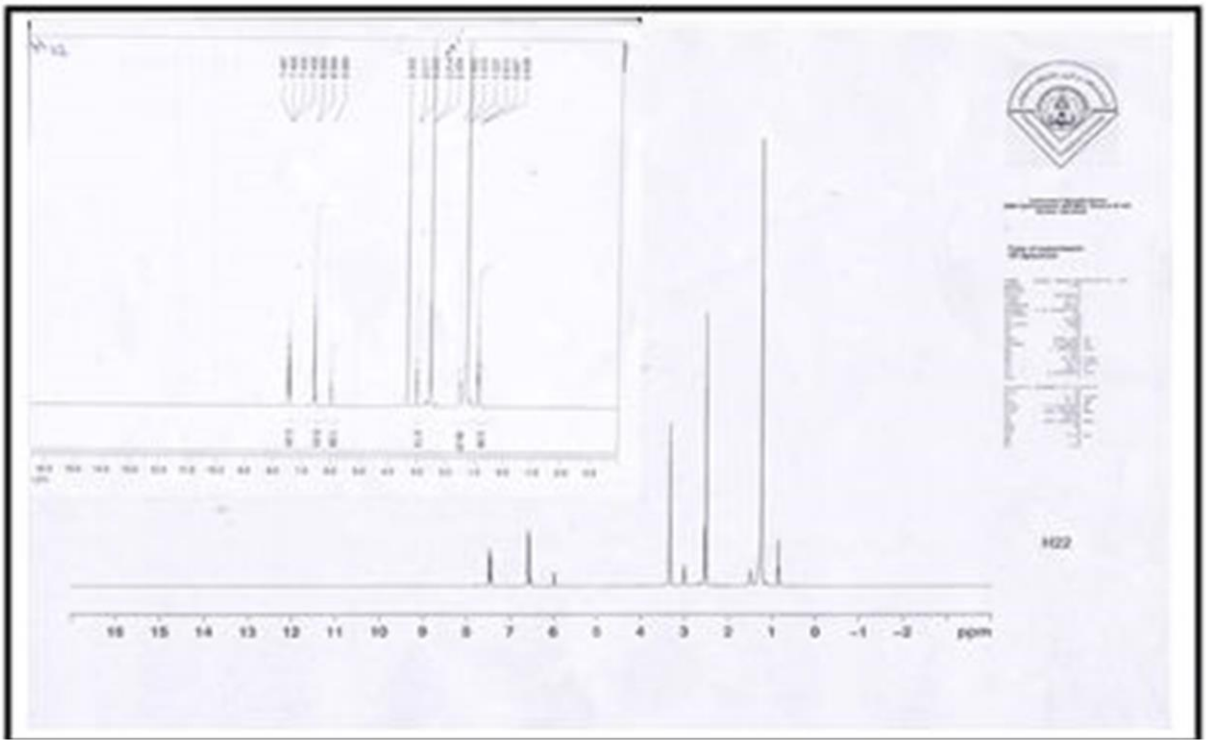


Fig3: HNMR Spectrum of H_{22}.

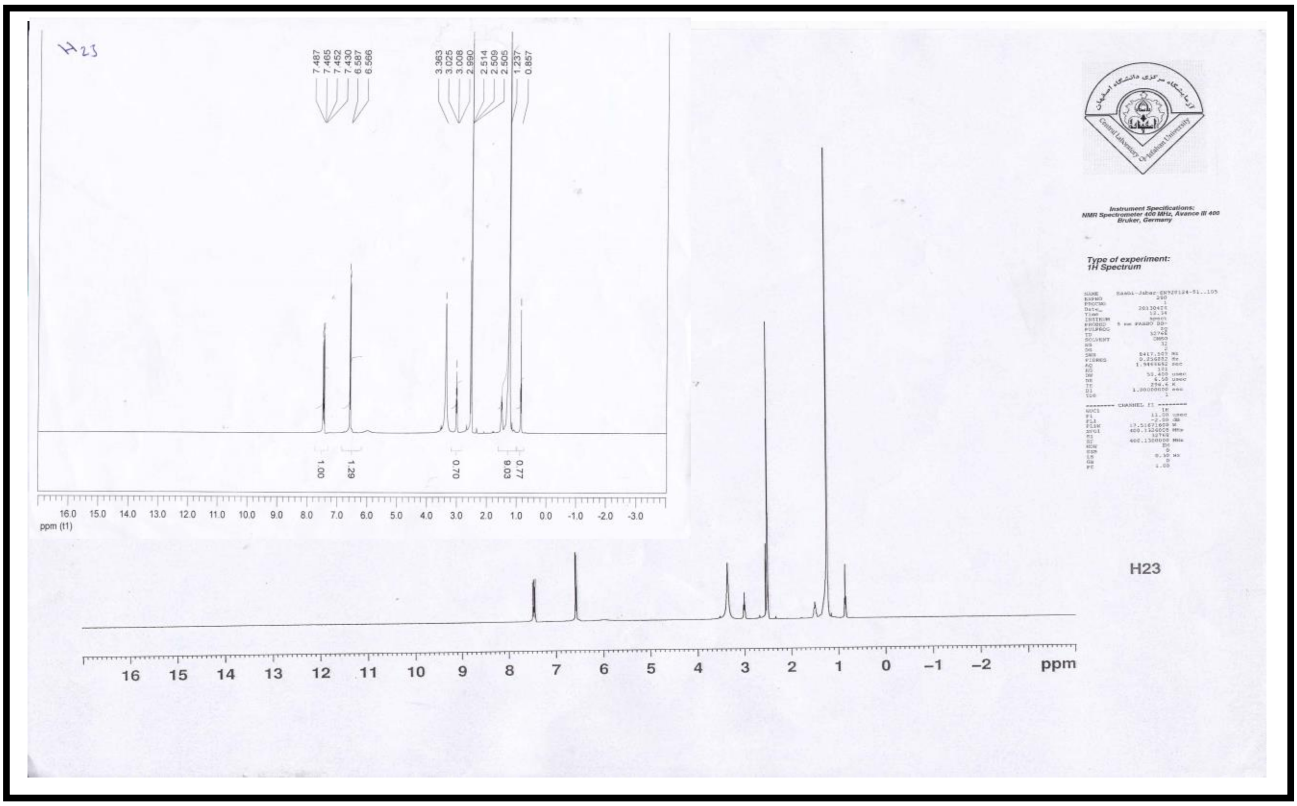


Fig4: HNMR Spectrum of H_{33}

Weight Loss Measurements

The results of the measurements are shown in Tables 4 and 5 for the corrosion of C-Steel in 0.5M HCl in the absence and in the presence of different concentrations of the Cationic Gemini surfactant (H_{22})&(H_{33}) at constant temp 25°C.The percentage of inhibition efficiency %IE and surface coverage parameter θ which represents the part of the surface covered by the inhibitor molecules were calculated using the following equations (Abdallah *et al*., 2008) :-

$$\%IE=[\ 1-\frac{W_{add}}{W_{free}}\ ]\ \times 100 \quad ----------- \quad (1)$$

$$\theta\ =\ [1-\frac{Wadd}{Wfree}\ ] \quad ----------- \ (2)$$

Where W_{free} and W_{add} are the weight losses of C-Steel in absence and presence of inhibitors

Fig 5representVariation of the Weight Loss as a Function of the Time in the absence of inhibitors at 25°C in 0.5M HCl

While Fig 6 and 7 represent the variation of the inhibition efficiency %IE as function of the time. The inhibition efficiency increased with increasing the inhibitor concentration . The corrosion rate R_{corr} where calculated using the following equation(Deng *et al.*, 2011):-

$$R_{corr} = \frac{\Delta W}{St} \quad \text{------------} \quad (3)$$

Where ΔW= is the weight losses of matel , S= is the surface area (cm^2),T= is the exposed time (min)

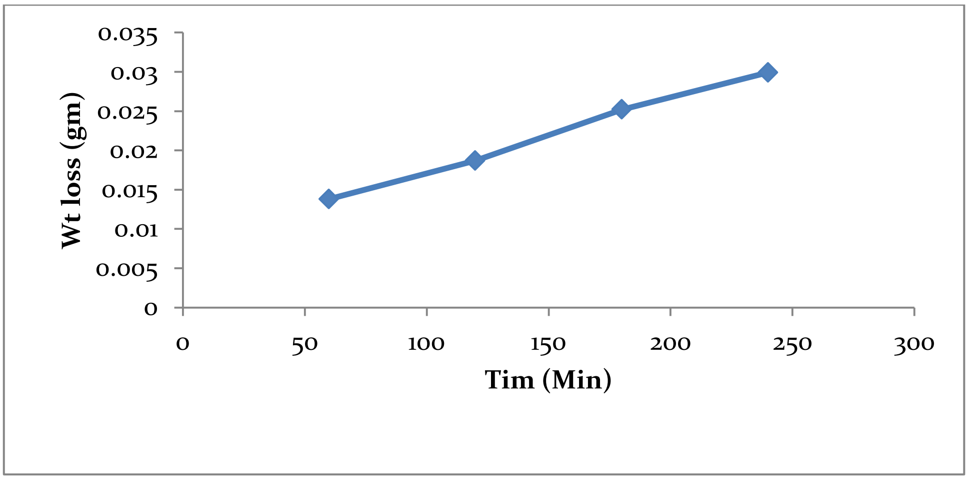


Fig5: Variation of the Weight Lossas a Function of the Time in the absence of inhibitors at 25°C in 0.5M HCl.

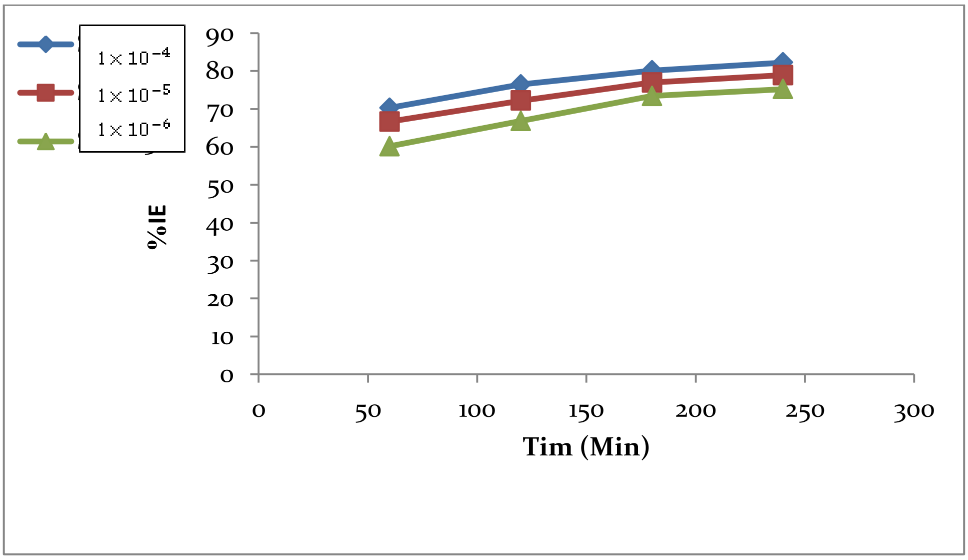


Fig 6 : Variation of the Inhibition Efficiency %IE as a Function of the Time in the Presence of Different Concentrations of (H_{22}) in 0.5M HCl at 25°C.

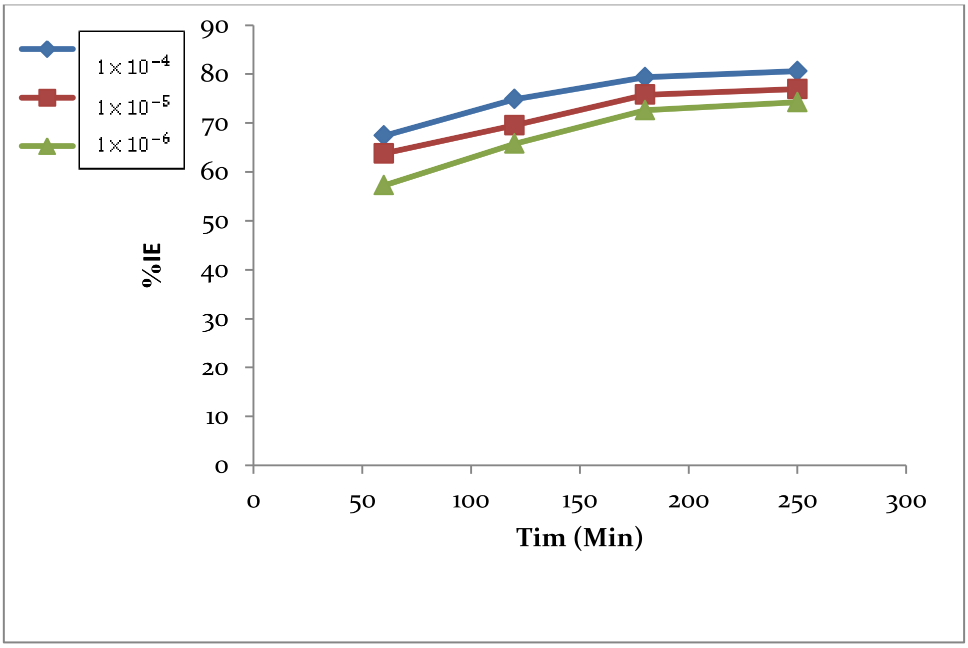


Fig 7 : Variation of the Inhibition Efficiency %IE as a Function of the Time in the Presence of Different Concentrations of (H_{33}) in 0.5M HCl at 25°C.

Table 4 : Effect of (H_{22}) on the Dissolution C- steel in 0.5M HCl.

Time (Min)	60				120				180				240			
Conc (M)	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE%	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE%	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE%	Θ	Wt-loss gm	Rcorr gm.cm^{-2}.min^{-1}	IE%	Θ
0.00	0.0138	81.32×10^{-7}	–	–	0.0187	91.38×10^{-7}	–	–	0.0252	10.17×10^{-6}	–	–	0.0299	15.01×10^{-6}	–	–
1×10^{-6}	0.0055	59.83×10^{-7}	60.14	0.6014	0.0062	33.72×10^{-7}	66.84	0.6684	0.0067	24.29×10^{-7}	73.41	0.7341	0.0074	20.12×10^{-7}	75.25	0.7525
1×10^{-5}	0.0046	50.04×10^{-7}	66.66	0.6666	0.0052	28.28×10^{-7}	72.19	0.7219	0.0058	21.03×10^{-7}	76.98	0.7698	0.0063	$10^{-7}17.13\times$	78.92	0.7892
1×10^{-4}	0.0041	44.60×10^{-7}	70.28	0.7028	0.0044	23.93×10^{-7}	76.47	0.7647	0.0050	18.13×10^{-7}	80.15	0.8015	0.0053	14.41×10^{-7}	82.27	0.8227

Table 5 : Effect of (H_{33}) on the Dissolution C- steel in 0.5M HCl

Time (Min)	60				120				180				240			
Conc (M)	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE%	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE%	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE%	Θ	Wt-loss gm	Rcorr $gm.cm^{-2}.min^{-1}$	IE%	Θ
0.00	0.0138	81.32×10^{-7}	–	–	0.0187	91.38×10^{-7}	–	–	0.0252	10.17×10^{-6}	–	–	0.0299	15.01×10^{-6}	–	–
1×10^{-6}	0.0059	64.18×10^{-7}	57.24	0.5724	0.0064	34.81×10^{-7}	65.77	0.6577	0.0069	25.02×10^{-7}	72.61	0.7261	0.0077	20.94×10^{-7}	74.24	0.7424
1×10^{-5}	0.0050	54.39×10^{-7}	63.76	0.6376	0.0057	31.00×10^{-7}	69.51	0.6951	0.0061	22.12×10^{-7}	75.79	0.7579	0.0069	$10^{-7}18.76\times$	76.92	0.7692
1×10^{-4}	0.0045	48.95×10^{-7}	67.39	0.6739	0.0047	25.56×10^{-7}	74.86	0.7486	0.0052	18.85×10^{-7}	79.36	0.7936	0.0058	15.77×10^{-7}	80.60	0.8060

Polarization Measurements.

Polarization behavior of C-steel in 0.5M HCl in the presence and absence of Cationic Gemini surfactant (H_{22})&$(H_{33})$is shown in Figs 8 .It was found that , both anodic and Cathodic reaction ofC-steel electrode corrosion were inhibited with increasing concentration of synthesized inhibitors . These results suggest that not only the addition of synthesized inhibitors reduce anodic dissolution but also retard the hydrogen evolution reaction.

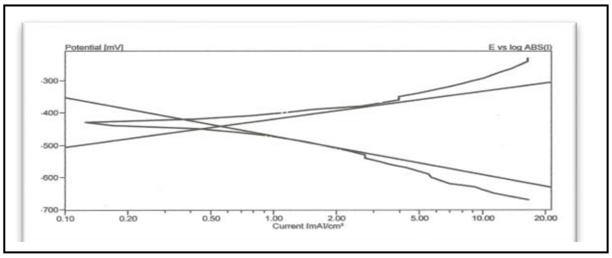
Electrochemical parameters such as corrosion potential (E_{corr}) , corrosion current density (I_{corr}), Cathodic Tafel constant (βc) and anodic Tafel constant (βa) were calculated from Tafel plots. Data in Tables6 and 7 represents the results of electrochemical param-eters . The addition of inhibitors causes a decrease of the current density, the maximum decrease in I_{corr} was observed for (H_{22})&(H_{33}). The Ecorr values of (H_{22})&(H_{33})inhibitor were shifted slightly toward both Cathodic and anodic directions and did not show any definite trend in 0.5M HCl. This may be contributed to the mixed –type behavior of the studied inhibitors . Moreover , these inhibitors caused change in the anodic and Cathodic Tafel slope indicating that , the inhibitors are affecting the anodic and Cathodic reaction mechanism without blocking the reaction sites of C-steel surface . Inhibition efficiency (%IE) was calculated by the relation(Savitri and Mayanna., 1996):-

$$\%\ IE = \left[1 - \frac{Iadd}{Ifree}\right] \times 100 \quad \text{-----------} \quad (4)$$

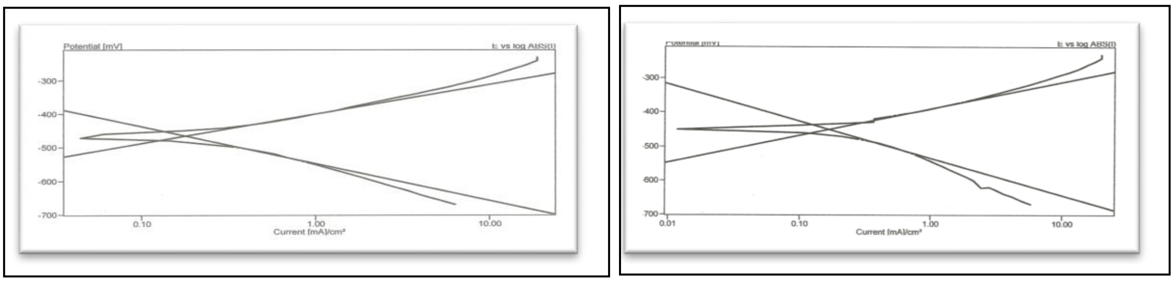
Where

I_{add} , I_{free} are the corrosion current in absence and presence of inhibitors .

Data in Table 6 and 7 shows that the inhibition efficiency increase-ed withincreasing theinhibitor concentration ,indicating the inhibiting effect of these compound.

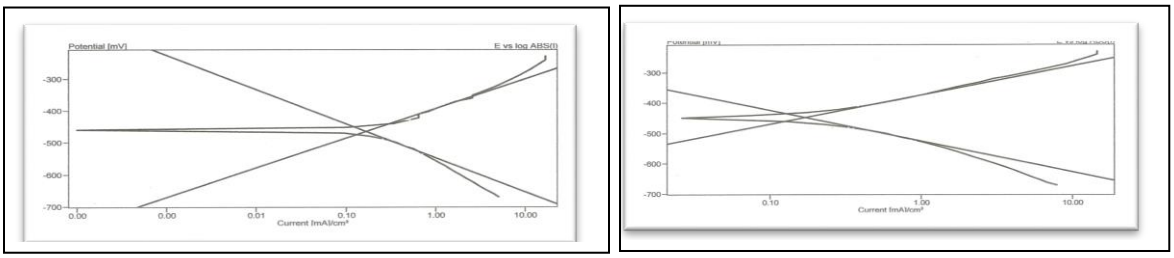


(0.5 M) HCl



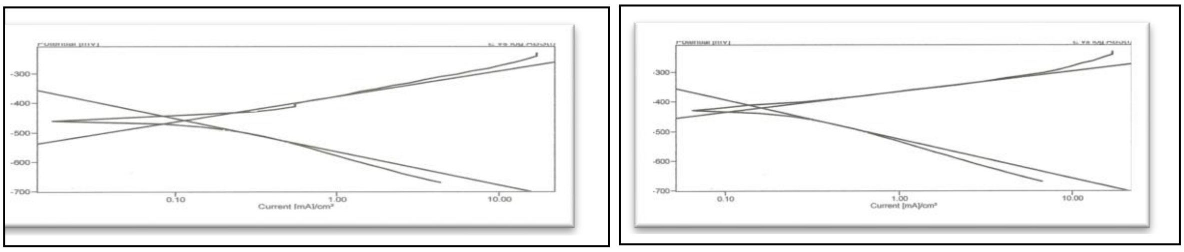
$(1\times 10^{-6}$ M) H_{22}

$(1\times 10^{-6}$ M) H_{33}



$(1\times 10^{-5}$ M) H_{22}

$(1\times 10^{-5}$ M) H_{33}



$(1\times 10^{-4}$ M) H_{22}

$(1\times 10^{-4}$ M) H_{33}

Fig 8 Galvano Static Polarization Curves of C-steel in 0.5M HClinabsence and PresenceInhibitor at 25°C.

Table 6:- The Values of Corrosion Parameters for the Corrosion of C-steel in 0.5M HCl by Galvanostatic Polarization in Presence (H_{22}).

Conc (M)	Icorr μA/Cm^2	Ecorr mV	βc mV.dec^{-1}	βa mV.dec^{-1}	IE %
0.00	555.38	-441.6	-119.7	86.9	–
1×10^{-6}	161.40	-451.6	-104.2	72.0	70.93
5×10^{-5}	150.84	-462.4	-100.9	80.3	72.84
1×10^{-4}	110.37	-454.3	-111.4	84.6	80.12

Table 7:- The Values of Corrosion Parameters for the Corrosion of C-steel in 0.5M HCl by Galvanostatic Polarization in Presence (H_{33}).

Conc (M)	Icorr μA/Cm^2	Ecorr mV	βc mV.dec^{-1}	βa mV.dec^{-1}	IE %
0.00	555.38	-441.6	-119.7	86.9	–
1×10^{-6}	165.54	-443.8	-103.5	73.1	70.19
5×10^{-5}	160.13	-440.7	-109.2	93.0	71.10
1×10^{-4}	122.53	-414.5	-118.4	66.7	77.93

The following conclusions could be predict from this study:-

1- The corrosion of c-steel in 0.5M HCl is inhibited by the addition of the prepared Surfactants

2- The inhibition efficiency increases with increases the concentration of these compounds .

3- These compounds act as mixed type of inhibitors .

4- the inhibition efficiency of Gemini surfactant (H_{22}) More than of of surface area for (H_{22}) on Surface of Iron compared with (H_{33}) and this results leads to increased the adsorption of this compound.

References

Abdallah M, Fouda A S., Shama S. A and Afifi E. A, (2008) African. J. of pure and Appl.Chem.,P.083.

Ac. J., Am J .,(1916)Chem. Soc. 38, 1077.

Ajmal M, Rawat J., Quraishi M. A., Br. Corros. J. (1999) 34:220.

Clubby B.G. (1990):"Chemical Inhibitors for Corrosion Control **".** Royal Sco. Chem ., Cambridge, p.141.

Craddock H. A., (2004) U.S. Patent Application 20040259740AI.

Deng S, Li X and Fu H., (2011) "Corrosion Science" , 53. 760-768.

Elayyach E, El Idrissi A, (2006)Hammouti B, Corros. Sci, 48, 2470-2479.

Esumi K, Goino M, Koide Y, J. Colloide and Surface.Sci, . (1996) 118, 161-166.

Esumi K, MiyaZaki M, Arai T, Koide Y, J. (1998)Colloid and Surface.Sci, 135, 117- 122.

Lgmri A, makarimb H. A. EI, Guenbour A, Prok. (2003) Org. Coat. 48,63-70..

Mohanan S, Maruthamuthu S, Kalaiselvi N, et al., .(2005) Corros, Rev. 23. 425- 444.

Niu L, Zhang H, Wwi , et al., Appl. Surs. Sci, 252, 1634-1624. (2005).

Obi-Egbedi N. O and Obot I. B. , (2011) " Corrosion Science " , Vol , P. 263-275 .

Ponchert C. J. , (1983) " Aldrich Library of IR " Aldrich Chemical Company, Inc.

Ponchert, C. J. 1983) " The Aldrich Library of NMR Spectra " , Edition II.

Popova A, Christov M, Raicheva S, et al. (2004), Corros. Sci. 46,1333-1350.

Saleh M. M, Asem. A A, J. (2006) Appl. Electrochem, 36, 899-905.

Savitri B.V and Mayanna S(1996), Ind.Chem.Technol. 3,256.

Selverstein R. M, Wbster F. W. , (1998) " Spectrometric Identification of Organic Compouds",5th Ed.

Selverstein R, Clayton G., (2000) " Spectrometric Identification of Organic Compouds",7th Ed, Johon Wand Sons.

Sputnik E., Ademovic Z. and Lisac,(1995),in: Proceeding of the 8th European Symposium on Corrosion Inhibitors (8SEIC)Ann. Univ. Ferrara, N.S.,SezV,Suppl., P.257.

Walker M. L., (2003)Chemical Abstracts Patent 2, 482,513.

Yu X., Zhang W and Garosshen T, (2004)European Patent 1,493,846 AI.

تحضير وتشخيص منشطات السطوح ودراسة تثبيطها لتاكل الكاربون - ستيل في الاوساط الحامضية

حوراء كريم **الاء علي حسين** **كوكب علي حسين**

قسم الكيمياء / كلية التربية للعلوم الصرفه / جامعة البصرة

الخلاصة

) ، H_{33} و H_{22} تم تحضير نوعين من المواد المنشطة للسطوح الكاتيونية بالنسبة للطرف المحب للماء هما (
.وتم استخدامها كمثبطات لتاكل سبيكة الفولاذ الكاربوني في IR, ^{1}HNMR شخصت هذه المركبات بتقنية
) وستخدمت طريقة (الفقدان بالوزن وتقنية الاستقطاب الخطي) واشارت 0.5 M HCl المحلول حامضي (
80.60 تساوي ($^{\circ}$C25 وحرارة 1X 10^{-4} وتركيز 240 min النتائج بان النسبة المئوية لكفاءة التثبيط عند زمن
على التوالي باستخدام طريقة الفقدان بالوزن . اما باستخدام منحنيات تافل H_{33}وH_{22} %) للمثبطات 82.27, ,
على التوالي وكذلك H_{22} وH_{33}%) للمنحنيات 80.12,77.93 فكانت النسبة المئوية لكفاءة التثبيط كالتالي (
اثبتت منحنيات تافل ان المركبات المحضرة هي من نوع المثبطات المزدوجة .