

## Synthesis and some applications of Anionic Palmitic Acid Schiff Base Salt Surfactants

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**Abstract:** Schiff bases derived from condensation reaction of benzaldehyde or anisaldehyde and diethylenetriamine were prepared. The products were reacted with palmitic acid (1 : 1 mol) to give the corresponding palmitic Schiff base salt surfactants. The chemical structures of the prepared compounds were confirmed using elemental analysis, FTIR and <sup>1</sup>H-NMR spectroscopy. Various surface properties of the synthesized surfactants were evaluated particularly, critical micelle concentration, effectiveness, efficiency, maximum surface excess and minimum surface area. These surfactants were also evaluated as corrosion inhibitors and as biocide agents Gram positive and Gram negative bacterial strains. The rheological properties, and the filter loss for oil-based mud (invert - emulsion mud) were evaluated, the result showed that they were a good emulsifiers and filter loss control agent for oil – base mud. It has been found that they have good corrosion inhibition for low carbon steel alloy and has good bactericidal effect.

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**Key words:** Surfactants, Corrosion inhibitors, oil base mud and biological activity.

### 1. Introduction:

Schiff base compounds are the condensation product of an amine and a ketone/aldehyde. Recent publications showed increased attention to these compounds as corrosion inhibitors especially in acidic environments for various metals like steel, aluminium and copper [1-7]. The greatest advantage of many Schiff base compounds is that they can be conveniently and easily synthesized from relatively cheap materials. The inhibition of steel corrosion by acids has been previously studied by various researchers using different organic compounds [8–12]. These compounds in general are adsorbed on the metal surface blocking the active corrosion sites. Several Schiff bases have been investigated as corrosion inhibitors for various metals and alloys in acidic media [1, 2, and 13].

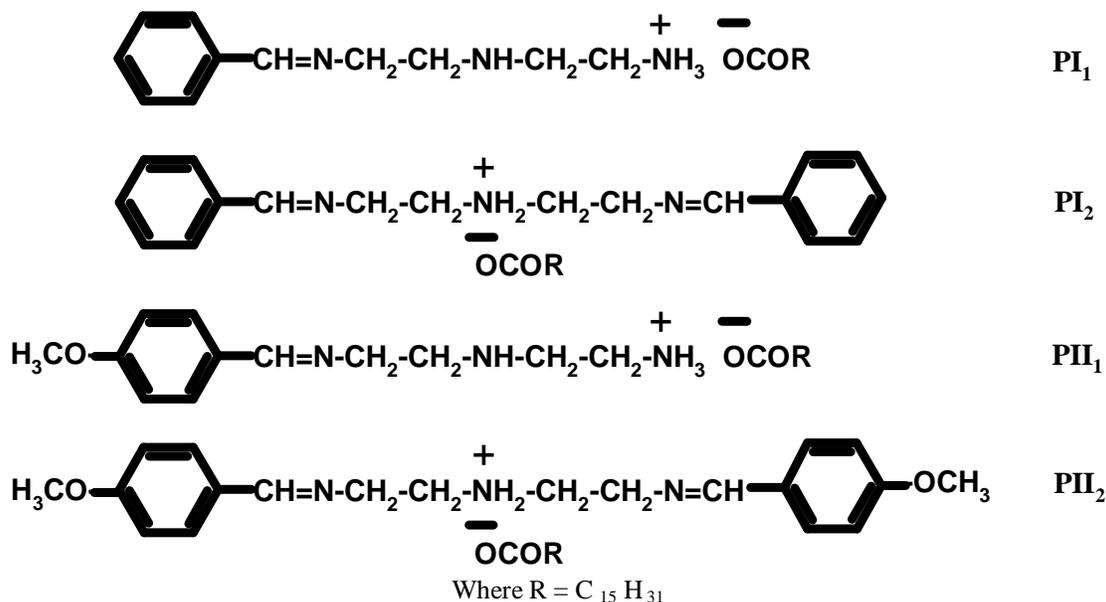
Schiff bases are characterized by the –N=CH– (imine) group which is important in elucidating the mechanism of transamination and racemisation reactions in biological systems [14&15]. Due to the great flexibility and diverse structural aspects, a wide range of Schiff bases have been synthesized and their complexation behavior studied [16]. On the other hand, in the rotary drilling there are a variety of functions and characteristics that are expected from drilling fluids (drilling mud or simply mud). The drilling fluid is expected to carry cuttings from beneath the bit, transport them up the annulus and permit their separation at the surface while at the same time the rotary bit is cooled and cleaned. A drilling fluid is also intended to reduce

friction between the drill string and the sides of the hole while maintaining, preventing corrosion fatigue of the drilling– pipe and allowing interpretation of electric logs. There are a various advantage of using oil – based drilling mud in rotary drilling, In summary, wells drilled with oil- based mud normally produce lower waste volumes than those drilled with water based mud, Also the penetration of the formation by water is avoided, thus preventing swelling or sloughing. One of the most important properties of these drilling fluids are their thermal stability and that they don't present rheological and thixotropic problems under the condition of drilling [17-20]. The use of Schiff base as an emulsifier in oil-base mud is a novel. The function of the emulsifier in oil-based mud is to impart weak gel strength and also emulsification of additional water which is picked up during the drilling operation that promotes a stable emulsion [21-22].

### 2. Material and Experimental Techniques:

Preparation of the surfactant compounds

Benzaldehyde, (1 or 2 mol) or anisaldehyde, (1 or 2 mol) was condensed with diethylenetriamine in ethanol forming the corresponding Schiff base, each products was reacted in water with palmitic acid (1:1 mol) forming palmitic acidamine salts surfactants (PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>) having the following structures :



**Fig. 1: The chemical structure of the prepared compounds**

#### Surface Tension Measurements:

Surface tension measurements were made for freshly prepared surfactant solutions with concentration range from ( $1 \times 10^{-1}$  to  $1 \times 10^{-5}$ ) mol/L. The test was done at 25°C using Du Nouy Kruss-K6. The surfactants solutions were prepared in 1M HCl solutions. The surface tensions were the average of three readings for the each sample.

#### Emulsification power:

Emulsification power of the synthesized surfactants was measured by vigorous shaking of 10 ml surfactant solution (0.1%) and 10 ml paraffin oil for 5 minutes at 25 °C. The emulsification power was expressed as the time required for separation of 9 ml of pure water.

#### Corrosion Measurements:

##### Weight loss Technique:

A weight-loss technique [ASTM G31-72 (Reapproved 2004)] was used to measure the inhibiting efficiency to corrosion of the prepared Schiff bases amphiphiles for mild steel in 1MHCl solutions at 25°C for 24h. The dissolved oxygen range is 6-8 ppm. The experiments were performed with mild steel specimens having a composition (wt %): 0.17 C, 0.035 Si, 0.51 Mn, 0.82 P, and the remainder is Fe. Each specimen was machined into regular shapes of 55.8-cm<sup>2</sup> cross-sectional area. The specimens were sequentially abraded with different emery papers, degreased with acetone, washed with distilled water and dried. Corrosive solutions is 1M HCl in the absence and presence of the inhibitors at concentrations ranging from to 2.7 to 270X10<sup>-6</sup>M

were prepared from doubly distilled water . The average of three coupons was recorded.

##### Polarization for corrosion (Tafel ):

Electrochemical tests have been evaluated by using a Voltalab -40 Potentiostat PGZ 301 at 25<sup>0</sup>C. HCl1 (1M) was used as corrosive solution in the absence and presence of the inhibitor. The concentrations ranging from 1 to 30X10<sup>-6</sup>M of compound PII<sub>2</sub> were prepared using doubly distilled water. The efficiency was determined from the following equation

$$\text{Eff. \%} = (\text{CR}_{\text{BI}} - \text{CR}_{\text{inh}}) / \text{CR}_{\text{BI}}$$

Where: CR<sub>BI</sub> is the corrosion rate in absence of inhibitor and CR<sub>inh</sub> is the corrosion rate in presence of inhibitor

##### Tests for oil – base mud:

The materials and chemical additives of oil – base mud were obtained from the Baroid Company to be used as a reference sample (R). The work with oil – base emulsion mud or oil – water ratio (70/30) were performed by using newly prepared surfactants (PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>) as primary emulsifiers with ratio (2%) of the mud formulation and compared to oil – base mud formulated with imported primary emulsifier (R) ( commercial one ) [23].

##### Mud formulation:

Mud Formulation were as follow : diesel oil (350 ml + primary emulsifier 2% (10 ml ) + tap water (150 ml) were mixed for 20 minutes and then (1.99%) viscosifier + secondary emulsifier (6 ml) + organophilic clay (1.5% ) + soda lime (1.59%) for all

muds formulation , All chemical additives were added slowly using stirring and mixed well in the mixer. So we have:

MR: Mud formulation of oil- base ratio (70/30) with the imported (commercial emulsifier) (R).

MPI<sub>1</sub>: Mud formulation of oil- base ratio (70/30) with the new prepared emulsifier PI<sub>1</sub>.

MPI<sub>2</sub>: Mud formulation of oil- base ratio (70/30) with the new prepared emulsifier PI<sub>2</sub>.

MPII<sub>1</sub>: Mud formulation of oil- base ratio (70/30) with the new prepared emulsifier PII<sub>1</sub>.

MPII<sub>2</sub>: Mud formulation of oil- base ratio (70/30) with the new prepared emulsifier PII<sub>2</sub>.

All the samples were aged to 300 °F for 16 hours and tested at 75 °F , The tests were conducted on both aged and unaged samples.

Biological activity:

The synthesized surfactants were screened for their biocidal activity using diffusion disc method. A filter paper sterilized disc saturated with measured quantity of samples (20 mg in 1 ml DMSO) is placed on plate containing solid bacterial medium (nutrient agar broth) or fungal medium (Dox's medium) which has been heavily seeded with the spore suspension of the tested organism. After inoculation, the diameter

of the clear zone of inhibition surrounding the sample is taken as inhibitory power of samples against the particular test organism.

### 3. Results and Discussion:

#### 3.1. Structure:

The chemical structure of the synthesized Schiff – based surfactants (alkyl amine salts) were confirmed using micro elemental analyses, which showed good coincidence between the calculated and found values of C, H, and N (%) Table1.

FTIR spectra showed the following bands;  $\nu_{\text{NH}}$  at 3453 and 3296  $\text{cm}^{-1}$ ,  $\nu_{\text{C=O}}$  at 1736  $\text{cm}^{-1}$ ,  $\nu_{\text{C=N}}$  at 1640 $\text{cm}^{-1}$ ,  $\nu_{\text{C-H}}$  at 2844  $\text{cm}^{-1}$  and  $\nu_{\text{N}^+}$  at 3179  $\text{cm}^{-1}$  which confirmed the expected functional groups found in the synthesized molecules.

<sup>1</sup>HNMR analyses of compounds (PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>) as representative samples showed the following; for PI<sub>1</sub> :  $\delta$  =1.29 ppm (H, C-H),  $\delta$ =0.96 ppm (S, 3H of terminal CH<sub>3</sub>),  $\delta$ =7.29-8.29 ppm (5H-benzylidene),  $\delta$ = 2.77 ppm (t, 2H, CH<sub>2</sub>),  $\delta$ =2.23ppm (t, 2H, CH<sub>2</sub>-COO), and  $\delta$ = 2.0 ppm (2H, NH<sub>2</sub> proton). The data of elemental analysis, FTIR and <sup>1</sup>HNMR spectra confirms the chemical structures of the synthesized amphiphiles as represented in Fig1.

**Table (1): Characterization of prepared Schiff base amine salt surfactants**

Compound	Yield%	C %		H %		N %	
		Calc.	Found	Calc.	Found	Calc.	Found
PI <sub>1</sub>	70	72.48	72.40	10.96	10.76	9.39	9.18
PI <sub>2</sub>	85	75.26	75.75	9.9	9.2	7.85	8.18
PII <sub>1</sub>	80	70.44	69.97	10.69	9.95	8.80	8.18
PII <sub>2</sub>	90	72.6	72.48	9.4	9.2	7.05	6.84

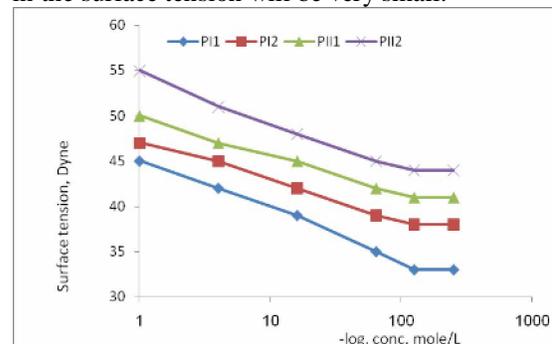
#### 3.2. Surface Properties:

Surface tension ( $\gamma$ ) and critical micelle concentration, (CMC)

Figure (2) represent the variation of surface tension ( $\gamma$ ) against  $-\log(\text{conc.})$  of the synthesized surfactants (PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>) at 25°C in acid solutions.

It is clear that the surface tension curve have two characteristic regions. One at the lower concentrations, which showed gradual decrease in the surface tension while the other at higher concentrations at which the surface tension stays almost constant with very small changes. The higher change in the first region indicates the fast adsorption of the surfactant molecules towards the interface. At the higher concentrations, the surface is almost saturated by the surfactant molecules and no further

molecules penetrate to the interface, hence, the change in the surface tension will be very small.



**Fig. 2: The surface tension of the prepared compounds.**

The intercept between these two regions indicate the critical micelle concentration (CMC) of each surfactant. Table (2) represents the critical micelle concentration (CMC) values of the synthesized Schiff base surfactants. The values of CMC in Table 2 revealed that the presence of the hydrophobic chain length of the synthesized surfactants produces a decrease in their values. That behavior could be explained as the number of methylene groups in the surfactant molecules increases their hydrophobicity which increases the hydrophobic chain solvent interaction. Hence, the molecules tend to form aggregates in the bulk of their solutions. As we can see the presence of the terminal methoxy group in compounds (PII<sub>1</sub> and PII<sub>2</sub>) increases their hydrophilicity, which was responsible for decreasing their CMC values and increasing the depression of the surface tension at this concentration, (Table 2).

From table (2) the highest CMC value was observed for PII<sub>1</sub> 24x10<sup>-5</sup> at 25°C while, the lowest value was observed for PII<sub>2</sub> 13x10<sup>-5</sup> at 25°C which referred to the difference in their structures where, the presence of the oxygen atom in the skeleton of PII decreases the water / hydrophobe repulsion that occurred through hydrogen bond formation [24].

Effectiveness ( $\gamma_{cmc}$ ), maximum surface excess ( $\Gamma_{max}$ ) and minimum surface area ( $A_{min}$ )

The difference between surface tension values of the surfactant solution at its CMC and that of the corresponding distilled water is defined as effectiveness ( $\gamma_{cmc}$ ). The most efficient is the one that gives the greatest lowering in surface tension at (CMC). According to the result of effectiveness shown in Table 2, PII<sub>1</sub> is a mostly found to be more efficient, It achieves the maximum reduction of the surface tension at CMC.

The maximum surface excess is expressed as the concentration of surfactant molecules at the interface per unit area ( $\Gamma_{max}$ ). While the minimum surface area is defined as the area occupied by each molecule in nm<sup>2</sup> at the interface. Using the adsorption law of molecules at the interfaces, ( $\Gamma_{max}$ ) values were calculated according to the following equation.

$$\Gamma_{max} = \left( \frac{d\gamma}{d \log c} \right) / (8.3 \times 10^7 \times RT)$$

Where  $d\gamma/d \log C$  is the surface pressure, R, universal gas constant and T, the absolute temperature. Regarding the results listed in Table 2 we observe that  $\Gamma_{max}$  decreases by increasing the molar ratio of the Schiff based structure for both PI<sub>2</sub> and PII<sub>2</sub> which may be attributed to desorption of molecules from the interface and their dissolution in the aqueous phase [25].

The minimum surface area occupied by each surfactant molecules at the air/water interface ( $A_{min}$ ) is calculated according to the following equation.

$$A_{min} = 1/N \cdot \Gamma_{max}$$

where ( $A_{min}$ ) values increase with the increase in molar ratio of Schiff base for both PI<sub>2</sub> and PII<sub>2</sub>

Standard free energies of micellization and adsorption ( $\Delta G_{mic}^o$ ,  $\Delta G_{ads}^o$ )

According to the Gibb's equations of thermodynamics, the thermodynamic functions of micellization and adsorption were calculated from the surface parameters as listed in (Tables 2) according to the Gibb's equations of thermodynamics as follows:

$$\Delta G_{mic} = -2.303RT \log (CMC)$$

$$\Delta G_{ads} = \Delta G_{mic} - (0.6023 \times 10^{-1} \times \pi_{cmc} \times A_{min})$$

From Table (2) the standard free energy change of adsorption ( $\Delta G_{ads}^o$ ) was found to be more negative than that for the micellization process ( $\Delta G_{mic}^o$ ), which refers to the higher tendency of these surfactants to adsorb at air/water interface rather than the micellization. The preference of adsorption is governed by the thermodynamic stability of the molecules at the air/water interface. Thus rising in  $\Delta G_{ads}^o$  can be traced to the presence of the methoxy group within the surfactant molecules, which increase the adsorption process at the air/water interface. The hydrogen bonds occurring between the water and surfactant molecules provide good stability for the adsorbed molecules at the interface. These results are in good agreement with the data obtained from  $A_{min}$  values [26].

**Table (2): Surface properties of prepared Schiff base amine salt surfactants**

Comp.	CMC, mol E-5	$\gamma_{cmc}$	cmc	$\Gamma_{max}$ E-10	$A_{min}$ nm <sup>2</sup>	- G <sub>mic</sub>	- G <sub>ads</sub>
PI <sub>1</sub>	19	41.8	30.2	0.96	1.73	21.14	24.28
PI <sub>2</sub>	20	45.0	27.0	0.90	1.84	21.07	24.07
PII <sub>1</sub>	24	33.6	38.4	1.13	1.46	20.69	24.08
PII <sub>2</sub>	13	38.4	33.6	1.02	1.63	22.24	25.54

### 3.3. Emulsion Stability:

The emulsifying power values of the prepared compounds are listed in table (3). As shown in the table (3) it is clear that all prepared surfactants have high emulsion stability. It is clear also that the PII<sub>1</sub> or PII<sub>2</sub> compounds have higher emulsifying power values than that of PI<sub>1</sub> or PI<sub>2</sub>. This is due to the solubility of the attached counter ions. It is well known that the emulsion stability of the surfactant molecule depends mainly on its hydrophob part, which increases, as the carbon chain length increases the emulsion stability of the compound. In our study the

hydrophob part in the prepared compounds is constant. Consequently, the emulsion stability depends on the counter ions attached with the prepared compounds. The solubilities of the counter ions of PII<sub>1</sub> and PII<sub>2</sub> are more than that of PI<sub>1</sub> and PI<sub>2</sub> due to the presence of ether group.

The emulsion stability of PI<sub>1</sub> is more than that of PI<sub>2</sub>. This is due to the solubility of counter ion of the compound PI<sub>1</sub> which is more than that of PI<sub>2</sub> due to the presence of imine and benzyl groups. For the same reason, the emulsifying power of the PII<sub>1</sub> is more than that of PII<sub>2</sub>.

**Table (3): Emulsion stability of 0.1% surfactants in 10% NaCl water**

Comp.	PI <sub>1</sub>	PI <sub>2</sub>	PII <sub>1</sub>	PII <sub>2</sub>
Time, Minute.	34	22	37	33

### 3.4. Corrosion Inhibition:

The inhibition efficiencies of the synthesized Schiff base amphiphiles were calculated by weight loss before and after immersion in the corrosive medium according to the equation:

$$(\%) = [(W_o - W) / W_o] \times 100$$

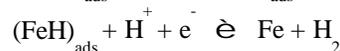
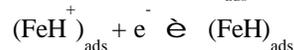
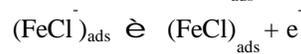
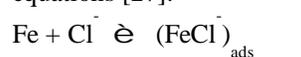
Where W<sub>o</sub> and W are the corrosion weight losses of the uninhibited and inhibited steels respectively.

Table 4 and Figures 3 represent the variation of inhibition efficiencies of the synthesized inhibitors in different acidic media for mild steel on wide range of doses (from 2.7 up to 270X 10<sup>-6</sup>M). It is clear that the inhibition efficiency towards corrosion process increases by increasing the inhibitor dose. The maximum corrosion inhibition was found at 30X10<sup>-6</sup>M for all the synthesized inhibitors in HCl solutions. Increasing the inhibition efficiencies with increasing the concentration of the synthesized inhibitors is mainly due to the adsorption of those inhibitors on the metal surface. The adsorption mechanism of the inhibitor molecules at metal/solution interfaces is depending on the chemical structure of the inhibitors and their response towards the environment governed by one or more of the following topics:

1. Electrostatic attraction between the charged inhibitor molecules and the metal surface.
2. Interaction between the p-electrons in the inhibitor molecules and the metal.
3. Interaction between uncharged moieties in the inhibitor molecules and the metal surface.

The chemical structures of the synthesized inhibitors comprise unsaturation sites (conjugation within benzene rings) and heteroatom in the imino groups. The conjugation in the benzenoid nucleus of benzaldehyde and anisaldehyde interacts with the metal surface forming a strong adsorption bonds. This interaction also occurs due to the imino group of the Schiff bases.

The hydrophobic part of the palmitic acid acts as the uncharged moiety which forms the thin film preventing chloride ions from the metal surfaces. The proposed mechanism of the steel dissolution in the acidic medium was described in the following equations [27]:



Meanwhile, imino groups are protonated in the acidic medium forming the protonated imine (-N<sup>+</sup>H=C-) which is adsorbed physically to the negative species formed during steel dissolution (FeCl<sup>-</sup>). In case of the synthesized inhibitors containing anisaldehyde moiety, the methoxy group containing uncharged electron pairs on the oxygen atoms. The uncharged electron pair interacts with the positively charged species produced during the steel dissolution in the acidic medium (FeH<sup>+</sup>).

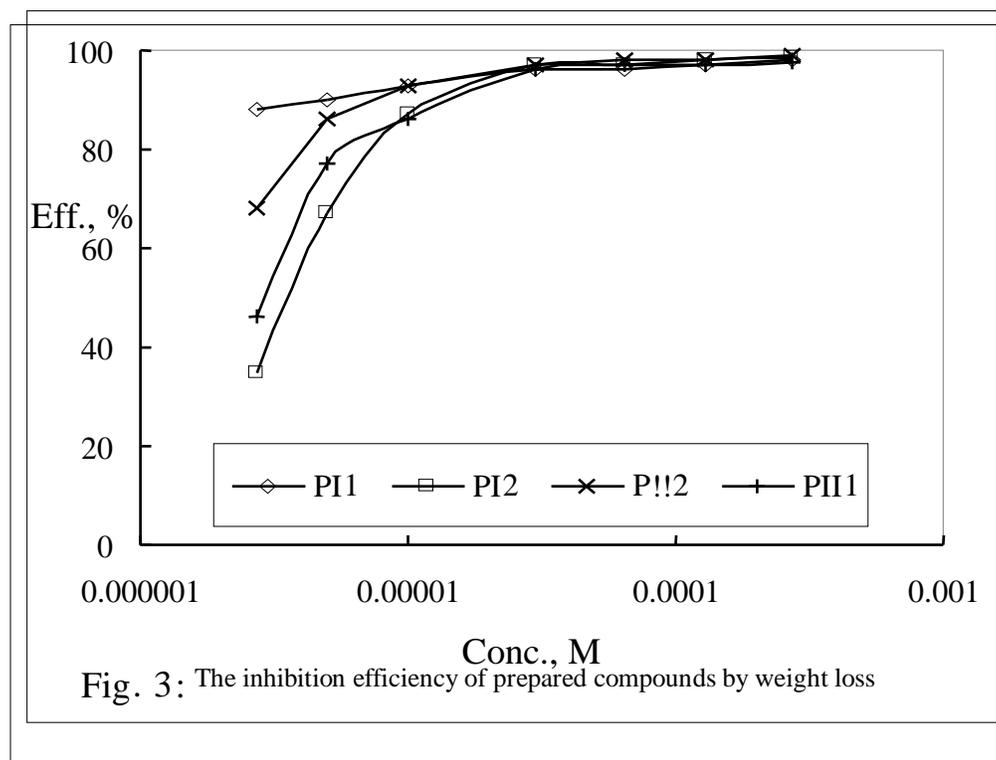
The experimental results of the corrosion processes of the mild steel in the acidic media showed high inhibition efficiencies of the synthesized inhibitors. The inhibition efficiencies of the synthesized inhibitors are 88%, 35%, 46% and 68% at lower concentrations (2.7X10<sup>-6</sup>M) for PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>, respectively. The maximum inhibitions (at higher concentration of 270X10<sup>-6</sup>M) are 98%, 98.4%, 97.7%, and 99%, for PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub> and PII<sub>2</sub>, respectively,

Analyzing the data of corrosion inhibition reveals that the inhibitors derived from two imino groups exhibit higher efficiencies than those obtained from one derivative. This could be referred to the combination of the three above mentioned topics in their inhibition mechanism. However, two Schiff base molecules derivatives are stronger than one

molecule. The above results was confirmed by the thermodynamic parameters of the micellization and adsorption process where it is found that the more negative  $\Delta G_{mic}^{\circ}$  and  $\Delta G_{ads}^{\circ}$  are the more corrosion efficiency increases.

**Table (4): The corrosion inhibition efficiency of the prepared Schiff base amine salt surfactans at different doses (weight loss method).**

Conc.M*10 <sup>6</sup>	Eff., %			
	PI <sub>1</sub>	PI <sub>2</sub>	PII <sub>1</sub>	PII <sub>2</sub>
2.7	88	35	46	68
5	90	67	77	86
10	93	87	86	93
30	96	97	96	97
65	96	97	97	98
130	97	98.2	97	98.3
270	98	98.4	97.7	99



#### Tafel polarization

Table 5 shows a typical record of Tafel polarization measurements for mild steel in 1M HCl in the absence and presence of the PII<sub>2</sub>. Corrosion current density ( $i_{corr}$ ) of bare mild steel electrode in this condition was 3769 Acm<sup>-2</sup>. It is clear that corrosion current density decreased with increasing the concentration of the PII<sub>2</sub>.

It's clear that addition of the PII<sub>2</sub> to acid media affected both the cathodic and anodic parts of the curves. Therefore, these compounds behave as mixed inhibitors and Corrosion potential is shifted to the positive direction more markedly. This shows that the effect of inhibitors on the anodic reaction is more observable than on the cathodic reaction. Increasing the concentration of the PII<sub>2</sub> caused corrosion potential to be nobler, although there was no specific relation between  $E_{corr}$  and inhibitors concentration.

**Table (5): Tafel polarization parameter values for the corrosion of mild steel in 1M hydrolic acid containing different concentrations of the PII<sub>2</sub>.**

Conc (MX10 <sup>-6</sup> )	-E Corr, mv	I. corr, mA/cm <sup>2</sup>	Rp ohm.cm <sup>2</sup>	Ba, mv	Bc, mv	Corr.rat, mmy	EFF., %
0.0	516	0.3769	220.65	155.7	-168.0	4.41	0.0
1	534.3	0.1939	392.35	221.1	-146.9	2.26	48.75
2	547.5	0.1086	497	261	-127.3	1.269	71.12
3	552.4	0.0999	486.7	224.9	-125.7	1.168	73.5
6	544.4	0.0806	553.68	266.8	-122.4	0.942	78.64
10						0.552	87.48
30						0.146	96.69

Table 5 shows the polarization parameters for corrosion of mild steel in the presence of different concentrations of the investigated compound. The corrosion inhibition efficiency increases when the concentration of the inhibitor increases. Depolarization of both anodic and cathodic branches after addition of the inhibitors indicated no dissolution of metal and the maximum efficiency was 96, 69% for concentration of 30X10<sup>-6</sup>M PII<sub>2</sub>.

### 3.5. Oil - Base mud

The prepared Schiff-base surfactants (PI<sub>1</sub>, PI<sub>2</sub>, PII<sub>1</sub>, and PII<sub>2</sub>) were evaluated as a primary emulsifier for oil-base mud with the oil-water ration

(70/30) and emulsifier concentration 2%. The evaluation incorporates the study of rheological properties (apparent viscosity (AV), plastic viscosity (pv) yield point (yp), gel strength G<sub>10</sub> second , G<sub>10</sub> mint, Thixtropy and the filter loss of the mud are formulated by the new prepared emulsifiers compared to the reference mud sample (MR). The test was carried under the condition of high temperature 350°F and high pressure 500 psi with continuous circulation for 16 hours. Table (6) shows the results of the test before and after aged for both the mud formulated with the new emulsifiers and a reference sample mud.

**Table (6) : Rheological properties ( apparent viscosity AV, plastic viscosity PV , yield point YP , Gel strength and filter loss ) after and before aged for 16 hours at 350 ° F and 500 (psi) .**

Mud example	Temperature F <sup>o</sup>	Rheological properties			Gel strength		Filter loss (ml)
		A.V ( CP)	P.V (CP)	Y.P (1b/100ft <sup>2</sup> )	G / 10 sec	G/10 mint	
M <sub>R</sub>	Initial	17	15	16	6	6	9
	300 ° F	13	11	5	2	3	12
MPI <sub>1</sub>	Initial	20	17	16	9	9	7
	300 ° F	17	13	8	3	4	9
MPI <sub>2</sub>	Initial	18	15	12	7	7	7,5
	300 ° F	15	12	7	4	5	8
MPII <sub>1</sub>	Initial	22	14	17	8	8	6
	300 ° F	18	16	11	4	5	10
MPII <sub>2</sub>	Initial	19	16	12	6	6	6
	300 ° F	15	11	6	2	1	9

Rheological properties:-

Before aged:- The apparent viscosity were 20, 18, 22, 19 (cp) for Mpl<sub>1</sub>, Mpl<sub>2</sub>, MplI<sub>1</sub>, and MplI<sub>2</sub> respectively while the (AV) for MR was 18 (cp), plastic viscosity (PV) were 17, 15, 14, 16 for MPI<sub>1</sub>, MPI<sub>2</sub>, MPII<sub>1</sub>, MPII<sub>2</sub> while the pv for MR was 15 (cp), The yield point were 16, 12, 17, 12 16/100ft<sup>2</sup> for MPI, Mpl<sub>2</sub>, MplI<sub>1</sub>, MplI<sub>2</sub> respectively while the yield point for MR was 16 1b/100Ft<sup>2</sup>.

Gel strength G<sub>10</sub> second recorded 9,7,8,6 1b/100Ft<sup>2</sup> and G<sub>10</sub> mint showed were also 9,7,8, 61b/100Ft<sup>2</sup> for the four oil-base mud formulated with

the new emulsifiers . So the Thixtropy for each one is equal to zero which is compatible with Thixtropy of reference sample MR which is also equal zero.

Filter loss of the mud formulated with the new emulsifier MPI, MP<sub>2</sub> MPII<sub>1</sub>, MPII<sub>2</sub> were equal to 7, 7.5, 6, 6ml while the filter loss of the reference sample was 9 ml

The decrease of filter loss of the mud formulated with the new emulsifiers and the reference sample mud indicates the stability of the mud.

After aged:-

The apparent viscosity ( $A_v$ ) and plastic viscosity ( $p_v$ ) yield point. ( $y_p$ ) decreased as a result of increasing temperature up to 350°F. For the 4 mud formulation with the new emulsifiers  $MpI_1$ ,  $MpI_2$ ,  $MpII_1$ ,  $MpII_2$  the apparent viscosities were (17, 15, 18, 15) cp while the apparent viscosity of the reference mud sample MR was 11 cp. Also plastic viscosities were 13cp for  $MpI_1$ , 12 cp for  $MpI_2$ , 16 cp for  $MpII_1$  and  $MpII_2$  where the plastic viscosity of MR was 11 cp after aged. The yield point was 8, 7, 11 and 6 lb/100ft<sup>2</sup> for 4 new emulsifier mud formulations where the yield point for MR was 5 lb/100ft<sup>2</sup>. This result indicates that mud formulation with new emulsifiers was better than or compatible with the reference mud sample. Filter loss of the mud formulations with the new emulsifiers were less than filter loss of reference mud sample (MR) after aged [28].

From the above results we can conclude that the Rheological properties, gel strength and filter loss of the mud formulated with the new Schiff base emulsifiers showed results which were better than the reference sample mud, and that the Schiff base surfactants were good emulsifiers for oil-base mud. They are in order  $PI_1 > PII_1 > PII_2 > PI_2$ . The best emulsifier is  $PI_1$ .

### 3. 6. Biocidal Activity

The biological biocidal activity of the synthesized surfactants amine salts against Gram-negative bacteria (*Escherichia coli*) and (*Neisseria*

*gonorrhoea*) Gram-positive bacteria (*Staphylococcus aureus*) and (*Streptococcus faecalis*) is represented in Table 7. The biocidal activity of the compounds under investigation ( $PI_1$ ,  $PI_2$ ,  $PII_1$  and  $PII_2$ ) is due to adsorbance at the water/cell membrane interface. This adsorption increases solubility through the cell membrane increasing its permeability towards the media ingredients and correspondingly. Thus biological reactions disturb within the cell cytoplasm. Table 7 shows that, the synthesized surfactants have a good biocidal activity against bacteria used in this investigation. Table 7 shows that, compounds  $PI_1$  and  $PI_2$  give relatively better inhibition zones against bacteria than compounds  $PII_1$  and  $PII_2$ .

The mechanism of action of such surfactants on bacteria is understood to be one of electrostatic interaction and physical disruption, as opposed to interference with a metabolic pathway, as is commonly the situation with antibiotic species [29]. After the cationic site of the agent attached to a significant lipophilic component binds to anionic sites of the cell wall surface it is then able to diffuse through the cell wall and bind to the membrane. Acting as a surfactant, it is able to disrupt the membrane and permit the release of electrolytes and nucleic materials, leading to cell death. The membrane activity of the surfactants depends on the character of the polar head groups (size and electric charge distribution) and hydrocarbon chains (length, saturation and multiple chains).

**Table (7): Biocidal activity for the prepared Schiff base surfactants expressed by Inhibition zone diameter (mm/mg)**

Sample	<i>Escherichia coli</i> (G-)	<i>Neisseria gonorrhoea</i> (G-)	<i>Staphylococcus albus</i> (G+)	<i>Streptococcus faecalis</i> (G+)
Control	0.0	0.0	0.0	0.0
$PI_1$	14	14	12	14
$PI_2$	14	15	13	13
$PII_1$	13	14	13	13
$PII_2$	12	13	11	12

### 4. Conclusions:

From the obtained results the following conclusion can be drawn:

The prepared surfactants have good surface properties; they reduce the surface tension of the water and have low CMC. The prepared compounds have strong adsorption on the metal surfaces so they prevent their corrosion in acid medium. The inhibition efficacy is very high in 1M HCl, about 99% for concentration of  $2.7 \times 10^{-4}$  for  $PII_2$ . The optimum dosage for all prepared surfactants is around  $3 \times 10^{-5}$  M which gives inhabitation efficiency of 96-

97%. It is found also that they are good emulsifiers for oil base mud compared with the commercial one.

The prepared surfactants have very good biocidal effect towards the tested gram positive and negative bacteria

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