

Gemini Surfactant Performance Evaluation as Inhibitive action of PAPM for Treatment of AISI steel Corrosion and Studying Temperatures Influence in Acidic Medium

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Abstract:-

To inhibit corrosion of the AISI 4130 steel in 1M H₂SO₄ solution at different temperatures, the gemini surfactant was used, namely N,N'-((1,4-phenylenebis(azanediyl)) bis (2-hydroxy propane-3,1-diyl)) bis (N,N-dimethyldecan-1-aminium) (PAPM). The gemini surfactant by electrochemical impedance spectroscopy technique and weight loss method has been evaluated at different temperatures 30, 40 and 50°C. The gemini surfactant showed a very good performance as a corrosion inhibitor in acidic solution, and inhibition efficiency increases with increase inhibitor concentration but decreased with increasing temperatures. Impedance technique results shown, that studied molecule act as mixed-type inhibitor toward AISI steel, also values of standard free energy of adsorption ΔG_{ads}° suggest the physisorption and chemisorption were occurred for inhibitor molecules on AISI surface. In addition, the inhibitor adsorption behavior on the AISI surface was investigated at specified temperatures and it coincide with Langmuir's adsorption isotherm. Furthermore, time effect on corrosion inhibition efficiency was studied where results shown that influence was slight. From quantum calculations, the inhibitor act as soft molecule were noted, also it was shown that the inhibitor more responding for reacting with the AISI surface and prefer the electrophilic attack because it contains on a nucleophilic centers. Experimental inhibition efficiency obtained from both two methods are on a good agreement to each other where optimum efficiency reached 90.32% for weight loss method and 87.17% for EIS technique. On other hand, theoretical inhibition efficiency and experimental inhibition efficiency were in a good agreement to each other, where as theoretical efficiency reached 92.35%.

Keywords: Gemini Surfactants, Corrosion Inhibitors, Temperature Influence, Weight Loss method, EIS, Quantum Methodology.

Introduction:-

Corrosion is the destructive attack of a metal through chemical or electrochemical reaction with its environment. The corrosion of metal and its alloys is a common problem in economic implications which costing billions of dollars in every year, therefore corrosion causes losses in economic factor. Economic losses caused by corrosion are divided into direct losses and indirect losses. Direct losses include the costs of replacing corroded structures and machinery or their components such as condensing tubes, pipelines and metal roofing. Indirect losses are an more difficult in assess, where include shutdown the corroded unit for example shutdown the corroded pipe lines in oil refinery (Revie and Uhlig, 2008; Sundaram and Sundaravadivelu, 2016).

Surface active agents (Surfactants) are organic compounds contains at least one lyophilic group (solvent-loving) and one lyophobic group (solvent-fearing) in surfactant molecule. In simplest conditions, the surfactant includes at least one non-polar group and one ionic group. If the corrosive medium is a water or an aqueous solution in this case the hydrophobic part in surfactant compound will be dsorb on metal surface while the hydrophilic part will be prevents corrosive materials to get closer for metal surface (Schramm, 2000; Farn,2006; Kiev,2004). Gemini surfactants possess corrosion inhibitive properties where these properties have been studied by Qi Zhang, *et al.* Four quaternary ammonium of gemini surfactants in series of hexanediyl-1,6-bis-(diethyl alkyl ammonium bromide) were synthesized and tested as corrosion inhibitors of aluminium in 1M HCl solution at 25 °C. The results

obtained showed that studied surfactants are efficient corrosion inhibitors for aluminium in hydrochloric acid solution and inhibition efficiency increases with surfactant concentrations (Zhang *et al.*, 2011). Also, Mohamed A. Hegazy and Aziza S. El-Tabei synthesized a new cationic gemini surfactant (4,4'-(3,3'-(1z,1'z)-pentane-1,5-diylidenebis (azan-1-yl-1-ylidene) bis (propane-3,1-diyl)) bis(4-dodecylmorpholine-4-ium bromide) and studied it as a corrosion inhibitor on carbon steel in 1 mol.L⁻¹ HCl solution (Hegazy and El-Tabei, 2013).

The use of corrosion inhibitors are one of the most important methods for protecting the surfaces of metals or alloys from corrosion and reducing corrosion damage in acidic solutions. The inhibitor interact with anodic or/and cathodic reaction sites to decrease the oxidation or/and reduction reactions. There are three main types of inhibitors, are organic inhibitors, inorganic inhibitors and mixed inhibitors and widely used in acidic solutions (Zadeh *et al.*, 2013; Singh and Mukherjee, 2010; Danaee *et al.*, 2013; Musa *et al.*, 2012; Liu *et al.*, 2012). There are general consensus by several researchers on that molecules which work as an inhibitors should be contain pair or pairs of electrons in hetero atoms such as O, N, S, etc., or contain polar function groups (e.g. nitro, hydroxy, amine, etc.) or possess plentiful of π -electrons, therefore these compounds will be provide a large protection for metals through their adsorption on the metallic surface, thereby they excellent to inhibit of corrosion (Khadom, 2017; Bouakkaz *et al.*, 2017; Subramanyam *et al.*, 1993; Galai *et al.*, 2017; Abdul Nasser *et al.*, 2012). Organic inhibitors can adsorb onto the metal surface by four distinct mechanisms (i) electrostatic attraction between charged molecules and metal, (ii) interaction between electron pairs of molecule and the metal, (iii) interaction between π -electrons of molecule and metal, and (iv) a combination of mechanisms such as (i) and (iii) (Shorky *et al.*, 1998).

The aim of present work is a systematic study to reduce of economic cost resulting from corrosion processes where the study included protecting for AISI steel from corrosion in acidic solution using gemini surfactant as inhibitor and studying influence of temperature and time on effectiveness of gemini surfactant.

Materials and Methods:-

Materials:-

Materials used in this work are products for Sigma-Aldrich (H₂SO₄ 98%). Double distilled water in all experiments was used. The chemical composition of AISI steel sample (wt%) is a (C: 0.2, Si: 0.13, Mn: 0.69, P: 0.02, S: 0.021, Cr: 1, Ni: 0.23, Mo: 0.16, Cu: 0.22, V: 0.002, W: 0.008, Co: 0.008, Sn: 0.02, Pb: 0.002, As: 0.009, Sb: 0.005 wt%, and the remaining for Fe. Density of AISI steel is a 7.85 g/cm³ (Zadeh *et al.*, 2013). The chemical structure of inhibitor (Gemini surfactant) N,N'-((1,4-phenylenebis (azanediyl))bis(2-hydroxy propane-3,1 -diyl))bis(N,N-dimethyldecan-1-aminium) is a shown in Fig. 1.

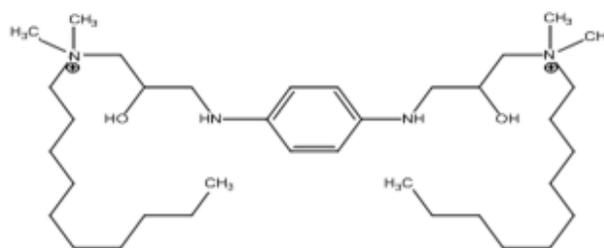


Fig. 1: Chemical structure of gemini surfactant (inhibitor) N, N'-((1,4-phenylenebis(azanediyl))m bism(2hydroxypropane-3,1-diyl) bis (N,N-dimethyldecan-1-aminium).

Inhibitor Evaluation Methods:-

Electrochemical Impedance Spectroscopy

Technique (EIS):-

To study effectiveness of gemini surfactant to inhibit of AISI steel corrosion using EIS technique, each sheet of AISI steel was cut into 1.5cm, 0.5cm for diameter and thickness respectively. Computer controlled electrochemical measurements ZAHNER Elektrik is a IM6Ex potentiostat model. Electrochemical impedance measurements in a glass cell were conducted, its overall volume 150 cm³ and consist of three electrodes, the reference electrode is a saturated calomel electrode (SCE), a platinum as counter electrode and the working electrode is a AISI steel type 4130. The potential scanning and scan rate of 1 mVs⁻¹ from -800 mV to -100 mV. The EIS experiments in frequency range from 100 KHz to 50 mHz and peak-to-peak A.C amplitude of 10 mV at open circuit potential versus saturated calomel electrode SCE were conducted. Duration for each experiment 30 minutes at room temperature. The inhibition efficiency

η % from charge transfer resistance was calculated using the Equation 1 (Ahmed *et al.*, 2018).

$$\eta \% = \left(\frac{R_p^0 - R_p}{R_p^0} \right) \times 100 \quad (1)$$

Where R_p^0 and R_p indicate the charge transfer resistance in presence and absence of inhibitor respectively. Also, the area of metal surface covered by molecules of inhibitor (Surface coverage Θ) was calculated through the Equation 2 (Zadeh *et al.*, 2013).

$$\text{Surface coverage } \Theta = 1 - \left(\frac{R_p}{R_p^0} \right) \quad (2)$$

Double layer capacitance C_{dl} of inhibitor concentrations using the Equation 3 has been calculated, where f_{max} is a frequency at the impedance maximum and R_p is a charge transfer resistance (Serrar *et al.*, 2018).

$$C_{dl} = \frac{1}{2\pi f_{max} R_p} \quad (3)$$

Weight Loss Method:-

To study effectiveness of the organic inhibitor to inhibit of AISI steel corrosion, each sheet of AISI steel was cut into 10cm, 3cm, 0.5cm for length, width and thickness respectively for using in weight loss method, where the total working area 73cm². AISI steel specimens using various emery papers were polished, grit size is a 400, 600, 800, then their rinsed by distilled water, acetone and dried it in a desiccator. Corrosion rate of AISI steel without inhibitor in aqueous solution of 1M H₂SO₄ as a corrosive medium was measured at a periods time 1, 2, 3 hours, and different temperatures 30, 40 and 50°C. The corrosion rate of AISI steel at same conditions with presence inhibitor at 0.01-0.05 M was measured. Inhibition efficiency and surface coverage (Θ) were calculated through the following Equations (Hegde and Nayak, 2018; Rbaa *et al.*, 2018).

$$\eta \% = \frac{W_1 - W_2}{W_1} \times 100 \quad (4)$$

$$\Theta = \frac{W_1 - W_2}{W_1} \quad (5)$$

Where, W_1 and W_2 are weight loss in AISI specimen at absence and presence of inhibitor respectively. The corrosion rate (C_R) in millimeter per year (mmpy) was calculated by Equation 6 (Hegde and Nayak, 2018).

$$C_R = \frac{87.6 \times W}{A \times t \times d} \quad (6)$$

Where W is a weight loss in (mg cm⁻² h⁻²), A is area of AISI specimen the exposed to acidic solution in cm²

(73cm²), t is a immersion time in hours, and d is a density of AISI steel (7.85 g cm⁻³).

Results and Discussion:-

Weight Loss Measurements:-

Weight loss experimentals was carried out according to ASTM procedure, where the AISI steel specimens in triplicate were immersed of 150 mL of 1M sulfuric acid solution in presence and absence of inhibitor at different times and varying temperatures. (Harbor, 1999).

Temperature Influence on Corrosion rate at Absence of Inhibitor:-

Corrosion rate of AISI steel in 1M H₂SO₄ without inhibitor was measured, the results of weight loss and corrosion rate obtained are illustrated in Table 1 and Fig. 2, where it was noted that the value of corrosion rate increased from 23.69 mmpy at 1 hour to 27.10 mmpy at 3 hours at temperature 30 °C, whereas at 40 °C the increase in corrosion rate was greater, where increased from 44.78 mmpy at 1 hour to 47.03 mmpy at 3 hours. At the 50°C, the increase of corrosion rate higher than corrosion rate at 30°C and 40°C, where increased from 53.35 mmpy at 1 hour to 62.26 mmpy at 3 hours. Hence, it can be conclude that the value of weight loss and corrosion rate increases with temperature rising at the proven time, also they increases with time increasing at proven temperature due to increase of kinetic energy of inhibitor molecules (Sato, 2012; Chrisanti, 2008).

Table 1: Shown the effect each of time and temperature on corrosion rate of AISI steel in 1M H₂SO₄ without inhibitor

Temperature	1 hr.		2 hrs.		3 hrs.	
	W (mg)	CR (mmpy)	W (mg)	CR (mmpy)	W (mg)	CR (mmpy)
30 °C	155	23.69	320	24.45	532	27.10
40 °C	293	44.78	601	45.93	923	47.03
50 °C	349	53.35	798	60.99	1222	62.26

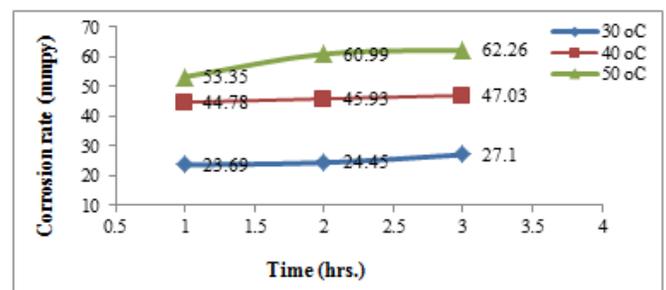


Fig. 2: Illustrates corrosion rate of AISI steel in 1M H₂SO₄ without inhibitor

Influence of Inhibitor Concentration and Temperature on Corrosion rate:-

The purpose of adding inhibitor (PAPM) is for controlling and prevention AISI steel corrosion in 1M H₂SO₄ solution where its evaluated using weight loss method. From the results shown in Tables 2-4 and Fig. 3-5 it can be conclude that each of weight loss and corrosion rate were considerably decreased with concentration increase at proven time, due to increased amount of used inhibitor thereby increasing surface area covered by inhibitor molecules, where increases the adsorption process on AISI surface and preventing the arrival of corrosive material to surface and finally the inhibition efficiency increases. AISI surface increased covered by inhibitor refer to the prevention of AISI dissolution where inhibition efficiency increase with increased of inhibitor concentration to reaches maximum 90.32 % (Saratha and Vasudha,2010; Nagm and Zake, 2007; Nwabanne and Okafor,2011; Ezeoke *et al.*, 2012). Subsequently, it can be conclude that inhibitor has high efficiency for inhibiting in acidic solution, due to adsorption of gemini surfactant (inhibitor) on AISI steel surface through non-bonding electron pairs of nitrogen and oxygen atoms or due to π-electrons of aromatic ring or both together. Corrosion rate and weight loss increases with temperature raise at inhibitor presence hence inhibition efficiency decreased with increasing the solution temperature from 30°C to 50°C. Inhibition efficiency decrease refers to that formed film on AISI surface is a less protective at high temperature because the de-sorption rate of the inhibitor is a faster in high temperature (Ayazi *et al.*, 2006; Jiang *et al.*, 2006; Ma *et al.*, 2000; Panchal *et al.*, 2012).

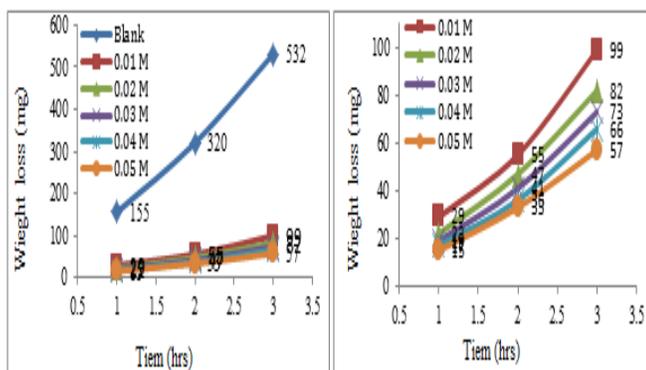


Fig. 3: Illustrated the weight loss of AISI steel in 1M H₂SO₄ with different concentrations of inhibitor at 30±1°C

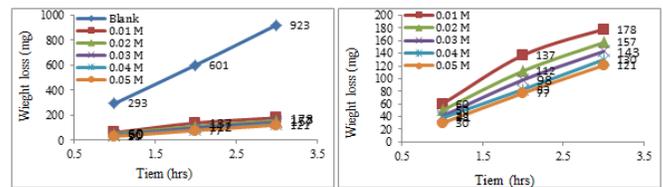


Fig. 4: Illustrated the weight loss of AISI steel in 1M H₂SO₄ with different concentrations of inhibitor at 40±1°C

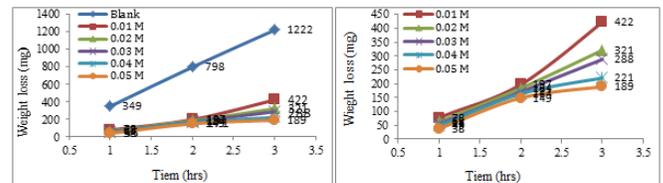


Fig. 5: Illustrated the weight loss of AISI steel in 1M H₂SO₄ with different concentrations of inhibitor at 50±1°C

Table 2: Corrosion data of AISI steel at different concentrations of inhibitor at 30±1°C

Time	1hr.				2 hrs.				3 hrs.			
	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %
1M H ₂ SO ₄	155	23.69	---	---	320	24.45	---	---	532	27.10	---	---
0.01 M	29	4.43	0.8129	81.29	55	4.20	0.8281	82.81	99	5.04	0.8139	81.39
0.02 M	22	3.36	0.8580	85.80	47	3.59	0.8531	85.31	82	4.17	0.8458	84.58
0.03 M	19	2.90	0.8774	87.74	41	3.13	0.8718	87.18	73	3.71	0.8627	86.27
0.04 M	17	2.59	0.8903	89.03	36	2.75	0.8875	88.75	66	3.36	0.8759	87.59
0.05 M	15	2.29	0.9032	90.32	33	2.52	0.8968	89.68	57	2.90	0.8928	89.28

Table 3: Corrosion data of AISI steel at different concentrations of inhibitor at 40±1°C

Time	1hr.				2 hrs.				3 hrs.			
	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %
1M H ₂ SO ₄	293	44.78	---	---	601	45.93	---	---	923	47.03	---	---
0.01 M	60	9.17	0.7952	79.52	137	10.47	0.7720	77.20	178	9.07	0.8071	80.71
0.02 M	50	7.64	0.8293	82.93	112	8.56	0.8136	81.36	157	8.00	0.8299	82.99
0.03 M	41	6.26	0.8600	86.00	98	7.49	0.8369	83.69	143	7.28	0.8450	84.50
0.04 M	38	5.80	0.8703	87.03	83	6.34	0.8618	86.18	130	6.62	0.8591	85.91
0.05 M	30	4.58	0.8976	89.76	77	5.88	0.8718	87.18	121	6.16	0.8689	86.89

Table 4: Corrosion data of AISI steel at different concentrations of inhibitor at 50±1°C

Time	1 hr.				2 hrs.				3 hrs.			
	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %	W mg	C _R mmpy	θ	η %
1M H ₂ SO ₄	349	53.35	---	---	798	60.99	---	---	1222	62.26	---	---
0.01 M	78	11.92	0.7765	77.65	197	15.05	0.7531	75.31	422	21.50	0.6546	65.46
0.02 M	63	9.63	0.8194	81.94	184	14.06	0.7694	76.94	321	16.35	0.7373	73.73
0.03 M	55	8.40	0.8424	84.24	171	13.07	0.7857	78.57	288	14.67	0.7643	76.43
0.04 M	49	7.49	0.8595	85.95	164	12.53	0.7944	79.44	221	11.26	0.8191	81.91
0.05 M	38	5.80	0.8911	89.11	149	11.38	0.8132	81.32	189	9.63	0.8453	84.53

Electrochemical Impedance Measurements:-

Inhibition efficiency of inhibitor (PAPM) in aqueous solution of 1M H₂SO₄ at room temperature has been measured by EIS technique. Electrochemical parameters of EIS technique are maximum frequency (f_{max}), double layer capacitance (C_{dl}), charge transfer resistance (R_p), solution resistance (R_s), phase angle(α) and metal surface irregularity (n). Charge transfer resistance has been calculated on a Nyquist method shown in Fig. 6A. It is clear from the results in Table 5 that change of impedance spectroscopy are indicate the inhibitor adsorption on AISI steel surface. The increase in charge transfer resistance and decrease in double layer capacitance may be attributed to increase of inhibitor adsorption on AISI surface, also the increase in R_p values may be ascribed to protective film formation on AISI steel surface. Charge transfer resistance increases with increase of inhibitor concentration, indicating to retardation of corrosion reaction in each of anodic and cathodic sites (Zarrok et al., 2013; Chitra et al., 2010). Diameter of capacitive loop in inhibitor presence is a larger than its absence, and increases with increase of inhibitor concentration as elucidated in Fig.7A this suggests the effectiveness of inhibitor increases with its concentration increase. Furthermore, Fig. 7A showed there are a little difference in diameter of capacitive loop at some concentrations, while in the other concentrations the difference in diameter of capacitive loop is a large, such behavior can be considered that adsorption is a physical adsorption in little difference, either in a large difference is a chemical adsorption. The adsorption on the metal surface decreases the double layer capacitance (Xiang-Hong and Xiao-Guang, 2013; John and Joseph, 2012). Decrease the C_{dl} values can be attributed to the decrease local dielectric constant and/or increase in thickness of electrical double layer (Zarrok et al.,2013; Yurt et al.,2005). Metal surface irregularity (n) has been determined using the relation $n = \alpha/(\pi/2)$, where α is a phase angle of CPE and its value should be larger than zero and less than one. In case inhibited solutions, the values of (n) are lies between 0.508 and 0.631 and its value increases with increasing of surfactant concentration (inhibitor) to reaches a maximum value 0.631 at 0.05 M as shown in Table 5, indicating reduction of surface inhomogeneity, due to adsorption of inhibitor on most active sites in AISI surface (The AISI surface is a more homogeneity). Low value of (n) in 1M H₂SO₄ solution

at inhibitor absence indicates surface inhomogeneity and/or formation of corrosion products on AISI surface (Mathina and Rajalakshmi,2016). The AC impedance of Bode plots increases with increasing of inhibitor concentration as shown in Fig. 7B. Low frequency may be attributed to the relaxation processes obtained by adsorption as shown in Table 5. Low of phase angle versus the frequency at decrease of inhibitor concentration indicate to the capacitive response decrease, such the phenomenon could be attributed to that corrosion effectiveness is a higher at low of inhibitor concentration. Maximum phase angle shifts to lower frequency after add inhibitor, indicating the increase of inhibition at constant system as shown in Table5 and Fig.7C (Meften,2016; Singh and Quraishi, 2012).

Table 5: Shows the EIS results of AISI steel at different concentrations of inhibitor at room temperature

Inhibitor concentration	R_p (Ω cm ²)	R_s (Ω cm ²)	C_{dl} (μ F/cm ²)	f_{max} (Hz)	Surface coverage(θ)	Metal surface irregularity (n)	Phase angle(α)	η (%)
1M H ₂ SO ₄	30.58	1.33	76.41	68.14	---	0.400	0.628	---
0.01 M	84.98	1.02	61.55	30.44	0.6402	0.508	0.799	64.01
0.02 M	88.64	0.38	60.12	29.88	0.6551	0.538	0.845	65.50
0.03 M	111.43	0.78	52.30	27.32	0.7256	0.571	0.898	72.55
0.04 M	128.71	0.45	49.52	24.98	0.7625	0.624	0.981	76.24
0.05 M	238.51	0.92	33.97	19.65	0.8718	0.631	0.992	87.17

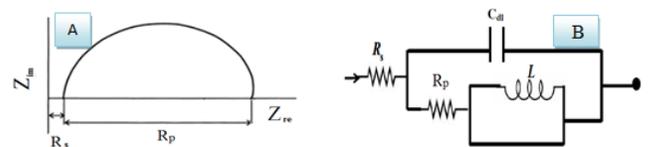


Fig.6: (A) Simple Nyquist plot, and (B) Electrochemical equivalent circuit used to fit the impedance spectra

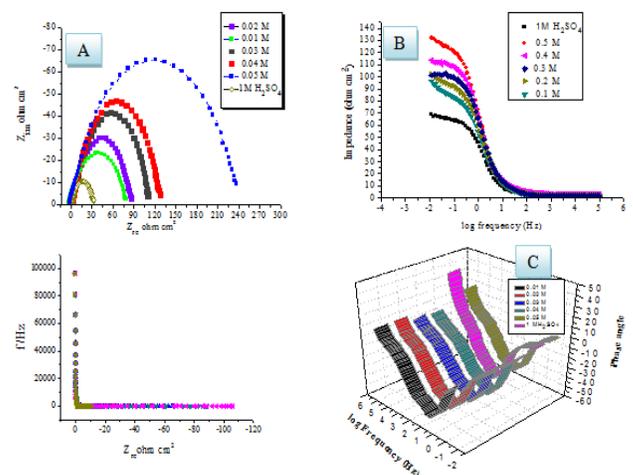


Fig.7: (A) Nyquist diagrams of AISI steel, (B) Bode plots of AISI steel, and (C) Bode-phase angle plots of AISI steel

Adsorption Behavior of Gemini Surfactant:-

In general the adsorption of inhibitor on metal surface is a essential step to explain inhibition mechanism. The adsorption provides information about the interaction between the adsorbed molecules and metal surface. Adsorption of inhibitors on metals surface depend on inhibitor structure, nature of corrosive medium, type of metal, pH of corrosive medium, temperature and electrochemical potential of metal-solution interface. From results of weight loss method previously mentioned, the AISI surface covered by inhibitor molecules of PAPM was noted increases considerably whenever increases the inhibitor concentration, indicating a large the adsorption on AISI steel surface. Several adsorption isotherms were assessed such as, Temkin, Frumkin, Langmuir and Freundlich isotherms, where the best fit obtained is a Langmuir adsorption isotherm. Langmuir adsorption by plotting C_{inh}/θ versus C_{inh} was determined for various concentrations of inhibitor using the Equation 7, where a straight lines have been given at correlation coefficient close to 0.999952, 0.999749 and 0.9994 as shown in Fig. 8. The best fit of correlation coefficient are $r_2 = 0.999952$, $r_2 = 0.999749$, $r_2 = 0.9994$ for gemini surfactant at 30, 40 and 50 oC respectively as shown in Table6. Also, it can be conclude that concentration directly proportional with C_{inh}/θ and the relation is a good linearity as shown in Fig. 8, suggesting the Langmuir model is suitable to describe the adsorption process of inhibitor molecules on AISI surface, furthermore indicates to strong adsorption of PAPM molecules on AISI steel surface (Abdallah *et al.*, 2016; Laabaissi *et al.*, 2017; El Aoufir *et al.*, 2017; Lgaz *et al.*, 2018; Adardour *et al.*, 2016).

$$\frac{C_{inh}}{\theta} = \frac{1}{K_{ads}} + C_{inh} \tag{7}$$

$$\Delta G_{ads}^{\circ} = -RT \ln (K_{ads} \times 55.5) \tag{8}$$

Where K_{ads} is a equilibrium constant of adsorption reaction, and its value from the intercept line on the C_{inh}/θ axis was calculated as shown in Table 6 and Fig. 8, where the intercept represents $1/K_{ads}$. The C_{inh} is a inhibitor concentration in the solution bulk. The standard free energy of adsorption ΔG_{ads}° was calculated through Equation 8, where R is a gases constant 8.314 J/k.mol, T is a temperature in Kelvin, and 55.5 is a water concentration in solution (Lgaz *et al.*, 2018).

In generally, the negative values of standard free energy of adsorption ΔG_{ads}° means that adsorption process spontaneously occurs, and its value if up to -20 kJ/mol or less negative from that, mean that adsorption correspond with physical adsorption, either these negative if a larger than -40 kJ/mol will be correspond with chemical adsorption. If the value of ΔG_{ads}° between -20 kJ/mol and -40 kJ/mol means that adsorption on metallic surface occur through physisorption and chemisorption together at the same time (mixed adsorption). The results obtained of gemini surfactant test as a inhibitor for AISI steel shown that ΔG_{ads}° values are -26.17, -26.33, -26.88 kJ/mol at 30, 40 and 50 °C respectively as the elucidated in Table 6, therefore the adsorption of PAPM molecules on AISI steel happened mainly via physisorption and chemisorption together (Zarrok *et al.*, 2013; Lgaz *et al.*, 2018; Tao *et al.*, 2009; Vennila and Manjula, 2016; Al-Senani and Alshabanat, 2018).

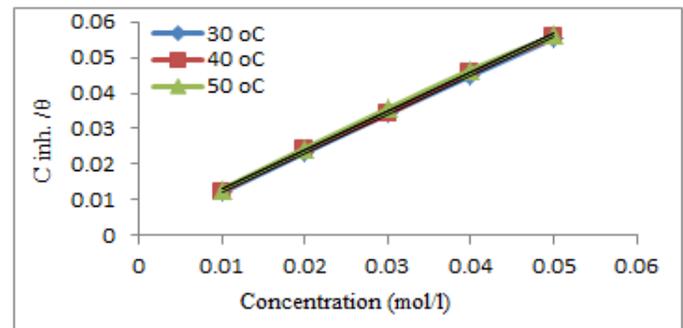


Fig. 8: Langmuir adsorption of gemini surfactant (inhibitor) on AISI steel surface at optimum efficiency

Table 6: Adsorption parameters of gemini surfactant (inhibitor) on AISI steel surface at optimum efficiency

Temperature (°C)	Slope	Intercept (1/K _{ads})	Correlation coefficient (r ²)	Equilibrium constant (K _{ads})	Free energy ΔG° (KJ.mol ⁻¹)	Adsorption type
30	1.076	0.00170	0.999952	588.23	-26.18	Langmuir
40	1.073	0.00223	0.999749	448.43	-26.34	Langmuir
50	1.087	0.00247	0.999400	404.85	-26.88	Langmuir

Theoretical Study Through Quantum

Methodology:-

Quantum methodology could help in the identify of appropriate sites to interact between the inhibitor and metal surface, also information provide about the configuration lowest adsorption energy onto the metal surface which cannot be experimentally

identified (Khadom,2017; Laabaissi *et al.*, 2017; Shahabi and Norouzi,2017). Electronic characteristics obtained by DFT/B3LYP/6-31G (d) are E_{LUMO} , E_{HOMO} , energy gap, solvation energy and dipole moment. Highest Occupied Molecular Orbital (HOMO) and Lowest Unoccupied Molecular Orbital (LUMO) are important electronic characteristics and correlated to each other for illustrating the inhibition processes and estimate compounds effectiveness as an inhibitors for corrosion (Al-Sabagh *et al.*, 2013; Ma *et al.*, 2006). The geometry-optimized structure of gemini surfactant is a non-planar as the elucidated in Fig.9 thereby diminishes of gemini surfactant adsorption area on AISI steel surface (Meften *et al.*, 2018).

From elucidated results in Table7 the high value of E_{HOMO} 12.357 eV indicate that molecule of gemini surfactant has strong tendency for donating in electrons to d-orbit of AISI steel to form a coordinate covalent bond with low energy, while the low value of E_{LUMO} -5.462 eV is a likely refer to ability of gemini surfactant on accepting electrons from anti-bonding orbit (4s2 orbit of AISI steel) to form back donation bond (Stable adsorption), consequently the inhibition efficiency will be sensitive to change in HOMO and LUMO energies. Fig. 10 shows the molecular frontier orbital for electrons density distribution of the gemini surfactant (Al-Sabagh *et al.*, 2013; Ma *et al.*, 2006; Meften *et al.*, 2018; Zhang *et al.*, 2005).

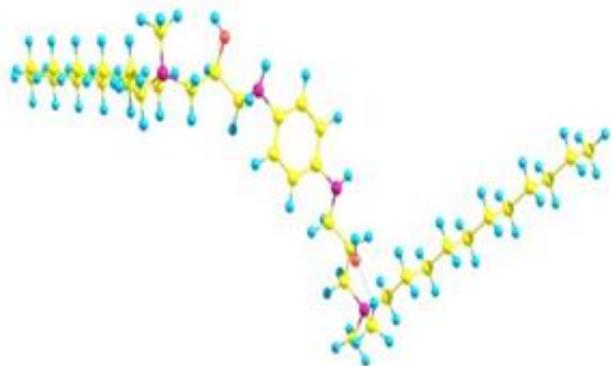


Fig.9: Geometry-optimized structure of gemini surfactant (inhibitor)

The energy gap (ΔE_{gap}) is a important parameter as a function for molecule reaction with the metallic surface through adsorption processes. Hard molecules characterized in large values of energy gap while soft molecules characterized in small values.

Hard molecules are less reactive from soft molecules due to a large gap between the last occupied orbital and first virtual orbit or because the soft molecules are more polarized. The elucidated results in Table 7 indicate that energy gap value of gemini surfactant is a small -17.819 eV, therefore the gemini surfactant is a soft molecule and more reactive with AISI steel surface, where adsorption increases then increase of inhibition efficiency (Al-Sabagh *et al.*,2013; Khalil,2003; Udhayakala *et al.*,2012). Energy gap using the following Equation $\Delta E_{gap} = E_{LUMO} - E_{HOMO}$ was calculated (Larouj *et al.*, 2016).

Table 7 : Electronic characteristics of gemini surfactant (inhibitor) by DFT/B3LYP/6-31G (d)

Electronic characteristics of inhibitor	Values
Energy of highest occupied molecular orbital	12.357 eV
Energy of lowest unoccupied molecular orbital	-5.462 eV
Energy gap	-17.819 eV
Solvation energy	144.68 kJ/mol
Dipole moment	1.298 Debye
Theoretical efficiency	92.35 %
Optimal experimental efficiency	90.32 %

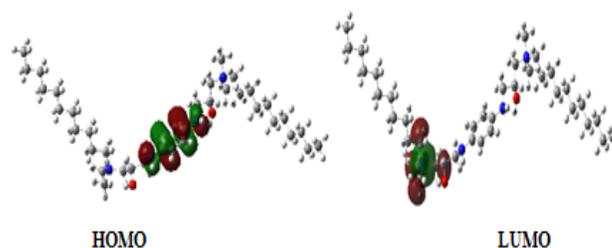


Fig.10: HOMO and LUMO Orbitals for electrons density distribution of gemini surfactant by DFT/B3LYP/6-31G (d)

Electrostatic Potential Surface (EPS) also called Molecular Electrostatic Potential (MEP) is a important for revealer the location of electrons density located in the atoms. Maximum negative region (dark red) is a nucleophilic center so it consider preferred site for electrophilic attack, while maximum positive region (dark blue) is a electrophilic center so it consider a preferred site for nucleophilic attack as elucidated in electrostatic map within the range $-1.087e-1$ a.u to $+1.087e-1$ a.u as shown in Fig.11. Through electrostatic potential surface (EPS) of gemini surfactant shown in Fig. 11 it was observed that negative region larger than

positive region therefore the gemini surfactant has ability to give electrons to d-orbit of AISI steel, this confirm the high value of EHOMO. The gemini surfactant on AISI surface has been adsorb through maximum negative region which improves chemical and physical adsorption processes (Shihab and Mahmood,2017; Maache et al.,2016). There are important case should be explain is a comparison between experimental inhibition efficiency and theoretical inhibition efficiency for gemini surfactant. Theoretical efficiency depending on the Equation 9 was calculated, where it was noted that experimental efficiency and theoretical are on a high agreement to each other (Sikemi et al.,2017). Optimal experimental efficiency reached 90.32% while theoretical efficiency reached 92.35% this confirms the accuracy of results obtained as shown in Table 7.

$$IE_{Theo} = 123.418 - 9.334 \times \text{Dipole moment} - 0.131 \times \text{Solvation energy} \quad (9)$$

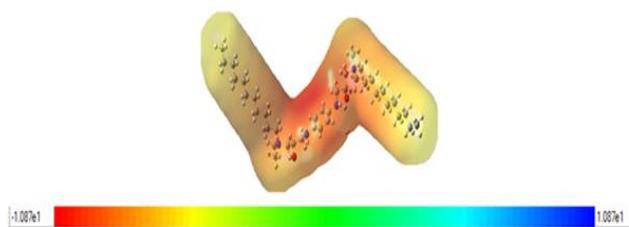


Fig.11: Electrostatic potential surfaces (EPS) of gemini surfactant with electrostatic map

Conclusions:-

In conclusion the main conclusions drawn from this study are that studied gemini surfactant consider excellent inhibitor for corrosion of AISI steel in H_2SO_4 solution, where inhibition efficiency increase with increasing inhibitor concentration and the inhibitor is a from a mixed type. The results obtained through EIS technique and weight loss method on excellent agreement to each other. EIS results showed occurred the adsorption for inhibitor molecules on AISI steel surface according to Langmuir adsorption isotherm. The ΔG_{ads}^0 results showed the physisorption and chemisorption were occurred on AISI surface. For temperatures clear effect on each of corrosion rate and inhibition efficiency where the efficiency decreased with temperature raise while the time has a slight effect on inhibition efficiency. From quantum results, that gemini surfactant (inhibitor) is a soft molecule and more reactive with the AISI surface were noted. Gemini

surfactant has two uses are a corrosion inhibitor and De-emulsifier. Finally the theoretical inhibition efficiency is a compatible with the experimental inhibition efficiency where reached to 92.35% for theoretical and 90.32% for experimental.

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