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RESEARCH ARTICLE

SYNTHESIS AND EVALUATION OF A NOVEL SERIES OF NONIONIC SURFACTANTS DERIVED FROM ITACONIC ACID ESTERS AS BIODEGRADABLE CORROSION INHIBITORS FOR ALUMINUM IN ACIDIC MEDIUM.

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Abstract

A novel series of nonionic polymeric surfactants based on triethanolaminediesteritaconate have been prepared and characterize using FTIR and ^{1}H-NMR spectra. The surface activity, the surface parameters and the free energies of adsorption and micellization of these surfactants at three different temperature were also determined and correlated to their chemical structures .The biodegradability test of all the prepared surfactants revealed that they have a higher tendency towards biodegradation as the biodegradation ratio of them ranged from 88-100% after 7 days only of the exposure to the microorganism which specified them as highly biodegradable compounds .The synthesized nonionic surfactants were evaluated at different concentration as corrosion inhibitor of aluminum in 1M HCl solution using gravimetric analysis and potentodynamic polarization measurement .It was observed that the synthesized surfactant with lowest CMC values showed inhibition efficiency reach 93.7% after 4 h immersion and the inhibition efficiencies increase by increasing concentration of the studied surfactants and based on the potentiodynamic polarization results, the synthesized compound behaved as a mixed type inhibitors. SEM of the metal surface supported the inhibition effect of these surfactants.

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Introduction:-

There have been recent moves to reduce the use of certain classes of surfactants polluting the environment and to replace them with more environmentally friendly and cost efficient surfactants The use of the nonionic surfactants is a current trend in research to replace the charged anionic and cationic surfactants by more environmentally safe surfactants also producing new biodegradable surfactants from renewable resources is another trend.(Sonesson et al,(2007);Kuntom et al,(1998);Berna et al,(1998);Larry et al.,(1998);Basu et al.,(1998).

Itaconic acid (IA) is an unsaturated dicarboxylic acid, nontoxic and readily biodegradable. (IA) is industrially produced in a high yield through the fermentation of starch. It was listed as one of the top value added chemicals from bio-mass by the US Department of energy. (Werpy et al.,(2004)), (IA) and its derivatives due to their unique structures and characteristics can be used as starting materials for the synthesis of polymers (Dwiartil et al,(2007).Furthermore, it shows great potential in synthesis of polymerizable surfactants, however, up to date, there

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are few reports related to the synthesis of itaconate - base surfactants (Parsath et al (2005); Junwei et al,(2011);Jun ,et al(2016).In the present paper we prepared a novel series of oxypropylatedtriethanolaminediesteritaconate base polymeric nonionic surfactants ,the surface activity , surface parameters ,biodegradability and efficiency of these surfactants as corrosion inhibitors against the dissolution of aluminum alloy in acidic medium were investigated using weight loss and potentiodynamic measurements.

Experimental procedures:-

Reagents:-

Itaconic acid (loba chemie,98%) ,fatty alcohols(Octayl , Layryl,Cetyl)(Adwic ,98%)triethylamine [sigma-Aldrich,98.8 %] acrylonitrile and allylalcohol (Alpha Chemie≥98%) ,fatty acids (decanoic ,myrestic and stearic acids) (FlukaChemika ≥ 98%) propylene oxide(Aldrich 99 % (T) p toluene sulphonic acid, hydroxyl amine hydrochloride and potassium hydroxide (Winlab 98%). All solvents were dried and supplied by (Al- Gomhuria Co .Egypt) Aluminum alloy used in this study has the following composition (wt %) Mg 0.0015 , Si 0.22, Fe 0.16, Cu 0.19 , Zn 0.0014, Ti 1.5 , Mn0.0011 and the remainder is Al, supplied by Zhejiang ShauanglinJining Metal Technology Co ,Ltd,Zhejiang, China.

Synthesis procedures:-

Preparation of itaconic monoester:-

The monoester was prepared by refluxing a mixture of itaconic acid (1mol) with fatty alcohols (octyl, lauryl, cetyl) (0.5 mol) respectively in benzene for six hours , using p-toluene sulphonic acid as a catalyst, after cooling reaction mixture , distilled water was added. The benzene layer containing the monoester was separated and dried overnight, and then vacuum distilled to obtain the crude product .Further purification was affected by fractional distillation under vacuum .(Azab et al, (2001))

Preparation of triethanolaminediesteritaconate:-

Triethanolamine (0.1mol) was esterified by (0.1 mol) of monoester itaconic acid using xylene as a solvent and p-toluene sulfonic acid as a catalyst .At the end of the reaction ,when the theoretical amount of water was removed (1.8ml), the product washed by $NaHCO_3$ solution at 40^0c to neutralize the catalyst, then triethanolamine diesteritaconate was extracted three times by petroleum ether(50 ml).Solvent was stripped off by rotator evaporator followed by complete drying of the ester using dry oven at 30^0c under vacuum (Negm,2000).

Oxypropylation of triethanolamine diesteritaconate:-

0.5wt% KOH solutions containing 0.01 mol of the ester was stirred and heated to 70^0c respectively, while passing a slow stream of nitrogen through the system to flush out oxygen. After stopping the nitrogen stream, the propylene oxide was dropping with continuous stirring and heating under an efficient reflux system to retain the propylene oxide .The reaction was conducted for different intervals of time ranging from 1-10 h. From the increment in the mass of the reaction mixture the average degree of propoxylation were determined (Morgos et al, (1983); Ahmed et al, (1996) .The selected average numbers of moles n are 5, 10, and 15 (monomer A).

Preparation of amide oxim (monomer B):-

Hydroxylamine hydrochloride (3.5g, 51mmole) in methanol (30ml) was added to sodium hydroxide (2.11g, 50mmole) in methanol (30ml) at- 25^0c, and insoluble solids were separated off by filtration. Acrylonitrile in methanol (20mmol, 40 ml) was dropped on this filtrate, after stirring for 24 h .at room temperature the mixture filtered again and evaporate .To the residue insoluble solid 50 ml of methylene chloride was added then the crude product was obtained by evaporation of the filtrate (Monomer B) (Eissa et al, 1994).

Preparation of nonionic surfactants (copolymerization reaction):-

The copolymer were obtained by the solution polymerization techniques.The monomers were placed in polymerization tubes and diluted with dimethyl formamide .The polymerization was initiate by adding 1 mol % benzoyl peroxide as a free radicals initiators.The tubes were flushed with nitrogen gas for about 20 min. then sealed and thermo stated at 65^0c for about 17-30hr depending on the monomer pairs and composition .The copolymer were obtained by repreciptation from petroleum ether ($40-60^0$) and finally vacuum at 60^0c.Then the product polymer was cooled and neutralized with Sodium hydroxide solution (Azab, 2005).Scheme 1 shows the chemical structures of the synthesized compounds.

Elemental Analysis:-

The structures of the investigated surfactants were confirmed by infrared (FTIR) and nuclear magnetic resonance 'H-NMR). Infrared spectroscopic analysis was performed by KBr disk method using a Fourier transform infrared spectrophotometer (FTIR) and 'H-NMR spectra were recorded using Varian-300Mercury 300 MHZ spectrometer with TMS as an internal standard and DMSO-D^6

Gel Permeation Chromatography:-

The molecular weights of the prepared surfactants were measured by GPC water Model 600 E and are provided in Table 2

Properties of the prepared surfactant:-

Surface tension andCritical micelle concentration (CMC) measurements:-

Surface tension was determined at room temperature by using a Du-Nouy international tensiometer with a platinum ring (Abdel-Salam et al, 2011), also interfacial tension were obtained using the same procedures as the surface tensions measurements (Han et al, 2009; Negm, 2013) and by plotting of the surface tension versus the - logarithm concentration of surfactant at temperatures 303,313 and 333K, the point of break was taken as the CMC value (Colwell et al, 1961).

Effectiveness (π_{CMC}):-

The effectiveness of a certain surfactant (π_{CMC}) is calculated from equation (1)

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

(γ_0) the surface tension of pure water and γ_{CMC} the surface tension of the surfactant solution at the critical micelle concentration (Negm, 2007).

Maximum Surface Excess Γ_{max}

The maximum surface excess Γ_{max}can be calculated according to equation (2)

$$\Gamma_{max} = \frac{-1}{RT}\left(\frac{\delta\gamma}{\delta \ln C}\right) \ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where R is the universal gas constant (8.314 J $mol^{-1}k^{-1}$) and T is the absolute temperature (t+273K), ($\delta\gamma/\delta\ln c$) is the slope of a plot of surface tension versus concentration curves below CMC at constant temperature.

Minimum surface Area (A_{min})

Minimum surface area (A_{min}) can be calculated using equation (3) (Negm et al, 2007)

$$A_{min} = \frac{10^{16}}{\Gamma_{max} N_{av}} \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

N_{av} is Avogadro's number and A_{min} is given in $nm^2 molecule^{-1}$

Emulsification power:-

Emulsification power was measured as mention previously in (Eissa et al, 2012)

Biodegradability:-

The biodegradability test in river water of the prepared surfactants was carried out using the surface tension method (DU-Nouytensiometer, Kruss type K_6) using a platinum ring (Falbe, 1986)

Gravimetric measurements:-

The inhibiting efficiency to corrosion of the prepared surfactants was measure using a weight – loss technique(Emregul et al ,2004)) .The experiments were performed using aluminum specimens have total surface area

3cm^2,corrosive solutions of 1M HCl and three different surfactants concentrations (100, 300, 500 ppm) prepared from doubly distilled water. The specimens were dipped in 100ml of the corrosive solution at30^{o}c for a period of four hours .The experiments were carried out on triplicate specimens in the present and absence of surfactant and the average corrosion rate and inhibitor efficiency were calculated using equation (4,5)(Negm et al, 2008).

$$C_r = \frac{W_2 - W_1}{AT} \qquad (4)$$

$$\mu = \frac{1 - W_{add}}{W_{free}} \times 100 \qquad (5)$$

Wherew$_1$ and w$_2$are the weight of the specimen after and prior to immersion in the test solution
A area of the specimen (cm^2), T is the immersion w$_{free}$ and w$_{add}$are the weight loss of aluminum in the absence and presence of the tested inhibitors, respectively.

Electrochemical measurement:-

The potentiodynamic polarization method was used to determined the cathodic and anodic polarization curves for aluminum in 0.1MHCl in absence and presenceof different concentration of the synthesized surfactant the working electrode was made of aluminum embedded in Araldite holder with area 1cm^2.Calomel electrode and Ptwirewas utilized as a reference and counter electrode respectively .The polarization curves were determined using Mensbergerpotentiostate PS6 with controlling softwarePS remote. All experiments were carried out at scanning rate of 2mv/sec. (El-Etre et al, 2017)

SEA observation of the metal surface:-

Thesurface morphologies of the metal before and after immersion in 1MHCl in presence and in absence of the synthesized surfactant were observed by SEM image using a JEOT (5400) scanning electron microscopy.

Results and discussion:-

Structure:-

The structure of the prepared compound confirmed using FTIR and 'H-NMR spectroscopy .FTIR spectra of surfactant C_3 as a representative samples for the other surfactants ,showed the following bands at 3401 cm^{-1} and3285cm^{-1} correspond to(NH) and(OH) group ,two absorption bands appeared at 2933cm^{-1} and 2927orresponded to asymmetric and symmetric stretching of C-H group; and two bands at 1655 and 1731 cm^{-1}corresponded the stretching of C=N and C=O respectively while the ether linkage appeared at 1095cm^{-1}.(Fig.1)

^{1}H-NMR spectroscopic analysis of surfactant C_2 as representative for the synthesized surfactant showed the characteristic signal shifts ∂ (ppm) at 0.984 ppm (t,3H of terminal CH_3) , 1.227 (m,28Hof CH_2),2.727(t,2H of CH_2-O-C=O),3.189-3.252 (m,6Hof repeated propylene oxide units),4.002(singlet ,1H of CH_2-CH-C=N-),and 7.9(broad s,1Hof OH) Fig 2.(The chemical structures and the preparation steps of the synthesized surfactants represented in scheme 1)

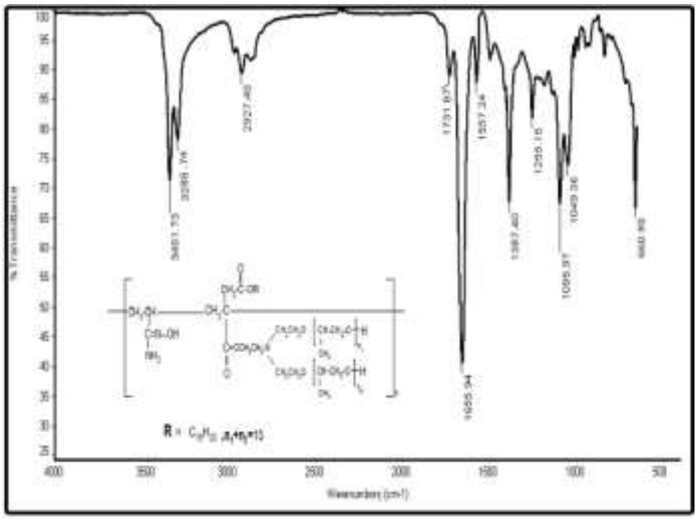
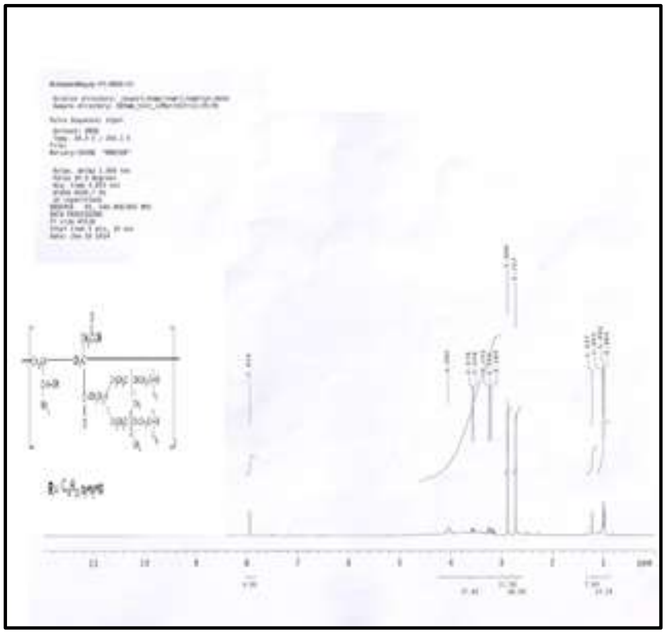
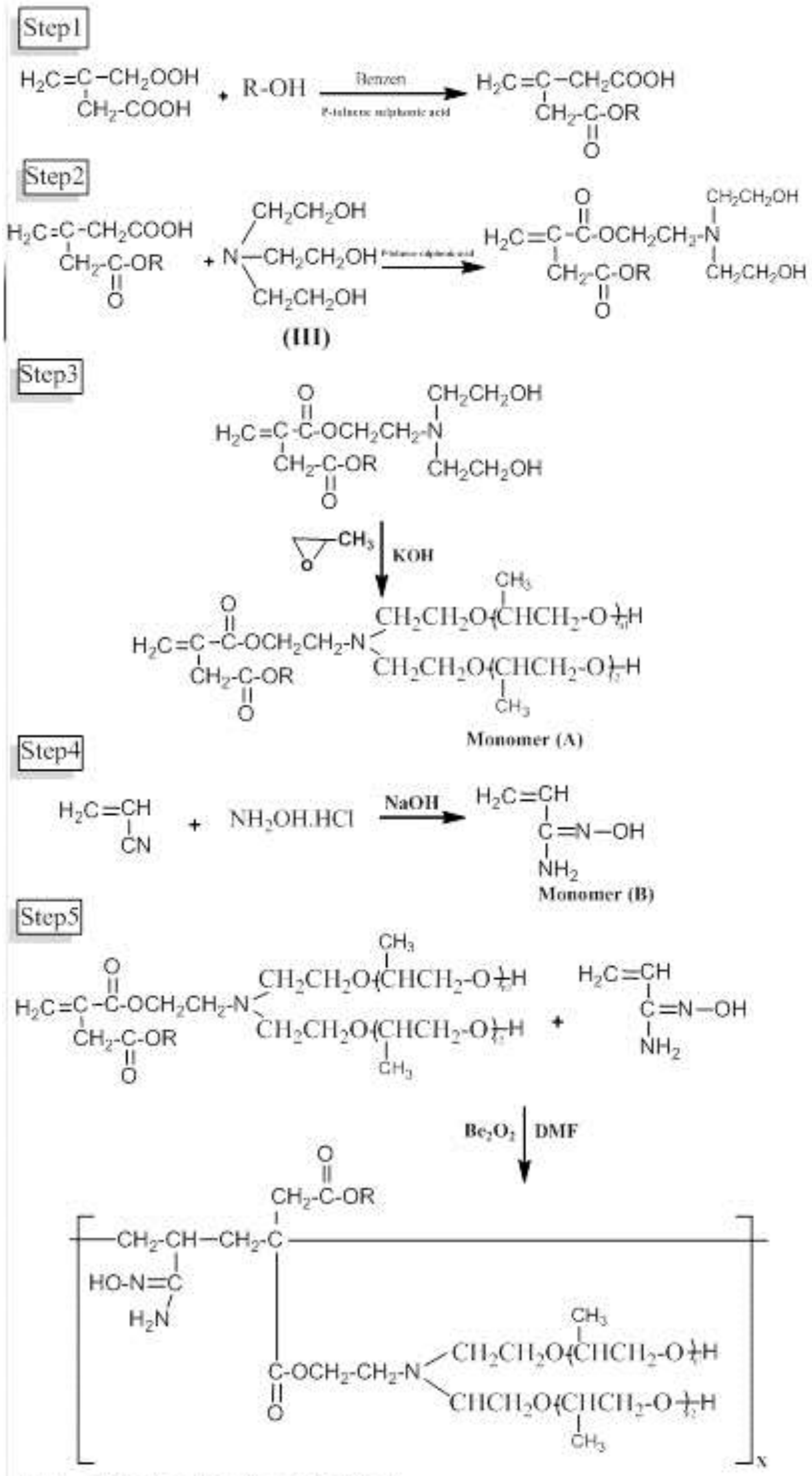


Fig (1):-IR spectra of the nonionic surfactant C3



Fig(2):-^{1}H-NMR spectra of nonionic surfactantC_2

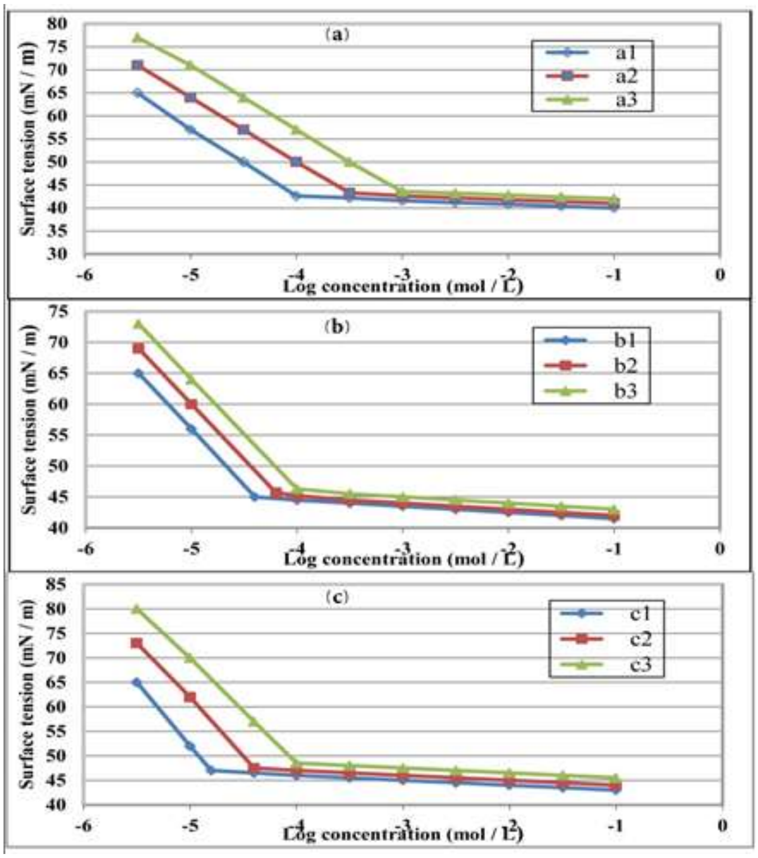


Where R= C_8H_{17}(a), $C_{12}H_{25}$ (b),$C_{16}H_{33}$(c)
$n_1 + n_2$= number of moles of propylene oxide [5(1),10(2) and15(3)]
X =number of repeating units of polymer

Scheme (1):-preparation of the nonionic surfactant

Surface Active Properties of the Synthesized Nonionic Surfactants:-

Fig3 represents the relationship between surface tensions versus -log concentration of the synthesized surfactants at 30°c. It can be seen from the figure that the surface tension decrease by increasing the concentration of the surfactant and the number of the polyoxypropylene chains attached to the surfactants. The critical micelle concentration (CMC) of these surfactants was determined by the intercept of the pre and post- miceller trend in figure these values are listed in Table 1.From the table it is clear that the CMC values increase by increasing the number of polyoxypropylene units attached to the polymer because increasing the hydrophilic character of the surfactant improves the solubilityof it in water and lower the tendency of the surfactant to form micelles(Negm et al , (2008);(2015).However ,the CMC values decrease as the number of methylene groups participated in the hydrophobic chains increases because the repulsion between these molecules and the aqueous phase is consequently increased and forces the surfactant molecules to the interface (Chandar et al,(2011) .It was observed also as a result of breaking of the hydrogen bonds by increasing the temperature from 30°c to 60°c the surfactants molecule separate from the aqueous phase to form micelles, consequently the CMC values also decrease. (Negm et al, 2011).



Fi g (3):-relation between surface tension and –log concentration of the nonionic surfactants

The maximum surface area Γ_{max} in mol/cm^{2}was calculated from equation (2) were listed in Table (1) and used to calculate (A_{min}) using Eq (3) .From the data in Table (1), it can be concluded that by increasing the number of polyoxyproplene unites in the nonionic chain Γ_{max} values decrease, as does increasing the temperature from 30°c to 60°c.However, by increasing the temperature theA_{min} values increase due to the coiling of the nonionic hydrophobic chains at the interface.

Table 1:-Surface and thermodynamics properties of the synthesized nonionic surfactants at 30, 40 and 60^0C

Surfactants	**Number of moles of propylene oxide**	**$T_{(K)}$**	**γ_{CMC} (mN/m)**	**CMC (mol/L)**	**π_{CMC} (mN/m)**	**Γ_{max} (mol/cm^2) 10^{-11}**	**A_{min} (A^2/mol) 10^{-8}**	**ΔG_{mic} KJ mol^{-1}**	**ΔG_{ads} KJ mol^{-1}**
A_1	5	303	43	O.0001	29	1.55	1.07	-23.2	-41.89
		313	42	0.00008	30	1.33	1.24	-24.55	-46.95
		333	41.5	0.00006	30.5	1.12	1.48	-26.91	-54.09
A_2	10	303	41.5	0.00032	30.5	1.309	1.268	-20.27	-43.56
		313	41	0.00028	31	1.087	1.53	-21.29	-49.85
		333	40	0.00022	32	0.93	1.78	-23.32	-57.62
A_3	15	303	41	0.001	31	1.15	1.44	-17.4	-44.29
		313	40.5	0.00079	31.5	1.08	1.53	-18.59	-47.6
		333	39.5	0.0006	32.5	0.83	2.00	-20.54	-59.69
B_1	5	303	43.5	0.00003	28.5	3.25	0.51	-26.23	-34.98
		313	43	0.000028	29	3.00	0.55	-27.28	-36.88
		333	42	0.000025	30	2.83	0.586	-29.33	-39.92
B_2	10	303	43	0.00006	29	2.897	0.573	-24.49	-34.5
		313	42.5	0.00005	29.5	2.73	0.608	-25.77	-36.57
		333	41	0.00004	31	2.59	0.641	-28.03	-39.99
B_3	15	303	42	0.0001	30	2.5	0.664	-23.27	-35.19
		313	41	0.000079	31	2.83	0.697	-24.58	-37.59
		333	40.5	0.000066	31.5	2.167	0766	-26.65	-41.12
C_1	5	303	46.5	0.000012	25.5	4.25	0.39	-28.54	-34.53
		313	45.5	0.000011	26.5	4.05	0.412	-29.71	-36.28
		333	44	0.0001	28	3.96	0.419	-31.61	-38.67
C_2	10	303	44.5	0.00005	27.5	3.96	0.419	-24.9	-31.89
		313	44	0.000039	28	3.71	0.447	-26.42	-33.95
		333	43	0.000031	29	3.62	0.458	-28.74	-36.74
C_3	15	303	44	0.00008	28	3.68	0.45	-23.76	-31.35
		313	43	0.000078	29	3.45	0.48	-24.58	-32.96
		333	42.5	0.00007	29.5	3.3	0.503	-26.48	-35.41

Thermodynamic properties of the synthesized surfactants:-

The free energy of adsorption and micelization of the synthesized surfactant were calculated according to the following equations (Ziyafaddin et al, 2010) and are listed in table 1

$$\Delta G_{mic} = 2.3RT\ (\log CMC)$$

$$\Delta G_{ads} = \Delta G_{mic} - (0.6023\ \pi_{CMC} A_{min})$$

Where R is the gas constant (8.314) T is the absolute temperature (K), $\pi_{CMC}$is the effectiveness in (mN/m) and A_{min} is the minimum surface area at interface by each molecule in nm^2.The thermodynamic data show the negativity of both ΔG_{mic}andΔG_{ads} which reveal the spontaneous behavior of these two processes. Also, the more negativity of ΔG_{ads} is evidence for the preferential tendency of the prepared surfactants towards adsorption at the air water interface rather than formation of micelles in the bulk of the solution **,** the values of **ΔG_{mic}**decrease by increasing the number of polyoxyproplene units in the nonionic surfactant molecules which could be attributed to the increase in the solubility of the different analogous as the result of hydrogen bonds formation. On raising the temperature the negativity of ΔG_{mic} and ΔG_{ads} are increased due to the stability of the adsorbed and micelized surfactant molecules than the freely dispersed ones in the aqueous phase.

Hydrophilic –Lipophilic Balance (HLB), Emulsion stability:-

The hydrophilic – lipophilic balance HLB of a surfactant is a measure of the degree to which it is hydrophilic or lipophilic, and is determined as described by Griffin (Griffin, 1949). The calculated HLB values of the synthesized compounds (listed in table 2) showed high solubility of them in both water and oil phase and according to their HLP valueswhich ranged between 7and 11the synthesized surfactant were classified as water in oil emulsifiers, also these HLB values qualifies these surfactants to be applicable in interfacial application mainly corrosion inhibition(Varka et al,2004) Table (2) shows also the emulsion stability of this surfactants and reveals that it increased with increasing the hydrophilic chain length.

Table 2:-surface tension, Interfacial tension, emulsification power and HLB of the synthesized surfactants

Surfactants	**Mol.Wt**	**Number of moles of propylene oxide**	**Surface tension (mN/m) 0.1 wt% at 30°C**	**Interfacial tension (mN/m) 0.1 wt % at 30°C**	**Emulsion stability (min) 1.0 wt %**	**HLB**
A_1	6230	5	40	14.5	45:09	9.65
A_2	8312	10	41	15.5	47:38	10.19
A_3	12632	15	42.5	16	52:12	12.32
B_1	6440	5	41.5	15	51:52	8.76
B_2	8960	10	42	15.5	54:33	9.31
B_3	11086	15	43	16	58:14	11.22
C_1	7280	5	43	16	60:45	7.71
C_2	9408	10	44	16.5	68:19	8.73
C_3	13768	15	45.5	17	72:32	10.53

Biodegradability:-

The biodegradability test was evaluated using a surface tension method (falbe ,1986).It is clear from the result in Table(3)that the presence of polyoxyproplyene units within the surfactants structure increases their ability towards biodegradation(Galal et al, 2012). The biodegradation ratio of all of the prepared surfactants ranged from 88-100% after 7 days only of the exposure to the microorganism. Furthermore, in surfactants $A_1$and$A_2$the biodegradation extent was reached 100%. These values specified the synthesized surfactants as highly biodegradable compounds which pass the international requirements level (70% after 28 days)

Table3 Biodegradability of the synthesized nonionic surfactants

Surfactants	**Number of moles of propylene oxide**	**1st day**	**2nd day**	**3rd day**	**4th day**	**5th day**	**6th day**	**7th day**
A_1	5	56	62	70	75	82	89	-
A_2	10	52	58	65	73	80	90	-
A_3	15	48	53	60	68	77	85	92
B_1	5	52	58	65	71	79	84	89
B_2	10	50	55	63	69	75	80	88
B_3	15	47	52	57	65	74	80	90
C_1	5	48	53	60	68	77	85	92
C_2	10	47	50	57	66	75	83	89
C_3	15	47	49	55	65	71	82	88

Weight Loss Measurements:-

The values of corrosion rates and inhibition efficiency obtained from the weight loss experiments are shown in Table 4. It is observed that the corrosion rate is gradually decreased by increasing the concentration of the inhibitors that may be attributed to the increase in the adsorbed amounts of the inhibitors on the metal surface which protect it from corrosive medium .It was also observed from the table as the polyoxypropylene unit increases the corrosion efficiency increase. The synthesized inhibitors have polyoxypropylene chains, amide oxime group and a great number of double bonds(C=O) and hetero atoms (N, O) in their chemical structures. This unique structure beside these highly electronegative groups make it can easily adsorbed on the metal surface which increases the efficiency of these inhibitors considerably .The corrosion inhibition efficiencies of the synthesized inhibitors are in the following order 3 > 2 > 1.

It was shown also from the table that the inhibition efficiency of the inhibitors within homologous series increases in the orderC$_3$ >B$_3$ >A$_3$ as the alkyl chain length increase and by correlated the data in (Table 1 and 4) it was found that as the CMC value of the synthesize surfactants decrease the corrosion inhibition efficiencies values are increase becausethe lower CMC values indicate high repulsion in the aqueous bulk between water and surfactant molecules which increases the adsorption tendency of the inhibitors molecules at the metal interface, increases the monolayer formation on the metal surface, and consequently increases the inhibitors tendency.

In Fig (4)The corrosion rates were plotted against the immersion time at constant concentration of inhibitors (C$_1$,C$_2$,C$_3$) .It is clear from the Figure that increasing the immersion time decreasing corrosion rates due the simultaneous adsorption of the inhibitors molecules at the interface (Negm et al,(2014).

Table 4:-Corrosion rates and Inhibition efficiencies of the synthesized nonionic surfactant

Surfactant	**Number of moles of propylene oxide**	**Concentration**	**Inhibition efficiency %**	**Corrosion rate (mg Cm^{-1}h^{-1})**
A$_1$	5	100	58.77	0.06
		300	70.86	0.04
		500	82.66	0.02
A$_2$	10	100	60.13	0.0581
		300	72.67	0.0398
		500	87.34	0.018
A$_3$	15	100	61.54	0.056
		300	73.74	0.0383
		500	88.67	0.016
B$_1$	5	100	60.81	0.0571
		300	72.72	0.0398
		500	88.56	0.0166
B$_2$	10	100	65.67	0.0500
		300	77.16	0.0333
		500	89.72	0.01499
B$_3$	15	100	66.43	0.0489
		300	78.32	0.0316
		500	91.50	0.0123
C$_1$	5	100	65.81	0.0498
		300	77.21	0.033
		500	85.65	0.0209
C$_2$	10	100	68.97	0.045
		300	80.06	0.0291
		500	93.02	0.010
C3	15	100	70.77	0.042
		300	80.69	0.028
		500	93.79	0.009

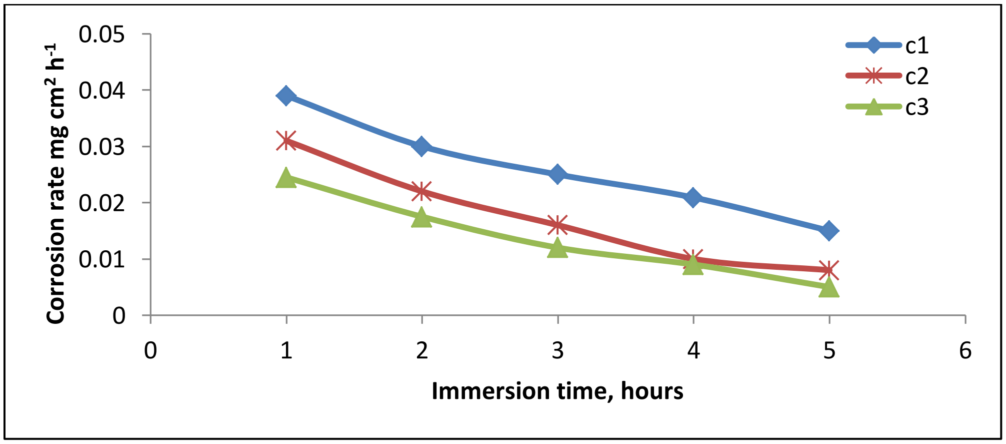


Fig 4:-Effect of immersion time on the corrosion rate in 1M HCl solution at constant concentration of C$_1$, C$_2$, C$_3$ at 30^{0}C

Potentiodynamic Polarization Measurements:-

The Potentiodynamic polarization curves of aluminum in1 M HCl solutions; free and inhibited with different concentrations of the surfactant (C3) as the (highly effective one) at a scan rate of 2mV/sec. are depicted in Fig (5).It can be seen from the Figure that the surfactants could be classified as a mixed type inhibitors as the increase of the surfactant concentration shifts the current potential curves towards lower values of current changed this means that these surfactants affect both anodic and cathodic reactions. It can be seen also from the Figure that cathodic and anodic polarization curves are parallel to the blank curve i.e. the addition of the inhibitors does not change the kinetics of the electrochemical reaction occurring on the metal surface (El-Etre et al, 2017).

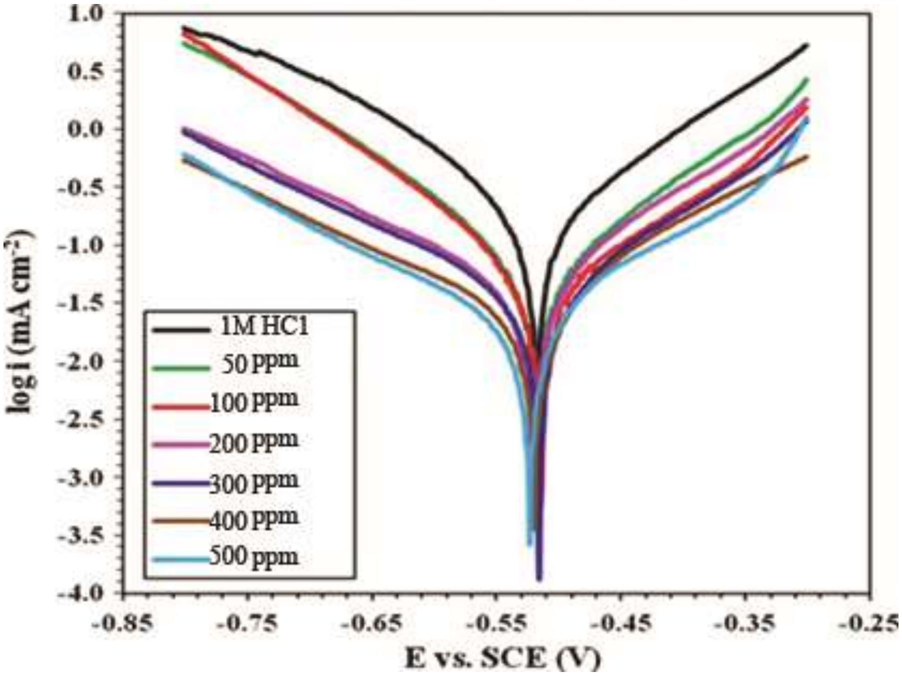
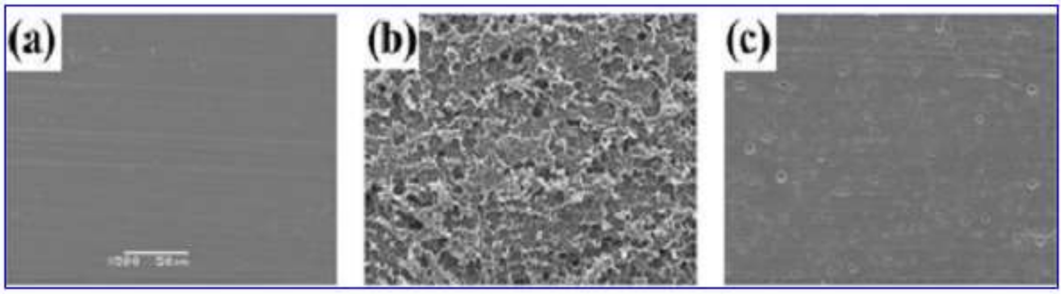


Fig (5):-Potentiodynamic polarization curves for aluminum in1M HCl in the absence and presence of different concentrations of the synthesized nonionic surfactant C_3

Scanning electron microscopy SEM:-

Fig (6) shows the morphologies of the surface of aluminum alloy, it can be seen from figure that before immersion aluminum surface seems smooth (a) while by immersion in the corrosive solution the surface appears highly corroded with huge amount of irregular deep voids distributed along it figure (6) (b).However, these deep voids drastically reduced in figure (C) due to the adsorption of the inhibitors on the metal surface which protect it from the corrosive solution.



Figure(6) Surface morphology of aluminum alloy(a) before immersion; (b) after 24 h immersion in 1 MHCl without inhibitor (c)after24 h immersion in 1M HCl and in the presence of500ppm of the inhibitor C3

Conclusion:-

New nonionic surfactants were synthesized and evaluated to be used as corrosion inhibitors of aluminum in1M HCl.The results of the study revealed the following:

1-The synthesized surfactants show good surface active properties, the negative values of $\Delta G_{ad\ s}$and ΔG_{mic} implies that the two processes are spontaneous. The more negativity of ΔG_{ads}confirming a higher tendency of the surfactant towards adsorption at the metal surface rather than micellization in the bulk of solution and among the studied system the lowest CMC values for surfactant C_3were support it to be the most effective corrosion inhibitors for aluminum in 1 M HCl.

2-The synthesized surfactants acts as environmentally friendly compounds as The biodegradation ratio of all of the prepared surfactants ranged from 88-100% after 7 days only of the exposure to the microorganism.

3- The result of gravimetric analysis and potentiodynamic measurement revealed that the studied surfactants act as goodinhibitors (referring to their corrosion inhibition efficiency values which reached 93.7% after 4 h immersion)

4- From the polarization data, it is clear that the inhibitor is a mixed type inhibitor.

5-Surface morphology of the metal supported the inhibitive effect of the synthesized surfactants.

References:-

1. Abdel-Salam, F.A. and El-Said, A.G. (2011): Synthesis and surface active properties of Gemini cationic surfactants and interaction with anionic azo dye (AR52).J Surfact. Deterg., 14:371-379
2. Ahmed, M.H.M., Sally P., Rusznaz ,k. I. and Farkas, L.(1996):Determination of the average ethoxylation degree. Tenside. Surf. Deterg., 33:410-411
3. Azab, M.M., Bader,S.K.andShaaban, A.F.(2001):Nonionic surfactants based on copolymers of dioctylitaconate with dioxypropyllateditaconic acid , J. Pig .Res. Tec .,30(6):388-394
4. Azab, M.M. Synthesis and copolymerization reaction of p-acryloxy monomer.(2005):Polym. –Int., 54:162-169
5. Basu, S .and Bhattacharyya , D.K. (1998):Utilization of acid oils in making surface-active compounds by lipase-catalyzed hydrolysis and esterification reactions. J Surfact .Deterg., 1:343-350
6. Berna, J.L, Moreno, A. and Bengoechea, C .(1998):Laundry products in bar form. J Surfact. Deterg., 1:263–271
7. Chandar, S.C.N., Sangeethe, D.andArumugham, M.N. (2011). Micellization of mettalo- surfactant N-Dodecyl Hexadecy l OctadecylSalicyldimineCobalt (111) complexes in non aqueous media J. Solut. Chem, 40:608-620
8. Colwell, C.E.andRixon, W.E. (1961): Consideration in the use of nonionic surface active agents. Am Dyest Re, 50: 679-682
9. DwiartiL, O.M. and Miura, S. (2007):Itaconic acid production using sago starch hydrolysate by AspergillumsTerreus TN 484-MI.Bioresour Technol,98,3329-3337
10. Eissa A.M.F., Mahmoud, A.A.and El-Sawy, A.A.(1994):Preparation and surface active properties of oxypropylateddiol monoesters of fatty acids with an amide oxime terminal groups .J.Crasas Y Aceites., 45:306-312
11. Eissa, A.M.F., El-Hefnawy, M., Badar. S., Radwan, M. and Deef Allah(2012) :synthesis and characterization of anionic polymeric surfactant based on sylphonated styrene .J Surfact.Deterg.,19:411-418
12. Emregul, K.C., and Atakol, O. (2004): Corrosion inhibition of iron in 1M HCl solution with Schiff base compounds. Mater Chem. Phys., 83:373-379
13. El-Etre1, A.Y., Ahmed, H. Tantawy1, Salah, E. and Doaa, F. S .(2017):Corrosion Inhibition of Aluminum by Novel Amido-Amine Based Cationic surfactant . J. Bas. and Environ**.**Sci.,2:128-139
14. Falbe,J.(1986).: Surfactants for consumer, Chap 4 Springer Verlage ,Heidelberg
15. Galal, H.S., Ghuiba F.M., Abdou,M. I., Badar ,E.A.A., Tawfik S.M. and Negm ,N.A.(2012): synthesis, thermodynamic properties of some biodegradable vanillin modified polyoxyethlene surfactants .J Surfact. Deterg., 15:735-743
16. Griffin, W.C. (1949): Classification of surface active agent by HLB. J. Soc. Cosmet .Chem., 1:311-319
17. Han,L., YeZ. and Chen H,Luo P.(2009):the interfacial tension between cationic Gemini surfactant solution and crude oil .J SurfactDeterg. , 12:185-190
18. Jun Xu, Fengzhi Cao, Tong Li ,Shaui Zhang , ChaunhuiGao,Yumin Wu(2016):Itaconic acid based surfactant:synthesis and characterization of sodium n-octylsulfitaconatediester anionic surfactant.,JSurfactDeterg 19:373-379
19. Junwei, D.,BinmS.and Jun, X.(2011):Synthesis and characterization of sodium nonyl phenol ethoxylate sulfoitaconateester.JSurf.Deterg.:1,443-49

20. Kuntom, A. and Kifli, H.(1998): Properties of soaps derived from distilled palm stearin and palm kernel.fattyacid.,J Surfact.Deterg,1:1429-1434
21. Larry N. and Britton ,L.N. (1998) :Surfactants and the environment .J.Surfact Deterg,1:109–117
22. MorgosJ. Sally P., FarksL. and Rusznak I.(1983):A novel way for ethoxylation with basic catalyst,J .Am .Oil Chem. Soc., 60:1901-1907
23. Negm, N.A.(2000).preparation and physicochemical properties of some amine surfactants ,PhD. Thesis Faculty of Science ,Ain Shams University
24. Negm N.A.(2013) :Isoxazolium cationic Schiff base Surfactants: surface and antimicrobial properties. ChimicaOggi Chemistry Today, 30: 5-8
25. Negm, N.A. (2007): Solubilization, surface active and thermodynamic parameters of Gemini amphiphles bearing nonionic hydrophilic spacers. J. SurfactDeterg., 2:771-780
26. Negm, N.A. and Aiad, I.A.(2007).Synthesis and characterization of multifunction surfactants on oil -field protection application. J.SurfactDeterg. , 10:87-92
27. Negm, N.A. and Zaki, M.F.(2008):Corrosion inhibition efficiency of nonionic Schiff base amphiphiles of p-amino benzoic acid for aluminum in 4N HCl. Collides Surf. A, 3:297-304
28. Negm, N.A., Ghuibam, F.M., Mahmoued, S.A. and Tawfik, S.M. (2008):Biocidal and anti corrosive activités of benzimidazol -3-ium cationicSchiff base surfactants Eng.Life Sci.,11(15):496-510
29. Negm, N.A., Tawfik, S.M., , Bader ,E.A., Mohamed, I.A .and Ferial, M.G.(2015) .Evolution of some nonionic surfactants derived from vanillin as corrosion inhibitors for carbon steel during drilling processes J.SurfactDeterg. , 18:413-420
30. Negm, N.A., Elkholy, Y.M., Ghuiba, F.M., Zahranm, M.K., Mohamed, S.A.andTawfik S. (2011): M Benzothiazol- 3- ium cationic Schiff base surfactants, synthesis, surface activity and antimicrobial applications against pathogenic and sulfur reducing bacteria in oil fields. J Adsorb. Sci. Technol, 32:512-518
31. Negm, N.A., El-Farargy, A.F., E.A. Abdel Halim, El Lboudy, S. and Ahmed, A.E.S.I. :(2014) Novel bio based nonionic surfactants: synthesis, surface activity and corrosion inhibition efficiency against aluminum alloy dissolution in acidic medium .J Surfactdeterg., 17: 1203-1211
32. Prasath, R.A .and Ramakrishnan.(2005):Synthesis, characterization and utilization of itaconate – based polymerizable surfactants for the preparation of surface –carboxylated polystyrene latexes. J Polym. Sci. Chem., 43:3257-32671
33. Sonesson, A.W., Callisen,T.H., Elofsson ,U.M.andBrismar, H. (2007): Imaging the detergency of single cotton fibers with confocalmicroscopy: the effect of surfactants and lipases. J SurfactDeterg, 10:211–218
34. Varka,E.M.,Argyropoulou,E.C.,Infante,M.R.andpegiodou,S.(2004):synthesis, characterization and surface properties of phynelamine-glcerol ether surfactants J SurfactDeterg, 7:409-414
    Werpy, T.and Peterson ,G.(2004) :Top value added chemicals from biomass, pacific northwest national laboratory and the national renewable energy laboratory, Washington D.C. USA ,1:41-44
35. Ziyafaddin,H.A.,Ravan,A.R.,Shafiga,M.N.andGulnara,A.A.(2010).Surfaceactivity,thermodynamicof micellization and adsorption properties of quaternary salts based on ethanolamine and decylbromide.J. Surfact. Deterg, 13:459-464