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 triethanolamine diesteritaconate have been prepared and characterized using FTIR and ¹H-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 potentiodynamic 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.

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 (Octyl, Lauryl, Cetyl) (Adwic, 98%), triethylamine (sigma-Aldrich, 98.8%), acrylonitrile and allylalcohol (Alpha Chemie ≥ 98%), fatty acids (decanoic, myristic and stearic acids) (FlukaChemika ≥ 98%), propylene oxide (Aldrich 99%) 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, Mn 0.0011 and the remainder is Al, supplied by Zhejiang ShuanglinJining Metal Technology Co., Ltd, Zhejiang, China.

Synthesis procedures:

Preparation of itaconic monoester:
The monoester was prepared by refluxing a mixture of itaconic acid (1 mol) 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 (0.1 mol) was esterified by (0.1 mol) of monoester itaconic acid using xylene as a solvent and p-toluene sulphonic acid as a catalyst. At the end of the reaction, when the theoretical amount of water was removed (1.8 ml), the product washed by NaHCO3 solution at 400c 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 300c under vacuum (Negm, 2000).

Oxypropylation of triethanolaminediesteritaconate:
0.5 wt% KOH solutions containing 0.01 mol of the ester was stirred and heated to 700c 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 250c, 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 650c for about 17-30hr depending on the monomer pairs and composition. The copolymer were obtained by reprecipitation from petroleum ether (40-600) and finally vacuum at 600c. 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-D6.

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 and Critical 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 of surfactant concentration at temperatures 303,313 and 333K, the point of break was taken as the CMC value (Colwell et al, 1961).

Effectiveness (πCMC):
The effectiveness of a certain surfactant (πCMC) is calculated from equation (1)

\[ \pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}} \] ............... (1)

(\(\gamma_0\)) the surface tension of pure water and \(\gamma_{\text{CMC}}\) the surface tension of the surfactant solution at the critical micelle concentration (Negm, 2007).

Maximum Surface Excess \(\Gamma_{\text{max}}\):
The maximum surface excess \(\Gamma_{\text{max}}\) can be calculated according to equation (2)

\[ \Gamma_{\text{max}} = \frac{1}{RT} \left( \frac{\delta \gamma}{\delta \ln c} \right) \] ............... (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 \(A_{\text{min}}\):
Minimum surface area \(A_{\text{min}}\) can be calculated using equation (3) (Negm et al, 2007)

\[ A_{\text{min}} = \frac{10^{16}}{\Gamma_{\text{max}} N_{\text{av}}} \] ............... (3)

\(N_{\text{av}}\) is Avogadro's number and \(A_{\text{min}}\) 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-Nouy tensiometer, Kruss type K6) 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...
3 cm² 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 at 30°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).

\[ C_r = \frac{W_2 - W_1}{A T} \quad (4) \]

\[ \mu = \frac{1 - W_{add}}{W_{free}} \times 100 \quad (5) \]

Where \( w_1 \) and \( w_2 \) are the weight of the specimen after and prior to immersion in the test solution, \( A \) area of the specimen (cm²), \( T \) 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 0.1M HCl in absence and presence of different concentration of the synthesized surfactant the working electrode was made of aluminum embedded in Araldite holder with area 1 cm². Calomel electrode and Pt wire was utilized as a reference and counter electrode respectively. The polarization curves were determined using Mensberger potentiostate PS6 with controlling software PS remote. All experiments were carried out at scanning rate of 2mv/sec. (El-Etre et al, 2017)

**SEA observation of the metal surface:**
The surface morphologies of the metal before and after immersion in 1M HCl in presence and in absence of the synthesized surfactant were observed by SEM image using a JEOL (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 C₃ as a representative samples for the other surfactants showed the following bands at 3401 cm⁻¹ and 3285 cm⁻¹ correspond to (NH) and (OH) group, two absorption bands appeared at 2933 cm⁻¹ and 2927 cm⁻¹ corresponded 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 1095 cm⁻¹.(Fig.1)

'H-NMR spectroscopic analysis of surfactant C₂ as representative for the synthesized surfactant showed the characteristic signal shifts \( \delta \) (ppm) at 0.984 ppm (t, 3H of terminal CH₃), 1.227 (m, 28H of CH₂), 2.727 (t, 2H of CH₂-O-C=O), 3.189-3.252 (m, 6H of repeated propylene oxide units), 4.002 (singlet, 1H of CH₂-CH-C=N-), and 7.9 (broad s, 1H of 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 surfactant C2
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 solubility of it in water and lowers 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).

The maximum surface area $\Gamma_{\text{max}}$ in mol/cm$^2$ was calculated from equation (2) were listed in Table (1) and used to calculate $(A_{\text{min}})$ using Eq (3). From the data in Table (1), it can be concluded that by increasing the number of polyoxypropylene units in the nonionic chain $\Gamma_{\text{max}}$ values decrease, as does increasing the temperature from 30°c to 60°c. However, by increasing the temperature the $A_{\text{min}}$ 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°C

| Surfactants | Number of moles of propylene oxide | T(K) | \( \gamma_{\text{CMC}} \) (mN/m) | CMC (mol/L) | \( \pi_{\text{CMC}} \) (mN/m) | \( I_{\text{max}} \) (mol/cm²) \( 10^{11} \) | \( A_{\text{min}} \) (Å²/mol) | \( \Delta G_{\text{mic}} \) (KJ mol⁻¹) | \( \Delta G_{\text{ads}} \) (KJ mol⁻¹) |
|-------------|-----------------------------------|------|---------------------------------|-----------|---------------------------|-----------------|-----------------|-----------------|-----------------|
| A₁          | 5                                 | 303  | 43                             | 0.0001    | 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          |
| A₂          | 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          |
| A₃          | 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                           | 0.006     | 32.5                      | 0.83            | 2.00            | -20.54          | -59.69          |
| B₁          | 5                                 | 303  | 43.5                           | 0.00003   | 28.5                      | 3.25            | 0.51            | -26.23          | -34.98          |
|             |                                   | 313  | 43                             | 0.00028   | 29                        | 3.00            | 0.55            | -27.28          | -36.88          |
|             |                                   | 333  | 42                             | 0.00025   | 30                        | 2.83            | 0.586           | -29.33          | -39.92          |
| B₂          | 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          |
| B₃          | 15                                | 303  | 42                             | 0.0001    | 30                        | 2.5              | 0.664           | -23.27          | -35.19          |
|             |                                   | 313  | 41                             | 0.00079   | 31                        | 2.83            | 0.697           | -24.58          | -37.59          |
|             |                                   | 333  | 40.5                           | 0.00066   | 31.5                      | 2.167           | 0.766           | -26.65          | -41.12          |
| C₁          | 5                                 | 303  | 46.5                           | 0.00012   | 25.5                      | 4.25            | 0.39            | -28.54          | -34.53          |
|             |                                   | 313  | 45.5                           | 0.00011   | 26.5                      | 4.05            | 0.412           | -29.71          | -36.28          |
|             |                                   | 333  | 44                             | 0.0001    | 28                        | 3.96            | 0.419           | -31.61          | -38.67          |
| C₂          | 10                                | 303  | 44.5                           | 0.00005   | 27.5                      | 3.96            | 0.419           | -24.9           | -31.89          |
|             |                                   | 313  | 44                             | 0.00039   | 28                        | 3.71            | 0.447           | -26.42          | -33.95          |
|             |                                   | 333  | 43                             | 0.00031   | 29                        | 3.62            | 0.458           | -28.74          | -36.74          |
| C₃          | 15                                | 303  | 44.5                           | 0.00008   | 28                        | 3.68            | 0.45            | -23.76          | -31.35          |
|             |                                   | 313  | 43                             | 0.00078   | 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 micellization of the synthesized surfactant were calculated according to the following equations (Ziyafaddin et al, 2010) and are listed in table 1

\[
\Delta G_{\text{mic}} = 2.3RT \log \text{CMC}
\]

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

Where R is the gas constant (8.314) T is the absolute temperature (K), \( \pi_{\text{CMC}} \) is the effectiveness in (mN/m) and \( A_{\text{min}} \) is the minimum surface area at interface by each molecule in nm². The thermodynamic data show the negativity of both \( \Delta G_{\text{mic}} \) and \( \Delta G_{\text{ads}} \) which reveal the spontaneous behavior of these two processes. Also, the more negativity of \( \Delta G_{\text{ads}} \) 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 \( \Delta G_{\text{mic}} \) decrease by increasing the number of polyoxypropylene 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 \( \Delta G_{\text{mic}} \) and \( \Delta G_{\text{ads}} \) 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 (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 values which ranged between 7 and 11, the 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 |
|-------------|--------|-----------------------------------|--------------------------------------|------------------------------------------|----------------------------------|-----|
| A1          | 6230   | 5                                 | 40                                   | 14.5                                     | 45:09                            | 9.65|
| A2          | 8312   | 10                                | 41                                   | 15.5                                     | 47:38                            | 10.19|
| A3          | 12632  | 15                                | 42.5                                 | 16                                       | 52:12                            | 12.32|
| B1          | 6440   | 5                                 | 41.5                                 | 15                                       | 51:52                            | 8.76 |
| B2          | 8960   | 10                                | 42                                   | 15.5                                     | 54:33                            | 9.31 |
| B3          | 11086  | 15                                | 43                                   | 16                                       | 58:14                            | 11.22|
| C1          | 7280   | 5                                 | 43                                   | 16                                       | 60:45                            | 7.71 |
| C2          | 9408   | 10                                | 44                                   | 16.5                                     | 68:19                            | 8.73 |
| C3          | 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 polyoxypropylene 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 A1 and A2, 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).

Table 3: 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 |
|-------------|-----------------------------------|---------|---------|---------|---------|---------|---------|---------|
| A1          | 5                                 | 56      | 62      | 70      | 75      | 82      | 89      | -       |
| A2          | 10                                | 52      | 58      | 65      | 73      | 80      | 90      | -       |
| A3          | 15                                | 48      | 53      | 60      | 68      | 77      | 85      | 92      |
| B1          | 5                                 | 52      | 58      | 65      | 71      | 79      | 84      | 89      |
| B2          | 10                                | 50      | 55      | 63      | 69      | 75      | 80      | 88      |
| B3          | 15                                | 47      | 52      | 57      | 65      | 74      | 80      | 90      |
| C1          | 5                                 | 48      | 53      | 60      | 68      | 77      | 85      | 92      |
| C2          | 10                                | 47      | 50      | 57      | 66      | 75      | 83      | 89      |
| C3          | 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 order $C_3 > B_3 > A_3$ 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 because the 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                   | 0.0333                               |
|            |                                   | 500           | 85.65                   | 0.0209                               |
| $C_2$      | 10                                | 100           | 68.97                   | 0.045                                |
|            |                                   | 300           | 80.06                   | 0.0291                               |
|            |                                   | 500           | 93.02                   | 0.010                                |
| $C_3$      | 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°C
Potentiodynamic Polarization Measurements:-

The Potentiodynamic polarization curves of aluminum in 1 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).

![Potentiodynamic polarization curves for aluminum in 1M HCl in the absence and presence of different concentrations of the synthesized nonionic surfactant C3](image)

**Fig (5):** Potentiodynamic polarization curves for aluminum in 1M HCl in the absence and presence of different concentrations of the synthesized nonionic surfactant C3

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.

![Surface morphology of aluminum alloy](image)

**Figure (6)** Surface morphology of aluminum alloy (a) before immersion; (b) after 24 h immersion in 1 M HCl without inhibitor (c) after 24 h immersion in 1M HCl and in the presence of 500ppm of the inhibitor C3
Conclusion:
New nonionic surfactants were synthesized and evaluated to be used as corrosion inhibitors of aluminum in 1M HCl. The results of the study revealed the following:
1- The synthesized surfactants show good surface active properties, the negative values of $\Delta G_{ad}$, and $\Delta G_{mic}$ implies that the two processes are spontaneous. The more negativity of $\Delta G_{ad}$ 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$_7$ were support it to be the most effective corrosion inhibitors for aluminum in 1M 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 good inhibitors (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 dioxypropyllatedidaconic 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.andArunumgham, M.N. (2011). Micellization of mettalo- surfactant N-Dodecyl Hexadecy I 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. DwirartL, O.M. and Miura, S. (2007): Itaconic acid production using sago starch hydrolysate by Aspergillus: Terreus 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 oxypropyllateditaconic acid, J. Crude oil .J  SurfactDeterg, , 12:185
11. Eissa A.M.F., Mahmoud, A.A.and El-Sawy, A.A.(1994): Preparation and surface active properties of oxypropyllated diol monoesters of fatty acids with an amide oxime terminal groups J.Crude oil .J  SurfactDeterg, , 12:185-190
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 polyoxyethylene 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 fatty acid. J Surfact. Deterg., 1: 1429-1434
21. Larry N. and Britton, L.N. (1998): Surfactants and the environment. J Surf. Deterg., 1: 109–117
22. Morgos, J. Sally P., Farkas L. 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): Isoniazid cationic Schiff base surfactants: surface and antimicrobial properties. Chimica Oggi Chemistry Today, 30: 5-8
25. Negm, N.A. (2007): Solubilization, surface active and thermodynamic parameters of Gemini amphiphiles bearing nonionic hydrophilic spacers. J. Surfact. Deterg., 2: 771-780
26. Negm, N.A. and Aiad, I.A. (2007). Synthesis and characterization of multifunction surfactants on oil-field protection application. J. Surfact. Deterg., 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. Colloids Surf. A, 3: 297-304
28. Negm, N.A., Ghuibam, F.M., Mahmoud, S.A. and Tawfik, S.M. (2008): Biocidal and anti corrosive activities of benzimidazol-3-imine cationic Schiff 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. Surf. Deterg., 18: 413-420
30. Negm, N.A., Elkholy, Y.M., Ghuiba, F.M., Zahran, M.K., Mohamed, S.A. and Tawfik, S. (2011): M-Benzothiazol-3-imine 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., 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. Surf. Deterg., 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., 43: 3257-32671
33. Sonesson, A.W., Callisen, T.H., Elofsson, U.M. and Brismar, H. (2007): Imaging the detergency of single cotton fibers with confocal microscopy: the effect of surfactants and lipases. J. Surf. Deterg., 10: 211-218
34. Varka, E.M., Argyropoulou, E.C., Infante, M.R. and Peggiodou, S. (2004): Synthesis, characterization and surface properties of phenylamine-glycerol ether surfactants. J Surf. Deterg., 7: 409-414
35. 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
36. Ziyafaddin, H.A., Ravan, A.R., Shafiga, M.N. and Gulnara, A.A. (2010). Surface activity, thermodynamic of micellization and adsorption properties of quaternary salts based on ethanolamine and decylbromide. J. Surf. Deterg., 13: 459-464