



Corrosion Inhibition of Aluminum by Novel Amido-Amine Based Cationic Surfactant in 0.5 M HCl Solution

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ABSTRACT:

A novel amido-amine based cationic surfactant, namely, 3-decanoylamino-propyl-ethyl-dimethyl-ammonium iodide (DAEI) was synthesized and its chemical structure was confirmed using FTIR spectroscopy and ¹H NMR spectra. The surface activities of synthesized compound were investigated. Free energies of adsorption and micellization processes were calculated. The inhibition effect of synthesized surfactant on the corrosion of aluminum in 0.5 M HCl solution was investigated using weight loss, hydrogen evolution and potentiodynamic polarization techniques. It was found that this inhibitor acts as a mixed-type inhibitor as well as the inhibition efficiency increases with increasing the inhibitor concentration, but decreases with raising temperature. Langmuir adsorption isotherm fits well with the experimental data. Thermodynamic functions for the adsorption process in 0.5 M HCl were determined and explained.

Keywords: organic synthesis, surfactant, corrosion inhibition, aluminum

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1. Introduction

Aluminum comprises 8% of the earth's crust. The annual market of the aluminum is 25 million tons which makes it the leader in the metallurgy of nonferrous metals [1]. The applications of aluminum and its alloys are varied from household to electrical engineering, packaging, transport and building. The resistance of aluminum against corrosion in aqueous media can be attributed to a rapidly formed surface oxide film. Because the aluminum oxide layer is very thin, it is easily degraded by physical or chemical methods. While physical methods can be minimized by delicate cleaning and operation of equipment, chemical degradation by environmental effects is very difficult to mitigate. The pH level is important as the oxide layer is only stable between a pH of 4.0 and 9.0, before and after that, it becomes soluble rather than solid. In order to maintain the good corrosion resistance of aluminum it is necessary to take into account a certain number of precautions. Some kinds of localized corrosion can occur if the metal is used in unfavorable conditions [2].

A class of compounds called surface – active compounds (or surfactants) [3] that decrease prominently the interfacial tension or interfacial free energy of the interfaces [4, 5]. Surfactant molecules are amphiphilic in character, i.e., they possess hydrophilic and hydrophobic regions [6, 7], having a long hydrocarbon tail and a relatively small ionic or polar head group. In polar solvents such as water, amphiphilic surfactant monomers assemble to form a micelle in such a way that their

hydrocarbon tails huddle in the core of the micelle, and the polar head groups project outwards into the polar bulk solution. As the amphiphile concentration increases, these properties deviate gradually from ideality and at the concentration where aggregation of monomers into micelles occurs; an abrupt change is observed. This concentration is called the critical micelle concentration (CMC) [8]. Adsorption of the surfactant molecules onto metal surface was found to be responsible for the corrosion inhibition of the metal and is in general directly related to its capability to aggregate to form micelles [9-14]. Corrosion inhibition by surfactant molecules are related to the surfactant's ability to aggregate at interfaces and in solution.

The present study aims to investigate the inhibition effect of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI) on the corrosion of aluminum in 0.5M HCl solution using weight-loss, hydrogen evolution and potentiodynamic polarization techniques as well as the thermodynamic functions for the adsorption were investigated.

2. Experimental

2.1. Materials

Aluminum 1050 provided by the Egyptian Copper Works Company, of the following chemical composition: 99.50% min Al, 0.05% max Cu, 0.25% max Si, 0.03% max Ti, 0.4% max Fe, 0.05% max V, 0.05% max Zn, 0.05% max Mn and 0.05% max Mg, was used.

Decanal, decanoic acid and butyl bromide were obtained from Acros organics company (Belgium). Dimethyl sulfate and ethyl iodide were purchased from Aldrich Company. Diethylether, HCl (37%), triethylamine, methylene chloride (98%), acetone and ethyl alcohol (99%), are high grade and obtained from AL-Nasr chemical company.

Solutions of 0.5 M HCl were prepared from 37 % HCl with density of 1.185 g/cm³ by diluting the appropriate volume of its calculated concentration with distilled water.

A solution of concentration of 10⁻² M was prepared from the synthesized cationic surfactant, accurate weighting and dissolving in distilled water, and used to prepare the desired concentration by dilution with distilled water.

2.2. Synthesis of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI)

Thionyl chloride was introduced drop by drop into a conical flask of 4 grams of decanoic acid till the mixture turned into paste, then refluxed for 2 hours at 60°C with continuous stirring, followed by drying in the air, yielding viscous clear yellowish liquid which refers to decanoyl chloride. Both of the required amounts of decanoyl chloride formed and 3-N-N-dimethylamino-1-propyl amine are dissolved in 10 ml of methylene chloride in two flasks separately.

Then decanoyl chloride is introduced drop by drop into the flask of 3-dimethylaminopropylamine in the presence of trimethylamine as a base catalyst in ice bath, followed continuously for one hour. Then the reaction mixture was stirred for three hours at room temperature. The product is obtained by filtration and the precipitate removed, then the solvent evaporated under reduced pressure to yield a viscous dark yellowish liquid (N-(3-dimethylamino-propyl) decanamide).

The required amount of the amido-amine compound formed is introduced into a flask of the required amount of ethyl iodide, then dissolved in 20 ml of dry acetone, then refluxed for 72 hrs at 70°C, then dried under vacuum distillation and washed with diethyl ether to remove the unreacted materials and dried again in the air to form brown viscous liquid. **Scheme 1** shows the chemical structure of the synthesized compound.

2.3. Elucidation of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI)

The synthesized compounds were characterized using IR and ¹H NMR techniques, as shown in figures (1– 4). The infrared spectra of the prepared surfactants were run on FTIR spectra recorded in KBr on a thermonicolet IS10 FTIR spectrophotometer.

The NMR spectra were also measured using Switzerland, Bruker Avance (III), with resonance frequency of 400 MHz and number of scans 128. This characterization is performed at 298 K, and the solvent used was DMSO – d₆ (SO(CD₃)₂). The chemical shift of DMSO – d₆ was 2.50(5). Tetramethylsilane (TMS) was used as an internal reference.

2.4. Critical Micelle Concentration and Surface-Active Properties.

The values of surface tension of the aqueous synthesized cationic surfactant were measured via Tensiometer – K6 processor (Krüss company, Germany) using the ring method at 298 K, between the measurements of values, the ring was initially washed with pure water and acetone. All values of aqueous solutions of prepared cationic surfactants were remained to stand 2 – 3 min before determined. The values of surface tension were decided 3 times for each sample through 3 min interval between each reading and the values were taken as the average of these recorded values.

The measurements of electrical conductivity of prepared cationic surfactant solutions were done using a digital conductivity meter (model type AD3000; EC/TDS and temperature meter) at 298 K. The measurement values were repeated three times for each solution.

2.5. Weight loss measurements

The aluminum samples used are of dimensions of 2 × 1 × 0.8 cm³. They were polished successively with fine grade emery papers, cleaned with acetone, washed with distilled water and finally dried, weighed and then introduced into test solution. The inhibition efficiency (IE %) was computed from the equation:

$$IE \% = \frac{\Delta w_f - \Delta w_i}{\Delta w_f} \times 100. \quad (1)$$

where, w_f and w_i are the weight losses per unit area in absence and presence of the inhibitor, respectively. The following equation was used to calculate the corrosion rate (CR) in grms/cm².hr:

$$CR = \frac{\Delta w}{A.T}. \quad (2)$$

where, w is the weight loss in grams, A is the area of specimen in cm² and T is the exposure time in hours.

2.6. Gasometry

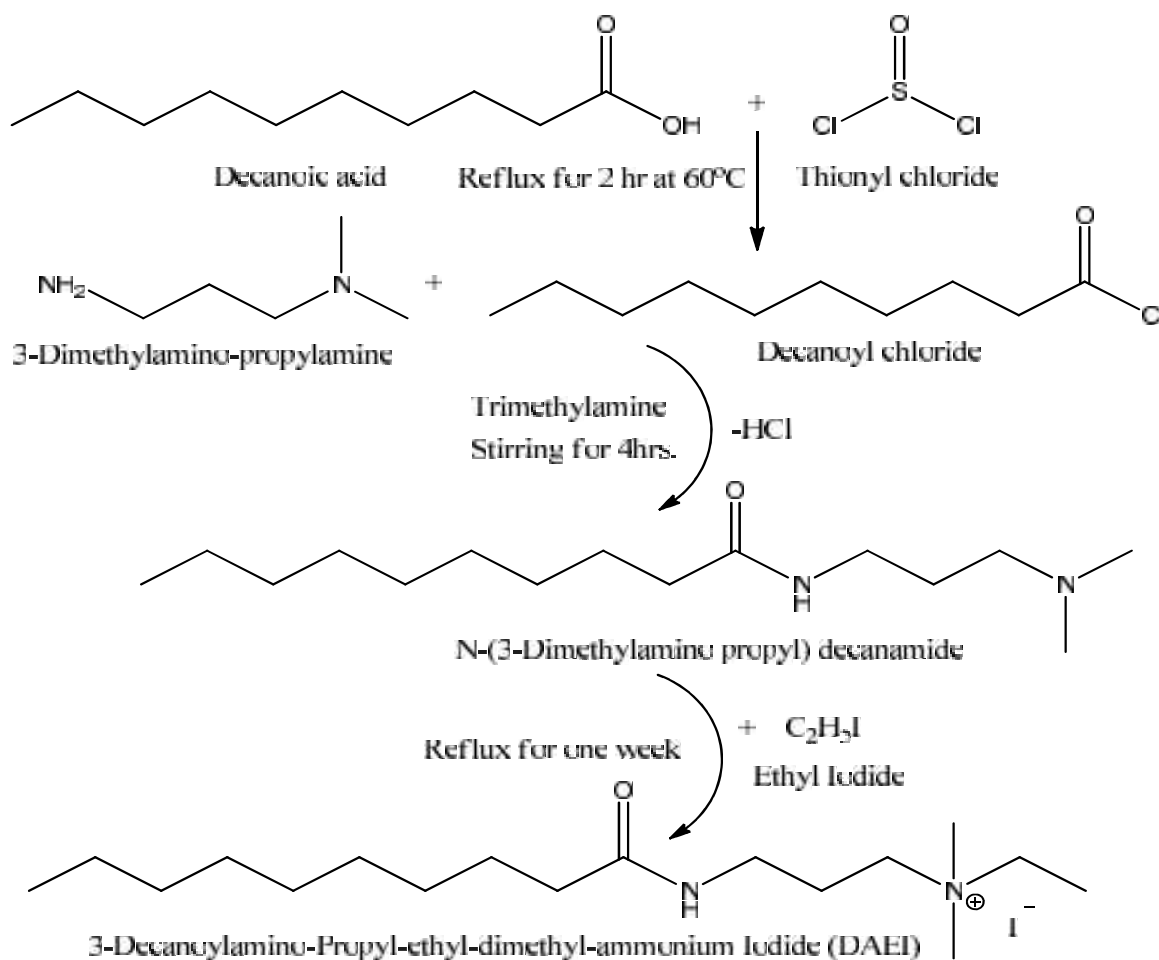
The progress of the corrosion reaction was determined by volumetric measurement of the evolved hydrogen. The aluminum sample was put in a Büchner flask containing the test solution. The flask is sealed with a rubber bung, and from its hose barb protruding from its neck, rubber tubing is connected to the bottom of an inverted measuring cylinder which is fitted above a basin. The cylinder and the basin are filled with distilled water. The hydrogen gradually displaces the distilled water and is collected at the top inside the cylinder, and its volume is measured directly with time. This experiment is done in absence and presence of different concentrations of the tested surfactant.

2.7. Electrochemical measurements

The Potentiodynamic polarization method was used to determine the anodic and cathodic polarization curves of aluminum in 0.5 M HCl both in absence and presence of different concentrations of the inhibitor. The working electrode was made of aluminum embedded in Araldite

holders with area, 1 cm². Before being utilized, the electrode was polished successively with different grades of emery papers until 2500 grade, degreased with acetone and then rinsed with distilled water. A Pt wire and calomel electrode was utilized as a counter electrode and reference

electrode, respectively. The polarization curves were determined using Meinsberger Potentiostat Galvanostat PS6 with controlling software PS remote. All experiments were carried out at scanning rate of 1 mV/sec.



3. Results and discussion

The chemical structure of the synthesized cationic surfactant was confirmed by the FTIR and ¹H NMR spectra.

3.1. Elucidation of N-(3-dimethylamino-propyl) decanamide

IR spectrum showed characteristic bands at 2927.41 cm⁻¹ (ν_{C-H} aliphatic fatty chain), 1633.41 cm⁻¹ (ν_{C=O} of amide),

3426.89 cm⁻¹ (ν_{NH}) and disappear of hydroxyl and carbonyl group bands of fatty carboxylic acid.

¹H NMR-400 MHz, d ppm: 0.91(t, 3H, **CH**₃-CH₂), 1.22(s, Fatty chain, CH₃-(**CH**₂)₆), 1.61(m, 2H, **CH**₂-CH₂-CO), 1.77(m, 2H, NH-**CH**₂-CH₂), 2.06(t, 2H, **CH**₂-CO), 2.70(s, 6H, **2CH**₃-N), 2.73(t, 2H, **CH**₂-N), 3.01(m, 2H, **CH**₂-NH), 7.98(t, 1H, **NH**) as showed figures (2.8 – 2.9).

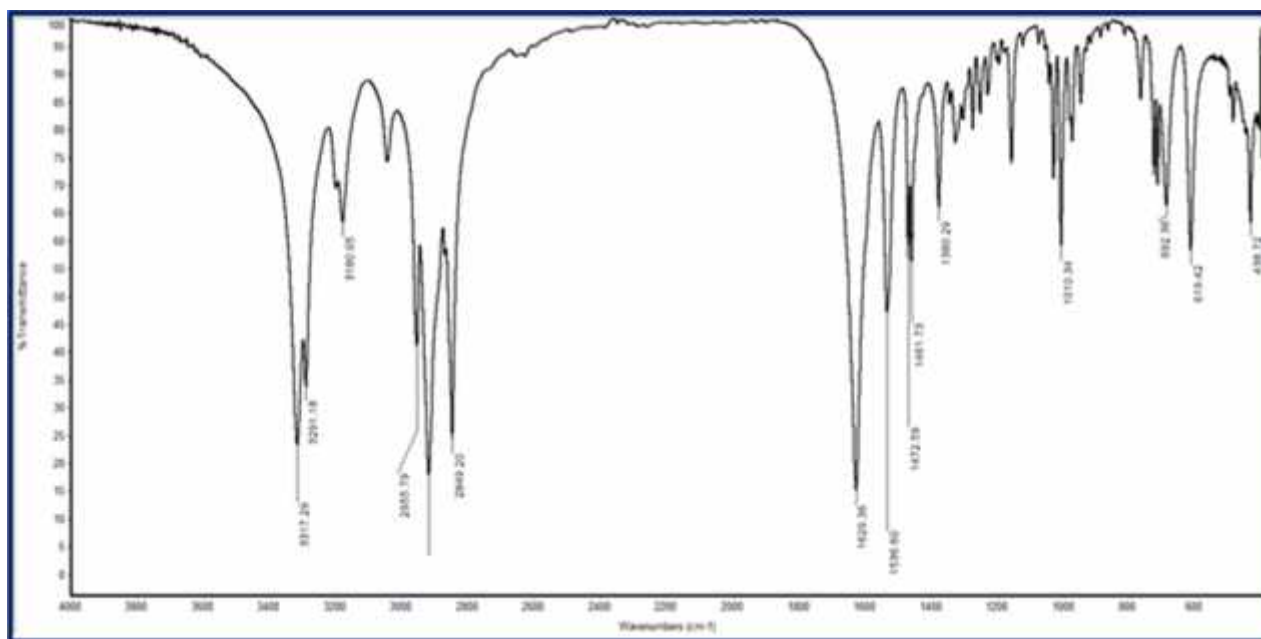


Fig (1): FT-IR spectra of N-(3-dimethylamino-propyl) decanamide.

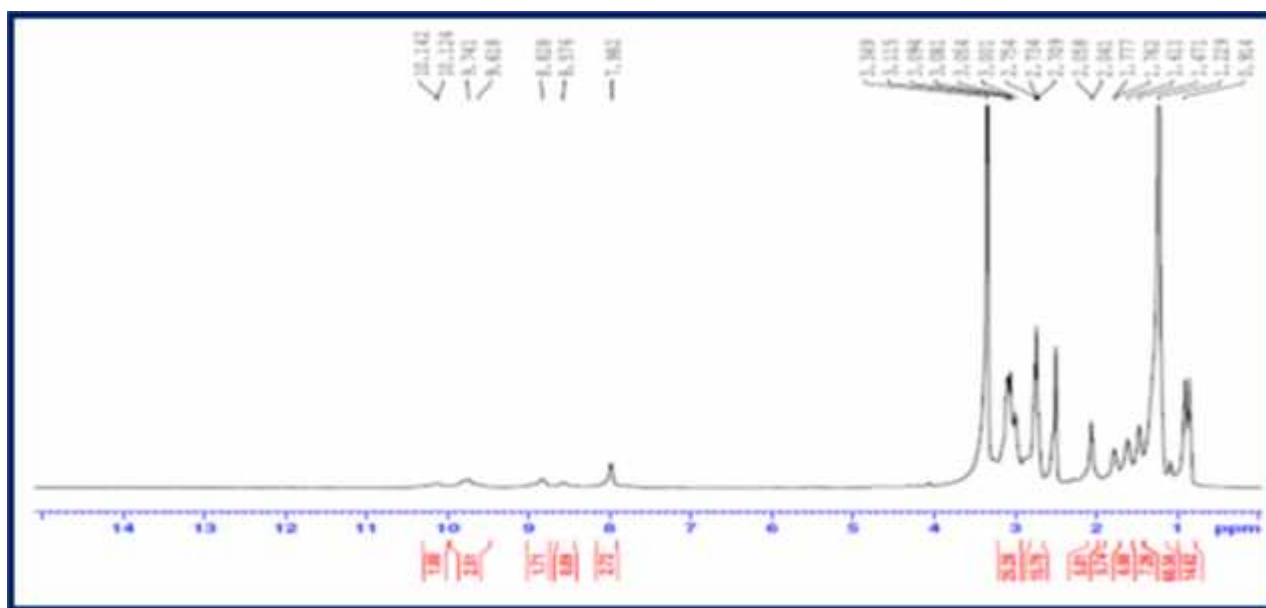


Fig (2): ¹H NMR spectra of N-(3-dimethylamino-propyl) decanamide.

3.2. Elucidation of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI)

Yellow viscous liquid, yield=80%, FT-IR (KBr pellet), cm^{-1} = 3441 (NH of amide), 2924, and 2854 (C-H , aliphatic fatty chain), 1648 (C=O of amide).

¹H NMR-400 MHz, d ppm: 0.84(t, 3H, $\text{CH}_3\text{-CH}_2$), 1.22(s, fatty chain (CH_2)₆), 1.46(m, 2H, $\text{-CH}_2\text{CH}_2\text{C=O}$), 2.08(m, 2H, $\text{-CH}_2\text{CH}_2\text{NH}$), 2.34(t, 2H, $\text{CH}_2\text{-C=O}$), 3.22(t, 2H, $\text{CH}_2\text{-N}^+$), 3.41(q, 2H, CH_2NH), 3.74(s, 6H, $\text{-(CH}_3\text{)}_2\text{-N}^+$), 8.01(t, 1H, NH).

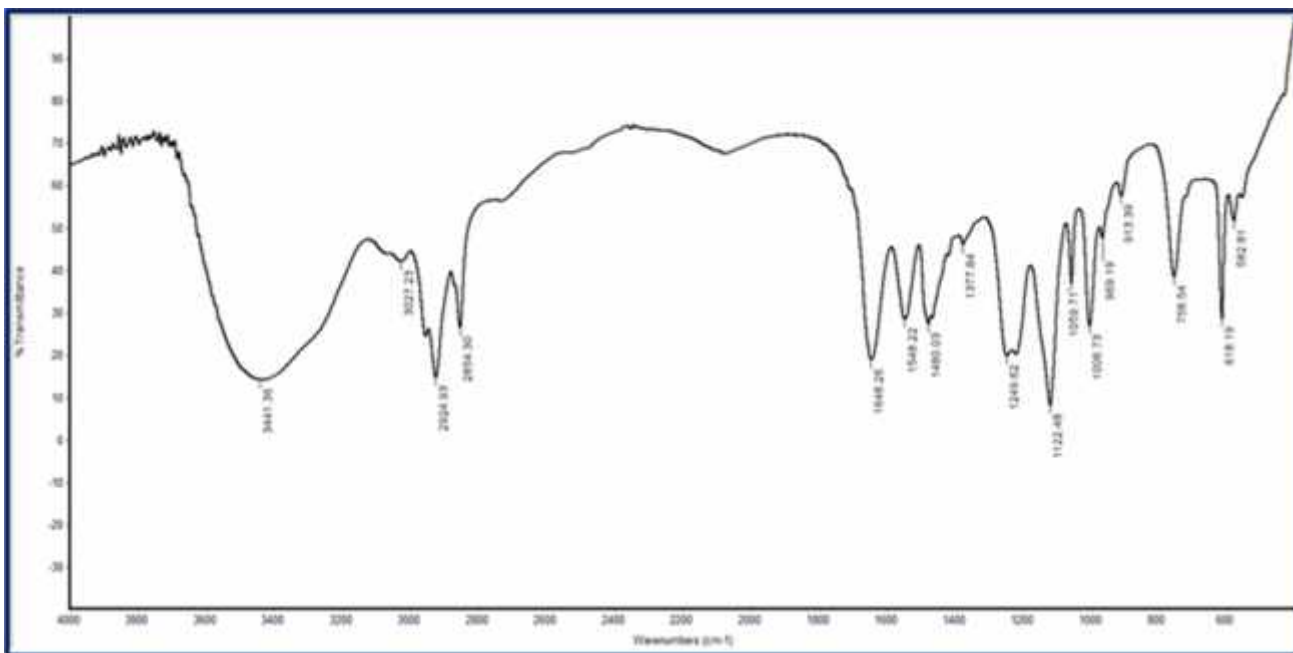


Fig (3): FT-IR spectra of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI).

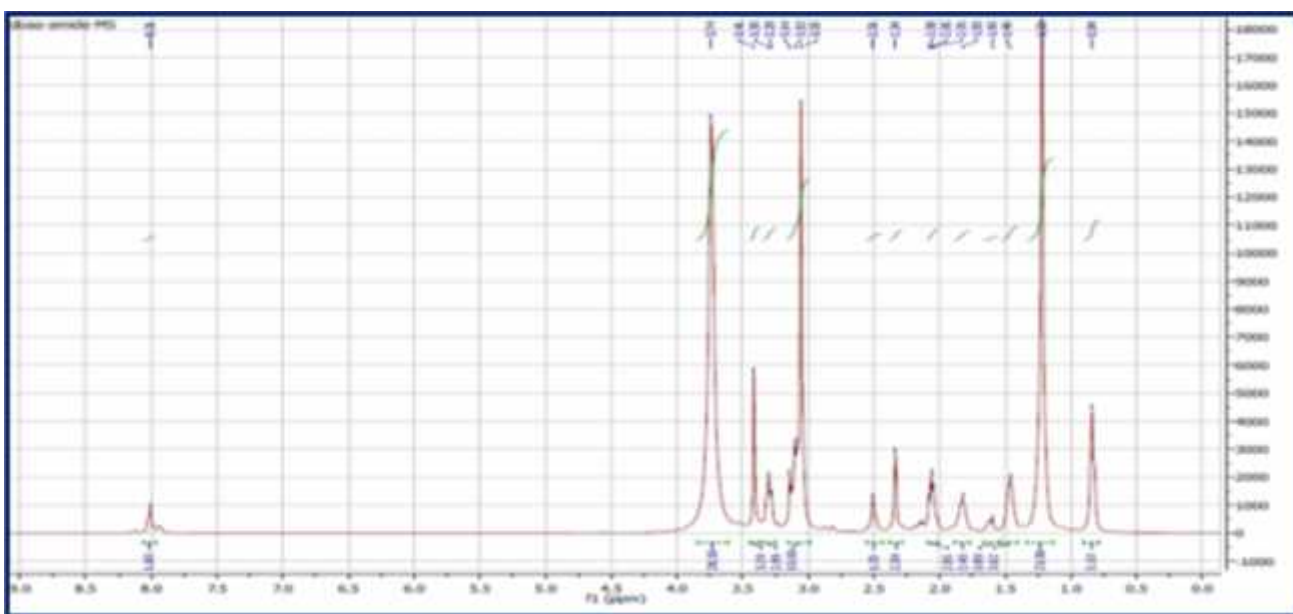


Fig (4): ¹H NMR spectra of 3-Decanoylamino-Propyl-Ethyl-Dimethyl-Ammonium Iodide (DAEI).

3.3. Critical Micelle Concentration and Surface-Active Properties.

Definition of Effectiveness (Γ_{CMC}) is the difference between the surface tension values of synthesized surfactant at the critical micelle concentration (C_{CMC}) in solution form and the surface tension values measured for pure water (γ_0) as follows:

$$\pi_{CMC} = \gamma_0 - \gamma_{CMC} \tag{3}$$

The values of the maximum surface excess, Γ_{max} represent the accumulation of synthesized cationic surfactant molecules at the air–water interface, and can be calculated by the following Gibb’s isotherm equation [15]:

$$\Gamma_{max} = \frac{-1}{2.303nRT} \left. \frac{d\gamma}{d \log C} \right|_T \tag{4}$$

where, $d \gamma / d \log C$ is the slope of γ vs. $\log C$; T is $t + 273$ ($^{\circ}K$); R is a gas constant (8.314); and n is the number of

ions dissociation for synthesized surfactants, n is taken to be 2 for conventional surfactants.

The values of maximum surface excess can be used to calculate the A_{min} values which defined as the average area occupied by single surfactant molecule interface when the solution is at equilibrium, using Eq. (5) [16].

$$A_{min} = \frac{10^{14}}{\Gamma_{max} \times N_A} \quad (5)$$

where, A_{min} is in nm^2 , N_A is Avogadro's number. The results listed in table (1) refer to that the higher values of Γ_{max} lead to crowding of surfactant molecules at the interface, which indicates to smaller values of A_{min} .

The calculation of free energy change of micellization (G°_{mic}) and adsorption (G°_{ads}) of prepared cationic surfactants were done through the following equations:

$$\Delta G^{\circ}_{mic} = (2 - \alpha)RT \ln CMC \quad (6)$$

$$\Delta G^{\circ}_{ads} = (2 - \alpha)RT \ln CMC - 0.06\pi_{CMC}A_{min} \quad (7)$$

where, R is a gas constant, CMC is the critical micelle concentration, α is a degree of counter ion dissociation.

From figure (5), the surface tension values are gradually decreased by increasing the synthesized surfactant concentration. That refers the surfactant molecules at the air/water interface are accumulated by raising the concentration. Also the figure exhibits two different regions, one at low concentration range characteristic by large change in the slope that called pre-micellization region. The other region appears at high concentration characterized by stable slope and called post-micellar region. The intercept between two characteristic regions called critical micelle concentration (CMC). The values of CMC were investigated via electrical conductivity and agreed with those obtained from the surface tension.

From table (1) it is noted that the standard free energies of micellization and adsorption values (G°_{mic} and G°_{ads}) are negative, this indicates to these two processes are spontaneous. In addition, the greater increasing in the negative value of G°_{ads} compared to those of micellization indicates to the ability of the molecules to be adsorbed at the interface.

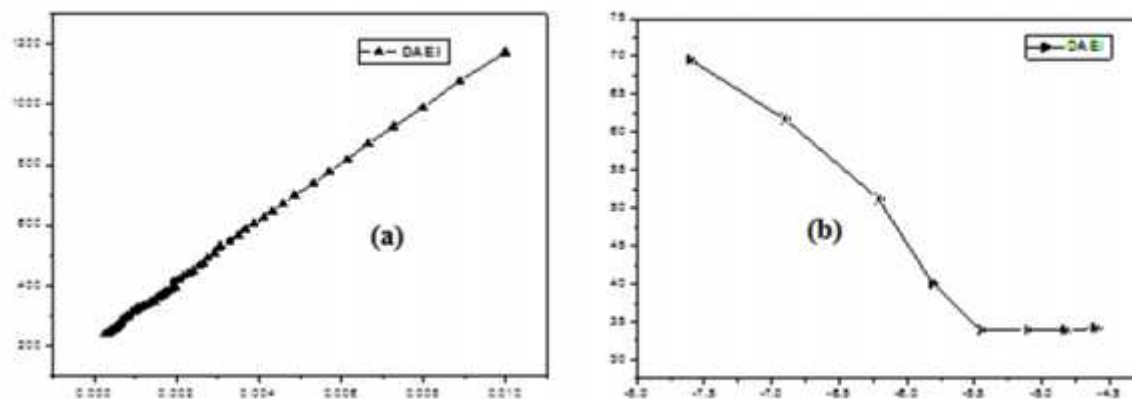


Fig (5): (a) The relation between electrical conductivity and concentration of DAEI at 298 K. (b) The relation between surface tension and $-\log$ concentration of DAEI at 298 K.

Table (1): Surface-active properties of the synthesized cationic surfactants.

| CMC ^a , M.L ⁻¹ | CMC ^b , M.L ⁻¹ | CMC _s , mN.m ⁻¹ | CMC _w , mN.m ⁻¹ | $\frac{0.8}{3}$ | $\frac{0.1}{7}$ | $\Gamma_{max} \times 10^{10}$, mol.cm ⁻² | A_{min} , nm ² | $-\Delta G^{\circ}_{mic}$, KJ.mol ⁻¹ | $-\Delta G^{\circ}_{ads}$, KJ mol ⁻¹ |
|---|---|--|--|-----------------|-----------------|---|--------------------------------|---|---|
| 0.00470 | 0.00481 | 33.27 | 38.73 | 0.8 | 0.1 | 3.23 | 0.51 | 15.53 | 16.71 |

^aCMC value obtained from surface tension measurements. ^bCMC value obtained from conductivity measurements.

3.4. Weight loss measurements

Figure (6) shows the weight loss – time curve for aluminum 1050 in 0.5 M HCl acid in absence and presence of different concentrations of the tested surfactant. As shown from this figure, by increasing the concentration of the surfactant, the weight loss of

aluminum samples are decreased. This means that the presence of this surfactant retards the corrosion of aluminum in 0.5 M HCl acid or in other words, this surfactant act as good inhibitor. The weight loss and inhibition efficiency values are listed in table (2).

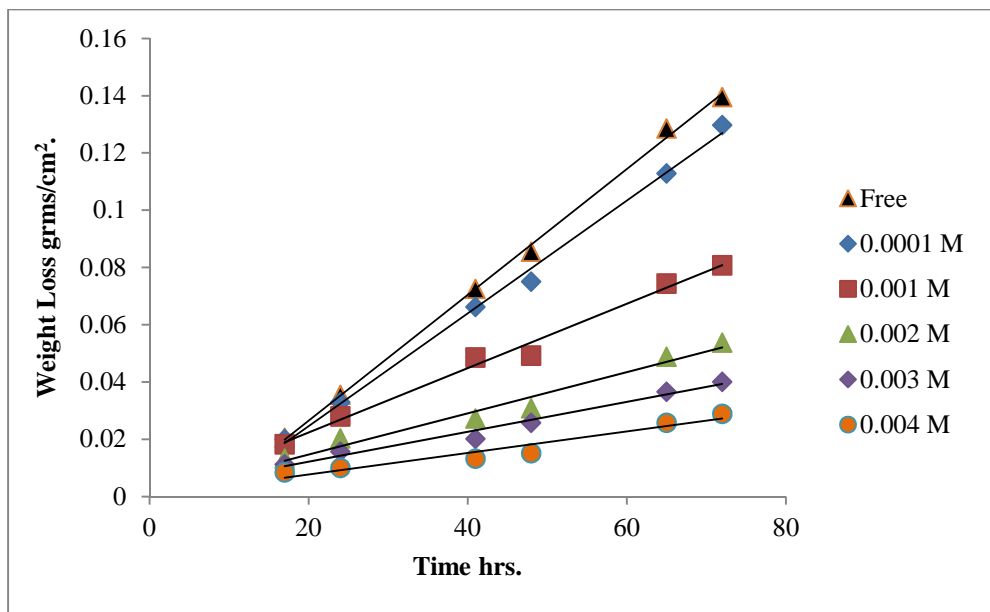


Fig (6): Weight loss – Time curves for the corrosion of aluminum 1050 in 0.5 M HCl in absence and presence of different concentrations of Surfactant (DAEI).

Table (2): Weight loss (gm/cm²) of the corrosion of aluminum 1050 in 0.5 M HCl solution with and without different concentrations of Surfactant (DAEI) at room temperature and different exposure times, hrs.

| Time hrs. | Free | | 0.0001 M | | 0.001 M | | 0.002 M | | 0.003 M | | 0.004 M | |
|-----------|-----------------------------|-----------------------------|----------|-----------------------------|---------|-----------------------------|---------|-----------------------------|---------|-----------------------------|---------|--|
| | Wt. loss gm/cm ² | Wt. loss gm/cm ² | IE % | Wt. loss gm/cm ² | IE % | Wt. loss gm/cm ² | IE % | Wt. loss gm/cm ² | IE % | Wt. loss gm/cm ² | IE % | |
| 17 | 0.0205 | 0.0201 | 19.5 | 0.0183 | 10.73 | 0.0132 | 35.61 | 0.0112 | 45.37 | 0.0084 | 59.02 | |
| 24 | 0.0355 | 0.0329 | 73.2 | 0.028 | 21.13 | 0.0203 | 42.82 | 0.0157 | 55.77 | 0.01 | 71.83 | |
| 41 | 0.0725 | 0.0662 | 86.9 | 0.0486 | 32.97 | 0.0272 | 62.48 | 0.0202 | 72.14 | 0.0132 | 81.79 | |
| 48 | 0.0855 | 0.075 | 12.28 | 0.0492 | 42.46 | 0.0308 | 63.98 | 0.0258 | 69.82 | 0.0151 | 82.34 | |
| 65 | 0.1285 | 0.1128 | 12.22 | 0.0744 | 42.10 | 0.0488 | 62.02 | 0.0366 | 71.52 | 0.0257 | 80.00 | |
| 72 | 0.1395 | 0.1297 | 7.03 | 0.0808 | 42.08 | 0.0537 | 61.51 | 0.0401 | 71.25 | 0.0289 | 79.28 | |

3.5. Effect of temperature

The effect of temperature on aluminum in 0.5 M HCl with and without 0.004 M of the tested surfactant after 48 hrs is shown in figure (7). From the figure, one can observe that, at all temperatures, the corrosion rate of aluminum in the presence of surfactant is lower than that in the free 0.5 M HCl solution. This means that this surfactant acts as inhibitor at all tested temperatures.

The increase of the temperature has a reverse relationship with the inhibition efficiency, which suggests the physical adsorption of surfactant on the aluminum surface. This behavior can be explained on the basis that the increase of the temperature leads to desorption of the adsorbed molecules of surfactants from the aluminum surface.

The activation energy E_a^{*}, for the corrosion of aluminum samples in 0.5 M HCl solutions in the absence and presence of 0.004 M of the surfactant were calculated from Arrhenius equation:

$$CR = A \exp - E_a^*/RT \tag{8}$$

while, the activation entropy (S*) and the activation enthalpy (H*) are calculated from transition – state equation:

$$CR = RT/Nh \exp \Delta S^*/R \exp - \Delta H^*/RT \tag{9}$$

where, CR is the corrosion rate of aluminum, A is the frequency factor, h planks constant ($6.62606957 \times 10^{-34}$ J.sec), N is Avogadro's number ($6.02214129 \times 10^{23}$ mol⁻¹)

and R is the universal gas constant (8.3144598 J.mol⁻¹.K⁻¹).

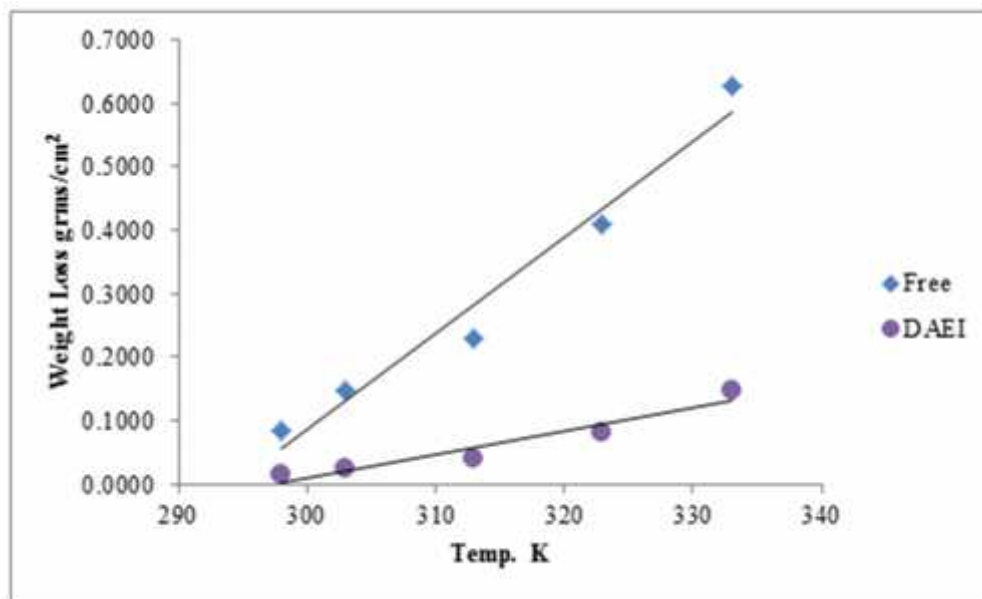


Fig (7): Weight loss – Temperature curves for the corrosion of aluminum 1050 in 0.5 M HCl in the presence and absence of 0.004 M of DAEI, after immersion time of 48 hours.

The calculated values of the activation energy (E_a^*), the activation entropy (S^*) and the activation enthalpy (H^*) are given in table (3). The value of activation energy (E_a^*) is markedly increased in the presence of the tested surfactant. This result suggests that the tested surfactant retards the aluminum dissolution through formation of barrier film of adsorbed molecules on the aluminum surface, which impedes the mass and charge transfer leading to decrease in the corrosion rate⁽¹⁶⁾.

The value of activation enthalpy (H^*) is positive with and without the surfactant in the 0.5 M HCl acid solution,

indicating that the corrosion process of aluminum in 0.5 M HCl is endothermic. However, the presence of the tested surfactant just increases the value of (H^*), which suggesting also more difficult corrosion of the metal [17].

The negative values of (S^*) also implies that the activated complex in the rate determining step represents an association rather than a dissociation step [18]. The value of (S^*) decreases upon the addition of the surfactant, suggesting the increase of orderliness due to the adsorption of the molecules of the tested surfactant forming barrier surface film at the aluminum surface.

Table (3): Activation parameters of the dissolution of aluminum 1050 in 0.5 M HCl in the presence and absence of 0.004 M of DAEI after immersion time of 48 hours.

| Solution | E_a^* (kJ.mol ⁻¹) | H^* (kJ.mol ⁻¹) | $- S^*$ (J.mol ⁻¹ .K ⁻¹) |
|--------------------------|---------------------------------|-------------------------------|---|
| 0.5 M HCl | 45.48 | 42.86 | 170.94 |
| 0.5 M HCl + 0.004 M DAEI | 52.53 | 49.91 | 162.35 |

3.6. Gasometry

As in the weight loss technique, in the hydrogen evolution method (gasometry), the volume of hydrogen evolved during the corrosion reaction of aluminum in 0.5 M HCl solution in absence and presence of different concentrations of surfactant was measured with time at room temperature (~ 25°C). The inhibition efficiency was calculated using the equation [19]:

$$I. E. \% = [1 - (V_{surf}/V_{free})] \times 100. \tag{10}$$

where, V_{surf} , is the volume of hydrogen gas evolved for inhibited solution by the tested surfactant and V_{free} for the uninhibited solution.

The values of evolved hydrogen volumes and inhibition efficiencies at different times are shown in table (4). The inhibition efficiency of the surfactant increases with

increasing the surfactant concentration, which indicate that the new surfactant act as good inhibitor for aluminum corrosion in 0.5 M HCl solution.

Table (4): Hydrogen volume (ml/cm²) of the corrosion of aluminum 1050 in 0.5 M HCl solution with and without different concentrations of Surfactant (DAEI) at room temperature and different exposure times, hrs.

| Time hrs. | Free | 0.0001 M | | 0.001 M | | 0.002 M | | 0.003 M | | 0.004 M | |
|-----------|---------------------------|---------------------------|-------|---------------------------|-------|---------------------------|-------|---------------------------|-------|---------------------------|-------|
| | Volume ml/cm ² | Volume ml/cm ² | IE % | Volume ml/cm ² | IE % | Volume ml/cm ² | IE % | Volume ml/cm ² | IE % | Volume ml/cm ² | IE % |
| 17 | 55 | 54 | 1.82 | 51 | 7.27 | 37 | 32.73 | 32 | 41.82 | 24 | 56.36 |
| 24 | 96 | 91 | 5.21 | 78 | 18.75 | 57 | 40.63 | 44 | 54.17 | 29 | 69.79 |
| 41 | 196 | 181 | 7.65 | 134 | 31.63 | 75 | 61.73 | 56 | 71.43 | 37 | 81.12 |
| 48 | 232 | 205 | 11.64 | 135 | 41.81 | 85 | 63.36 | 72 | 68.97 | 43 | 81.47 |
| 65 | 349 | 313 | 10.32 | 209 | 40.11 | 139 | 60.17 | 111 | 68.19 | 76 | 78.22 |
| 72 | 379 | 359 | 5.28 | 228 | 39.84 | 154 | 59.37 | 123 | 67.55 | 87 | 77.04 |

3.7. Potentiostatic polarization

The Potentiodynamic polarization curves of aluminum in 0.5 M HCl solutions; free and inhibited with different concentrations of surfactant were traced at scan rate of 1 mV/sec and shown in Fig (8). The respective electrochemical parameters e.g. current (I_{corr}), corrosion potential (E_{corr}) anodic and cathodic Tafel slopes (β_a and β_c), the degree of surface coverage (θ), corrosion rate (CR) and the percentage of inhibition efficiency (%IE) are given in table (5). The inhibition efficiency and surface coverage were calculated by using the following equations:

$$I.E. \% = 1 - I_{surf}/I_{free} \times 100. \tag{11}$$

$$= 1 - I_{surf}/I_{free} . \tag{12}$$

where, I_{surf} and I_{free} are the corrosion current in the presence and absence of the surfactants, respectively. It can be seen that, upon the addition of the surfactants, both

the corrosion current density (I_{corr}) and the corrosion rate (CR) decreased significantly and the percentage inhibition efficiency (IE %) increased.

Figure (8) shows that the increase of the surfactant concentration shifts the current – potential curves towards lower values of current. The values of cathodic Tafel slope (β_c), anodic Tafel slope (β_a) were slightly changed on increasing the concentration of the investigated surfactants. This means that there is no change in the mechanism of the inhibition in presence and absence of the surfactants; there is no change in the mechanisms of both hydrogen evolution and aluminum dissolution [20]; and that these surfactants affect both anodic and cathodic reactions, so it is mixed type inhibitors [21]. There is no appreciable shift in the corrosion potential (E_{corr}) after the addition of the surfactants, which strengthens the conclusion that the tested surfactants are mixed type inhibitors [22].

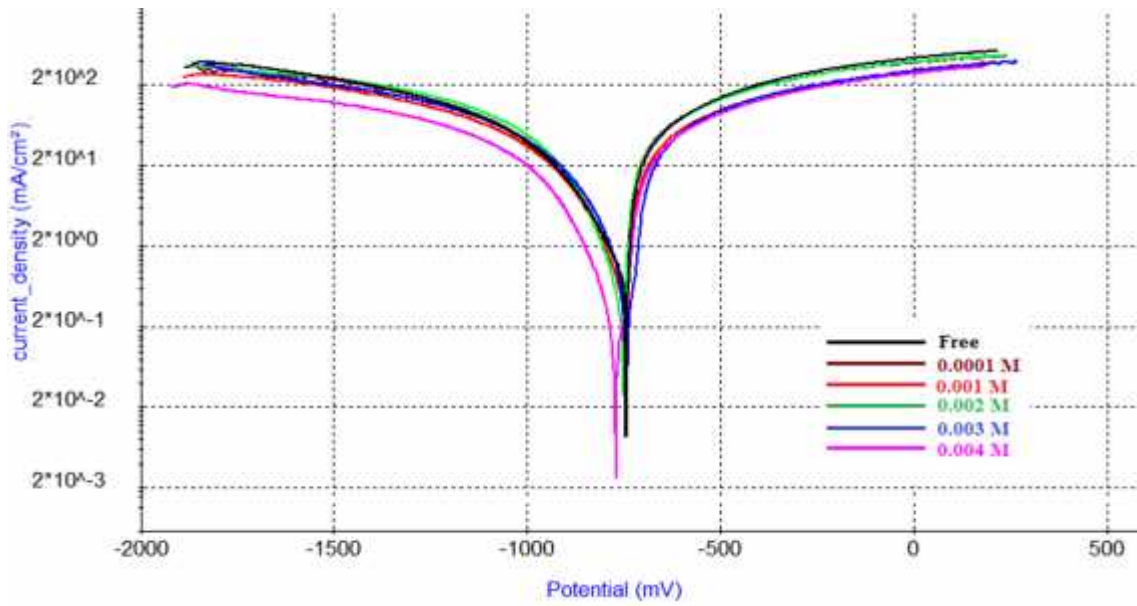


Fig (8): Anodic and cathodic polarization curves for aluminum 1050 in 0.5 M HCl solution and different concentrations of the surfactant (DAEI), at room temperature and scan rate of 1 mV/sec.

Table (5): Corrosion parameters obtained from potentiostatic polarization measurements of aluminum 1050 in 0.5 M HCl and different concentrations of surfactant (DAEI) at 298 K and scan rate 1 mV/sec.

| Conc. M | -c mV.decade ⁻¹ | a mV.decade ⁻¹ | CR mm/Jear | I.E. % | θ | I _{Corr.} mA | -E _{Corr.} mV |
|---------|-------------------------------|------------------------------|---------------|--------|--------|-----------------------|------------------------|
| Free | 62.90 | 15.07 | 4.91 | - | - | 0.23 | 743.07 |
| 0.0001 | 62.97 | 10.44 | 3.93 | 19.98 | 0.1998 | 0.18 | 741.34 |
| 0.001 | 49.45 | 14.17 | 2.49 | 49.27 | 0.4927 | 0.11 | 741.29 |
| 0.002 | 42.80 | 11.81 | 1.66 | 66.13 | 0.6613 | 0.08 | 750.17 |
| 0.003 | 31.41 | 15.16 | 1.13 | 76.91 | 0.7691 | 0.05 | 738.90 |
| 0.004 | 37.64 | 15.64 | 0.49 | 90.07 | 0.9007 | 0.02 | 764.80 |

3.8. Adsorption isotherm

The values of surface coverage (θ) for different concentrations of the studied surfactants have been used to explain the best isotherm for adsorption of these surfactants on the aluminum 1050 surface. Attempts were made to fit θ values to various isotherms including Frumkin, Freundlich, Flory – Huggins and Langmuir. The results are best fitted by Langmuir adsorption isotherm according to the following equation:

$$C/\theta = (1/K) + C \tag{13}$$

where, K and C are the equilibrium constant of adsorption process and surfactant concentration, respectively.

Plotting C/θ versus C gave straight lines, as shown in figure (9). The straight line with approximately unit slope value has an intercept of 1/K, suggesting that, the adsorption of these surfactants on aluminum 1050 in 0.5 HCl follows Langmuir adsorption isotherm. From these results, one can postulates that there is no interaction between the adsorbed species.

The equilibrium constant of adsorption K is related to the standard free energy of adsorption by the equation:

$$K = 1/55.5 \exp - \Delta G_{ads}^{\circ}/RT . \quad (14)$$

where, R is universal gas constant, the value 55.5 is the concentration of water in the solution in mole/litre and T is the absolute temperature. The negative values of G_{ads}° obtained indicate that the adsorption process of these surfactants on the surface of aluminum 1050 is spontaneous [23].

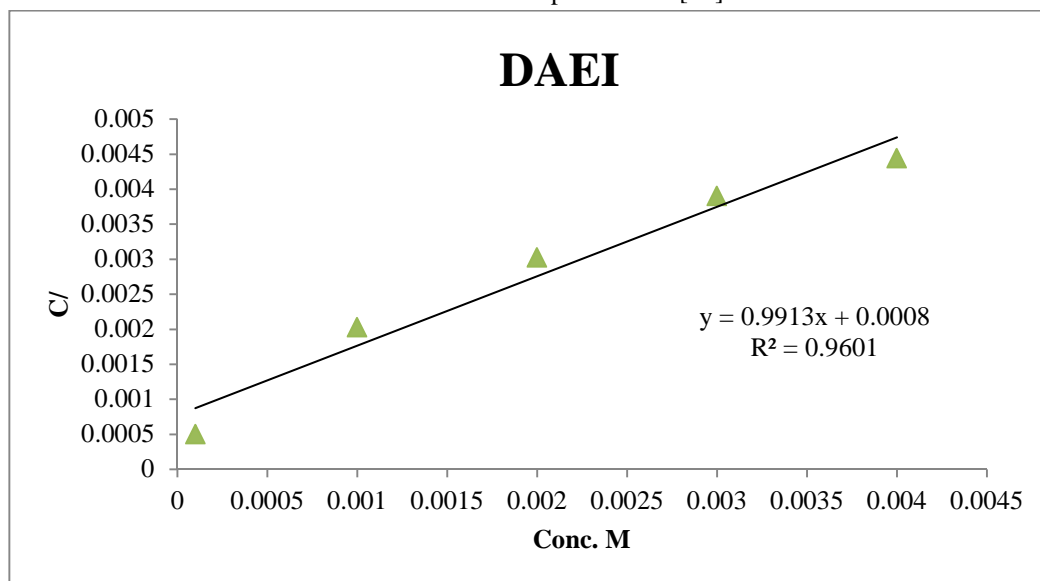


Fig (9): Langmuir Adsorption Isotherm for surfactant (DAEI) on aluminum 1050 in 0.5 M HCl.

Table (6) The Equilibrium constant of adsorption (K) and the adsorption free energy of surfactants derived from amide adsorbed on the surface of aluminum 1050 in 0.5 M HCl at room temperature.

| The Surfactant | $K \times 10^{-3}$ | $- G_{ads}^{\circ}$ (kJ.mol ⁻¹) |
|-------------------|--------------------|---|
| Surfactant (DAEI) | 1.250 | 27.625 |

4. Conclusion

- The greater increasing in the negative value of G_{ads}° compared to that of micellization indicates the ability of the molecules to be adsorbed at the interface.
- Addition of DAEI inhibits the corrosion of aluminum 1050 in 0.5 M HCl solution.
- The inhibition efficiency of DAEI increases with increasing its concentration.
- The inhibition efficiency of DAEI decreases with increasing temperature.
- DAEI is a mixed type inhibitor in 0.5 M HCl solution.
- The adsorption of the surfactants on aluminum 1050 in 0.5 M HCl solution follows Langmuir isotherm.
- The negative values of G_{ads}° show the spontaneity of the adsorption process.

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