SYNTHESIS OF BIO-BASED CORROSION INHIBITORS BASED ON ROSIN FOR LINE-PIPE STEEL

A. M. ATTA[a,b*], G. A. EL-MAHDY[a, c], A.M. ELSAEED[b],
H. A. AL-LOHEDAN[a],
[a]*Surfactants research chair, King Saud University, Chemistry Department, College of Science, P.O.Box - 2455, Riyadh - 11451, Saudi Arabia*
[b]*Petroleum application department, Egyptian petroleum research institute, Cairo, Egypt*
[c]*Chemistry department, Helwan university, Helwan, Cairo, Egypt*

The synthesis and characterization of a series of bio-based surfactants based on gum rosin as natural products were investigated. Surface activities of these surfactants were investigated to correlate their structure and their performances. The new rosin adduct was prepared by reacting rosin with linoleic acid by Diels Alder mechanism. The adduct was esterified with poly(ethylene glycol) to produce nonionic surfactants. The chemical structure of the prepared surfactants was characterized by ^{13}C and ^{1}H NMR analyses. The surface activities of the surfactants were measured from the adsorption isotherm measurements which were determined from the relationship between the concentrations and surface tension of surfactants in aqueous medium at different temperatures. Critical micelle concentration (cmc) values were determined for water soluble surfactants. Surface-active parameters such as area per molecule at the interface (A_{min}), surface excess concentration (Γ_{max}) and the effectiveness of surface tension reduction ($\Delta\gamma$) were measured from the adsorption isotherms of the modified surfactants. Corrosion inhibition behavior of RPEG600 and RLA- PEG600 compounds on steel surface were investigated by electrochemical impedance spectroscopy (EIS) and electrochemical polarization measurements. Electrochemical data show that both compounds suppressed the anodic and the cathodic reaction and   act essentially as a mixed-type inhibitor. The results showed that corrosion inhibition of steel largely depends on the molecular structure and concentration of the inhibitors.

1.Introduction

Rosin is one of bio-based polymer obtained from pine trees. The chemical composition is chiefly composed of 90% rosin acids and 10% non-acidic resinous materials such as turpentine. It has recently been used as a novel material for sustained applications such as paper sizing, coatings and drug release [1-10]. The rosin chemical structure was modified by either epoxidation or esterification of unsaturated double bonds or carboxylic group, respectively. On the other hand, isomerization of conjugated rosin acid double bonds facilies their reaction as diene in Diels Alder reactions   [11-14]. The functionality of resin acid using Diels Alder reaction increased industrial applications of rosin [15].

The use of naturally occurring raw materials in surfactant synthesis is expected to provide new types of surfactants with better biodegradability. Further, in order to achieve long term sustainable production. It will become necessary to use renewable sources [16]. In our previous works, we succeeded to prepare cationic, anioinic and nonionic surfactants and used as petroleum additrives and corrosion inhibitors for carbon steel alloys because they have ability to adsorb at

---

steel surface corrosive media interfaces to prevent the acids or salts to attack carbon steel [17-24]. The rosin based nonionic surfactants of N,N-polyoxyethylene dehydroabietylamines with different numbers of oxyethylene units also exhibited anticorrosion activity [25]. The previous studies aim to prepare the rosin based surfactants without change the lengths of the hydrophobic groups. There are some reports used unconjugated fatty acids as dienophile in Diels Alder reaction [26-30]. There is no any previous work to prepare Diels Alder adducts between rosin acid and fatty acids. Rosin acids are a novel source of hydrophobic groups with a tricyclic hydrophenanetherene structure that can be used for the synthesis of surfactants with natural origins. The aim of the present work was to prepare the rosin acid adducts with linoleic acid to increase the hydrophobic moiety of rosin with linear alkyl groups followed by esterification with polyethylene glycol to prepare new nonionic surfactants. The application of the prepared nonionic surfactants as corrosion inhibitors for carbon steel alloys in acidic medium is another goal of the present study.

2. Experimental

2.1 Materials

Rosin acids are the main component of gum rosin. The physical properties of rosin including M.p and acid number are 161°C and 183 mg KOH/ g of resin acid, respectively. The structures of some of the important resin acids isomers are including abietic, levopimaric, palustric, neoabietic, delydroabietic, dihydroabietic and tetrahydroabietic acids. In the present work, the rosinwere heated at 150 °C for 4h and at 200°C for 0.5h in nitrogen atmosphere to produce leveopimaric acid (LPA). Linoleic acid (LA), p-toluene sulfonic acid (PTSA), poly (ethylene glycol), PEG, has molecular weight 600 g/mol designated as PEG 400 and PEG 600 were supplied from Aldrich Chemicals Co. (USA) and used as received. Corrosion tests were performed on a carbon steel sheet having the following chemical composition (wt %): 0.3% C, 0.02% Si, 0.03% Mn, 0.045% Sn, 0.04% P and the remainder Fe. A steel disc of the same chemical composition was mounted in Teflon with an exposed surface area of 0.785 cm^{2}was used in all electrochemical measurements. A steel specimen acts as a working electrode (WE) and a saturated calomel electrode (SCE) was used as a reference electrode (RE), along with a platinum sheet as a counter electrode (CE). The prepared electrode was mechanically polished with different grades of silicon carbide papers, degreased in ethanol to obtain a fresh oxide-free surface, washed with bi-distilled water and dried at room temperature.

2.2 Technique

2.2.1 Preparation of polyoxyethylene rosinate ester (RPEG 600):
RPEG 600 was prepared by reacting rosin with PEG 600. Gum rosin (0.1 mol; 30 g) was heated under nitrogen to 180 °C and the reaction temperature maintained for 1 h at this temperature. PEG 600 (0.11 mol; 66 g) was added and heated to remove water from the reactants. PTSA (1%) based on total weight of reactants was added to the reaction mixture. The theoretical amount of water was removed from the reaction mixture and the temperature was kept at 120 °C for 1 hour and the reaction left for 3 hours at 170 °C. The reaction temperature was cooled to obtain brown powder of adduct. The product (RPEG 600) was separated by salting out use saturated NaCl solution and extracted with isopropanol using separating funnel. The purified products were isolated after evaporation of isopropanol.

2.2.2 Synthesis of rosin / linoleic acid adduct (RLA):
Gum rosin (0.33 mol; 100 g) was heated under nitrogen to 180 °C and the reaction temperature maintained for 1 h at this temperature. Linoleic acid (0.33 mol, 92.5 g) was heated under stirring in the presence of nitrogen for 2 h at 150 °C. The reaction was followed by thin-layer chromatography [petroleum ether/diethyl ether (7:3), Rf = 0.23]. Purification of product was achieved by column chromatography [silicagel using petroleum ether/diethyl ether (7:3) and

petroleum ether/ ethyl acetate (1:1) as eluent]. Fractions containing product **were** collected and the solvent was removed in vacuum. The purified productwas recrystallized from petroleum ether/diethyl ether (4:1). The M.p. 42–43 °C and yield (75 %) were determined.

2.2.3 Synthesis of polyoxyethylene rosinate / linoleic acid ester (RLA-PEG 600):

RLA-PEG 600 was prepared by esterification of RLA with PEG 600. RLA (0.1 mol) was mixed with PEG 600 (0.11 mol) and heated under nitrogen to remove water from the reactants. PTSA (1%) based on total weight of reactants was added to the reaction mixture. The esterified water was azotropically removed from the reaction mixture and the temperature was kept at 150 °C for 3 hour. The product was purified by salting out use saturated NaCl solution and extracted with isopropanol using separating funnel. The purified products were isolated after evaporation of isopropanol.

2.3 Measurements

Infrared spectra of the prepared compounds were recorded in polymer/KBr pellets using Mattson-Infinity series FTIR Bench Top 961.

^{1}H-NMR (400 MHz Bruker Avance DRX-400 spectrometer) was used to study the chemical structures of the prepared surfactants.

The surface tension measurements of different aqueous solution of the prepared surfactants in water and 1M HCl was measured at 25 °C by means of the pendent drop technique using drop shape analyzer model DSA-100 (Kruss, Germany). The error limits of these measurements are on the order of 0.1 mN/m or less. Pendent drops were formed on the tip of a Teflon capillary with an outside diameter of 0.1 in. and inside diameter of 0.076 in.

2.4 Electrochemical measurements

Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were conducted using multichannel system, which comprises a Solartron 1470E system (potentiostat / galvanostat) and Solartron 1455A as frequency response analyzer . The electrochemical impedance spectroscopy was measured at open circuit potential with a 10 mV AC perturbation at frequency ranging from 10 kHz to 10 mHz with 10 points per decade. Potentiodynamic polarization experiments, was measured with scan rate of 5 mV s−1. The data were plotted and analyzed using CorrView, Corr- Ware, Zplot and ZView software. To prove reproducibility, the polarization curve tests and the EIS measurements were repeated three times.

3. Results and discussion

The Diels-Alderreaction is one of the most important C-C bond forming organic synthesis reactions in a one-step reaction it enables the regio- and stereoselective construction of five, six and seven membered carbocycles and heterocycles [**31**]. There is only few examples of this cycloaddition are described for unsaturated fatty acids. The reaction is based on converting of unconjugated fatty acids, such as linoleic or linolenic acids, which have been converted into conjuenic acid by conjugation of the double bonds undergoes *Diels-Alder* reactions at high temperature with dienophiles bearing electron withdrawing groups [**32**]. Not reported yet are *Diels-Alder* cycloaddition reactions of leveopimaric acid as dienes and fatty acid deriveddienophiles. In this respect, the present work aims to prepare a biobased surfactants from Diels-Alder reaction between modified rosin ester and fatty acid. These extensions of the Diels-Alder reactionwith unsaturated fatty acids are addressed in this contribution. The Diels-Alder addition of linoleic acid with rosin without any solvent at 150 °C under nitrogen yieldedthe Diels–Alder adduct after a reaction time of 2 h in anisolated yield of 78% (Scheme 1).

The compound RLA was separated from the reaction mixture by column chromatography and recrystallized from petroleum ether/diethyl ether (4:1).
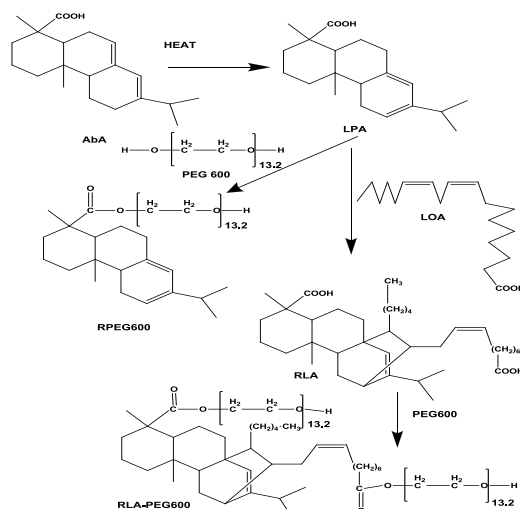
Scheme 1: Reaction procedure of RPEG600 and RLA-PEG600

3.1. Preparation of nonionic surfactants

The present work deals with synthesis of nonionic surfactants by reacting the carboxylic acid of rosin acid with PEG which has molecular weights 600 (PEG 600). The strategy of synthesis is based on preparation of nonionic surfctants having different hydrophile-lipophile balance (HLB) to study effect of surfactant structure on its properties. The esterification of rosin acids with PEG used to increase hydrophilicity of rosin acids as illustrated in the scheme 1. The structures of the produced surfactant was confirmed by using IR spectroscopy. TheIR patterns of RPEG 600 was represented in *Figure 1a.* The stretching bands at 1745 cm^{-1} for carbonyl (C=O) of ester and the peak at 3450 cm^{-1} for OH are observed and indicated the formation of ester group as repreesented in Scheme 1.
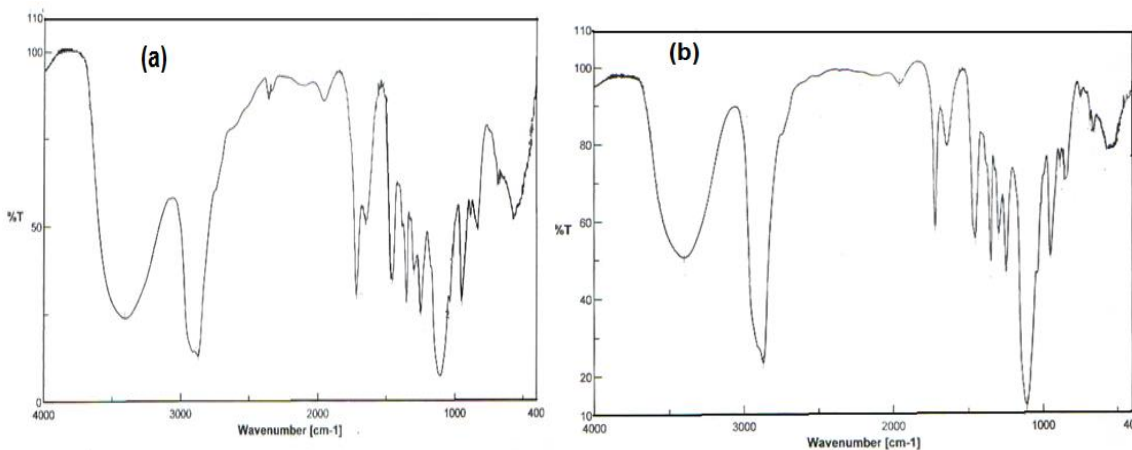

Fig. 1. FTIR spectra of a) RPEG600 and b) RLA-PEG600

On the other hand, the Diels Alder adduct RLA was esterified with PEG 600 to produce RLA PEG600 as represented in scheme 1. IR spectrum of RLA PEG600 was was represented in Figure 1 b. The appearance of peaks at 3435 and 721 cm^{-1} (which attributed to OH stretching vibration and C-(CH$_2$)n-C bending vibration of the long alkyl chain moiety of the ester) indicate the incorporation of LA.

^{1}HNMR and ^{13}CNMR spectra of RLA and RLA PEG600 wer represented in Figures 2 and 3, respectively. They were usedto confirm the structure of nonionic surfactants based on LA as hydrophobic group. New signals of methylene (CH$_2$)$_{16}$, CH$_3$ and CH=CH protons of LA appear as

an intense broad peak at δ = 1.35, 0.87 and 6.1 ppm were used to confirm the incorporation of LA with rosin as represented in Figure 2 a.The apperance of new protons of oxyethylene units at δ = 3.6 ppm, −OH proton of PEG at δ = 2.5 ppm, indicated the esterification of RLA with PEG 600. The disapperance of peak at 11.1 ppm (COOH) indicated the complete esterification of both rosin and LA acid. Moreover the apperance of band at 66-70.1 ppm (O-CH2)in ^{13}CNMR spectrum of RLAPEG600 (Figure 3b) indicated the esterification of PEG600 with RLA. The apperance of bands at 126-130 and 173-178ppm (Figure 3) were attributed to C=C and COO group of LA.
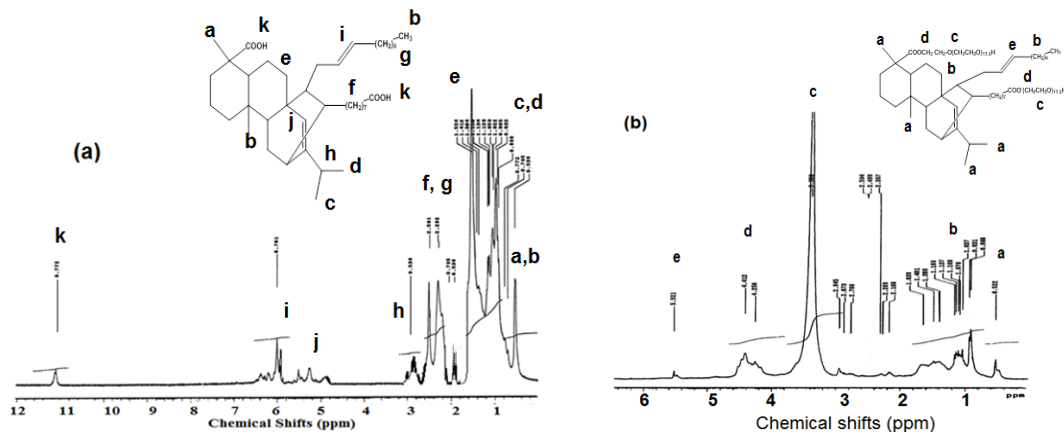

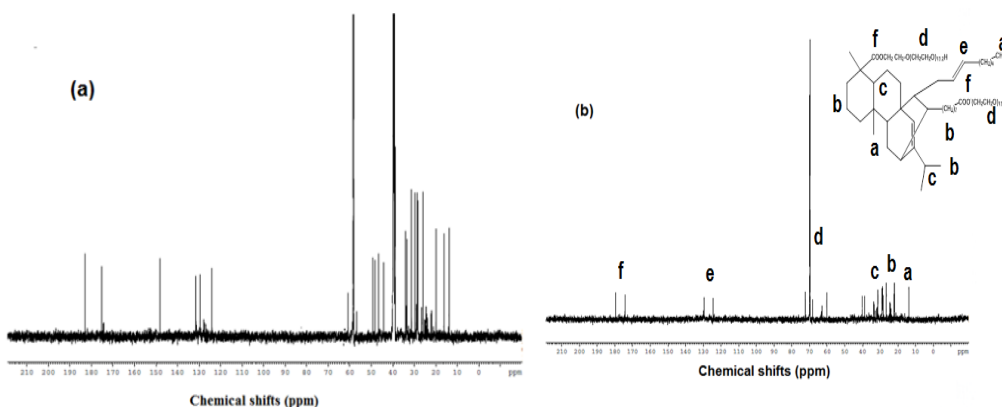Fig. 2. ^{1}HNMR spectra of a) RPEG600 and b) RLA-PEG600

Fig. 3. ^{13}CNMR spectra of a) RPEG600 and b) RLA-PEG600

3.2. Surface Activity of the prepared surfactants

It is important to investigate the surface activity of the prepared surfactants in both aqueous and 1M HCl solutions. It was previously concluded that [33,34], the surface tension of the aqueous nonionic surfactant solutions was not affected by 1 M HCl. The data of critical micelle or aggregation concentrations (cmc) were affected by 1MHCl [33,34]. In the present work the surface tension of the prepared rosin surfactant will be evaluated in both distilled water and 1 M HCl to study the adsorption characteristics at air/water interface and micellization of the surfactants in bulk solutions either in distilled or acidic aqueous solutions. The dynamic surface tension for different concentrations of the prepared surfactants was measured at water/air interface at temperature of 25 °C. The relation between the surface tension of RPEG600 and RLA- PEG600 in aqueous solution and ageing time at different concentrations were represented in figure 4. The adsorption isotherms of the prepared surfactant in water at temperature of 25 °C were plotted in figure 5.The data represented in figure 4 indicated that the prepared surfactants reached the surface tension equilibrium after time intervals ranged from 3 to 10 minutes. Moreover, the equilibrium time was reduced with increasing the surfactant concentrations and replacement of water with 1M

1052

HCl. These data indicated that the prepared surfactants are strongly adsorbed at interfaces in 1M HCl solutions. It is well known that the micellization, aggregation and adsorption of surfactants are based on the critical micelle concentrations (cmc), which were determined by the surface balance method as represented in figure 4. The cmc data were determined in water and 1 M HCl aqueous solution at 25 °C from abrupt changes of the plotted data of surface tension (γ) versus the solute concentration (ln C) and listed in table 1.
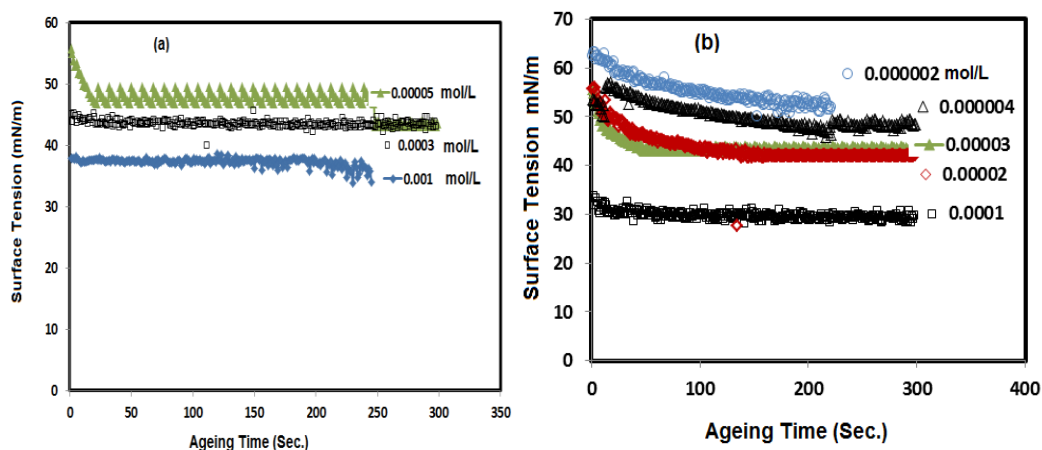
Fig. 4: Relation between surface tension and ageing time for different aqueous concentrations of
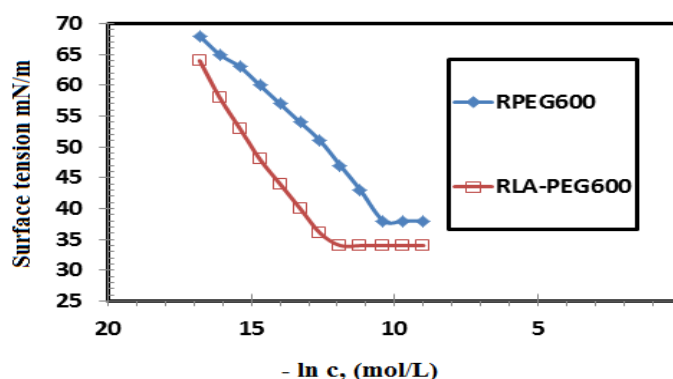a) RPEG600 and b) RLA-PEG600

Fig. 5:Adsorption isotherms of RPEG600 and RLA-PEG600

Table 1: Surface activity parameters of RPEG600 and RLA-PEG600

surfactants	medium	cmc x 10^5 mol/L	γ_{cmc} mN/m	$\Delta\gamma$ mN/m	$(-\partial\gamma/\partial\ln c)_T$	Γ_{max} x 10^{10} mol/cm^2	A_{min} nm^2/molecule
RPEG 600	Water	1.40	38.2	34.0	3.12	1.26	0.132
	1M HCl	0.68	38.3	33.9	3.58	1.44	0.115
RLA PEG600	Water	0.25	33.1	39.1	7.61	3.07	0.054
	1M HCl	0.12	34.2	38.0	8.31	3.35	0.050

The cmc data indicated that the RLA-PEG600 has low cmc than RPEG 600 which indicated that the RLA-PEG600 has low solubility in both water and 1M HCl and forms aggregates at lower concentration of 1M HCl more than in aqueous solution. This can be attributed

the increased hydrophobicity of the surfactants by incorporation of LA. It was previously concluded that decreasing the cmc values indicated a high tendency of surfactants to adsorb at the liquid interface [35].

The adsorption effectiveness of the prepared surfactants expressed by the maximum reduction of surface tension which was calculated from the equation, $\Delta\gamma = \gamma_{water} - \gamma_{cmc}$, the concentration of the prepared surfactants at the solvent-air interface, Γ_{max}, and the area per molecule at the interface, A_{min}, were calculated and are listed in Table 1 too. The surface excess concentration of the prepared surfactants at the interface can be calculated from the surface or interfacial tension data using the following equation [36]: $\Gamma_{max} = 1/RT \times (-\partial\gamma/\partial lnc)T$, where$(-\partial\gamma/\partial lnc)T$ is the slope of the plot of γ *versus* ln c at constant temperature (T), and R is the gas constant (in J mol^{-1} K $^{-1}$). The Γ_{max} values were used for calculating the minimum area (A_{min}) at the aqueous–air interface. The area per molecule at the interface provides information about the degree of packing and the orientation of the adsorbed surfactants, when compared with the dimensions of the molecules obtained from models. From the surface excess concentration, the area per molecule at the interface is calculated using the equation: $A_{min} = 10^{16}/N \Gamma_{max}$, where N is Avogadro's number Also, the area occupied at the interface is increased [36]. It was observed that A_{min} of RPEG 600 has a higher value as compared to RLA-PEG600. This can be due to the easier packing of RLA-PEG600 surfactants at the interface; thus the molecule occupies a smaller area, that is, RLA-PEG600 surfactants possess a higher adsorption at the interface than RPEG 600.These data indicated that the prepared RLA PEG600 favors micellization in bulk 1 M HCl solution compared to aqueous solution, which may reflect its greater tendency to adsorb at the metal/liquid interface more than the air/water interface. It was also suggested that the RLA PEG are more packed at the water/air interface, causing more efficient adsorption. A possible explanation is that the terminal location of the hydrophilic polyoxyethylene allows oxyethylene molecules to adapt a flexible loop-like conformation at the interface [37, 38].It can be concluded that the adsorption of RLA-PEG 600 at the interface increases with incorporation of LA in its chemical structure. This can be attributed to the interaction between the two head oxyethylene groups decreases coiling of oxyethylene located at the end of the RLA-PEG 600 molecules. Consequently, RLA-PEG 600 is easily packed at the air–water interface and highly adsorbed.

3.3. Electrochemical impedance spectroscopy (EIS)

Nyquist plots of steel in 1 M HCl in the presence of RPEG600 and RLA- PEG600 as corrosion inhibitors are given in Fig. 6a and 6b, respectively. The impedance data for the blank solution is depicted in the inset of Fig. 6. These Fig.6. Nyquist diagram for steel in 1 M HCl solution containing different inhibitor concentrations (RPEG600) showing experimental (square)and fit data (circle).
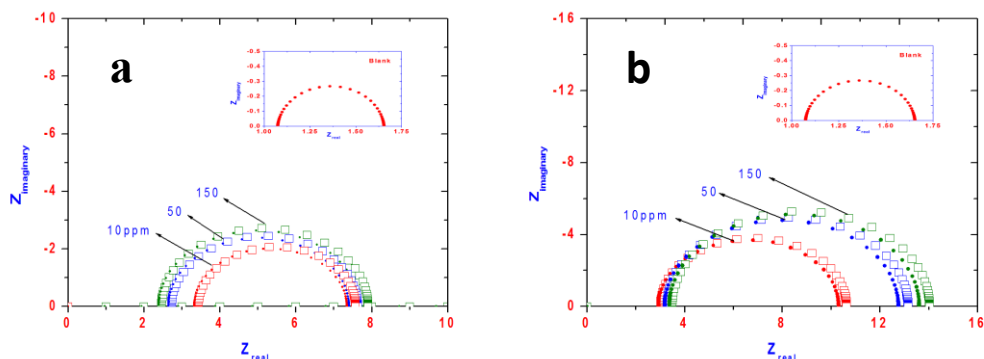

Fig. 6. (a) Nyquist diagram for steel in 1 M HCl solution containing different inhibitor concentrations (RPEG600) showing experimental (square)and fit data (circle), (b) Nyquist diagram for steel in 1 M HCl solution containing different inhibitor concentrations (RLA- PEG600) showing experimental (square) and fit data (circle)

1054

curves have been obtained after 1 h of immersion in the corresponding solution. It has been reported that the Nyquist semicircles are generally associated with the charge transfer at the electrode/electrolyte interface [39]. The diameter of the capacitive loop is regarded as the charge transfer resistance. It is evident that the smaller the charge transfer resistance, the faster the rate of an electrochemical reaction. The electrochemical process was modelled by electrical equivalent circuit (Fig.7) consisted of solution resistance (Rs) double layer capacitance (Cdl) and charge transfer resistance (Rct).
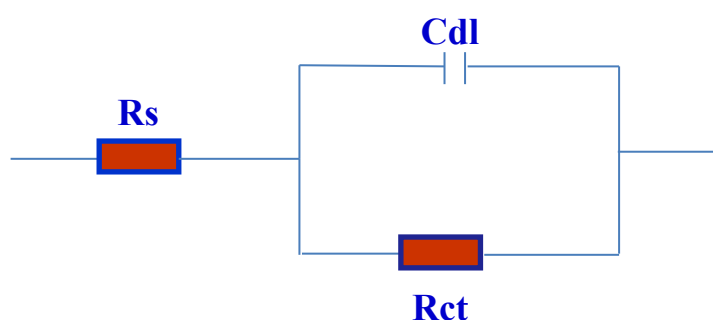
Cdl

Rs

Rct

Fig. 7: Equivalent circuit used for fitting the impedance data

The parameters obtained for RPEG600 and RLA- PEG600 by curve fitting are listed in Table 1 and 2, respectively. As it can be seen in Table 1 and 2, addition of both inhibitors to HCl solution resulted in a decrease in Cdl and an increase in charge transfer resistance. The value of Rct gives information about the corrosion rate and consequently inhibitor performance. The higher the Rct value is, the greater the resistive behavior of the steel, implying a more effective inhibitor. The increase in charge transfer resistance Rct for the inhibited system can be explained by an increase of the resistive behavior of steel owing to the formation of the adsorbed inhibitor molecules on steel surface.

Table 2: Inhibition efficiency of RPEG600 values for steel in 1M HCl with different concentrations of inhibitor calculated by Polarization and EIS methods

	Polarization Method					EIS Method		
Conc.	Ba (mV)	Bc (mV)	E_{corr} (V)	i_{corr} $\mu A/cm^2$	IE%	R_p Ohm	Cdl ($\mu F/cm^2$)	IE%
Blank	147.00	141.00	-0.4034	745	_____	1.80	334	____
10 ppm	100.56	107.93	-0.4469	345	53.69	3.99	238	54.88
50	118.84	126.48	-0.4583	274	63.22	4.90	179	63.26
100	121.80	141.73	-0.4930	123	83.48	7.97	146	77.54

Table 3: Inhibition efficiency of values of RLA- PEG600 for steel in 1M HCl with different concentrations of inhibitor calculated by Polarization and EIS methods

	Polarization Method					EIS Method		
	Ba (mV)	Bc (mV)	E_{corr} (V)	i_{corr} $\mu A/cm^2$	IE%	R_p Ohm	Cdl ($\mu F/cm^2$)	IE%
Blank	147.00	141.00	-0.4034	745	_____	1.80	334	____
10 ppm	88.48	103.65	-0.4307	170	77.12	7.61	218	76.34
50	82.58	131.79	-0.4620	71	90.46	12.51	160	85.61
100	107.03	136.94	-0.4731	56	92.48	13.85	128	87.00

The decrease in double layer capacitance for the inhibited solution compared to uninhibited one is usually explained by the displacement of water molecules from the surface due to adsorption of inhibitor molecules and/or an increase in the thickness of double layer [40-44]. In addition, the lower values of Cdl of the inhibited system can be attributed to the formation of the inhibitive layer, which give rise to more protection of the steel surface. The adsorption of the inhibitor molecules on steel surface leads to an increase in the thickness of the adsorbed layer and is accompanied by reduction in the double layer capacitance. The inhibition efficiency is calculated by charge transfer resistance obtained from Nyquist plots, according to the Eq. (1) [45]:

$$IE\% = 1 - R_{ct}* / R_{ct} \tag{1}$$

where $R_{ct}*$ and R_{ct} are the charge transfer resistance values without and with inhibitor, respectively. IE% values were calculated and listed in Table1 and 2 for RPEG600 and RLA-PEG600, respectively. It is obvious that the inhibition efficiency increases with increase in inhibitor concentration reaching a maximum value at 150 ppm concentration. The results obtained from EIS can also show a better inhibition effects of RLA- PEG600 compared with RPEG600. The results can be accounted to more adsorption of RALA- PEG600 molecules on steel surface compared to the RPEG600 molecules.

3.4 Electrochemical polarization measurements:

Figs. 8a and 8b show cathodic and anodic polarization curves for steel carried out at in 1 M HCl without and with various concentrations of RPEG600 and RLA- PEG600 inhibitor, respectively. The parameters of the electrochemical polarization curves as anodic Tafel slope (ba), cathodic Tafel slope (bc), corrosion potential (Ecorr) and corrosion current (Icorr) are displayed in Table 1 and 2 for RPEG600 and RLA- PEG600, respectively. It is observed that the addition of RPEG600 and RLA- PEG600 affects both the anodic and cathodic parts of the curves. It is clear that both anodic and cathodic curves shifted toward lower current densities in the presence of RPEG600 and RLA- PEG600. The decrease in cathodic and anodic current density suggests that RPEG600 and RLA- PEG600 act essentially as an effective mixed type inhibitor. It can be concluded that the inhibitors suppressed anodic dissolution rate of steel and retarded cathodic reactions rates. The lower corrosion current density indicates the formation of the inhibitive film on a steel surface, which protects the steel surface effectively.
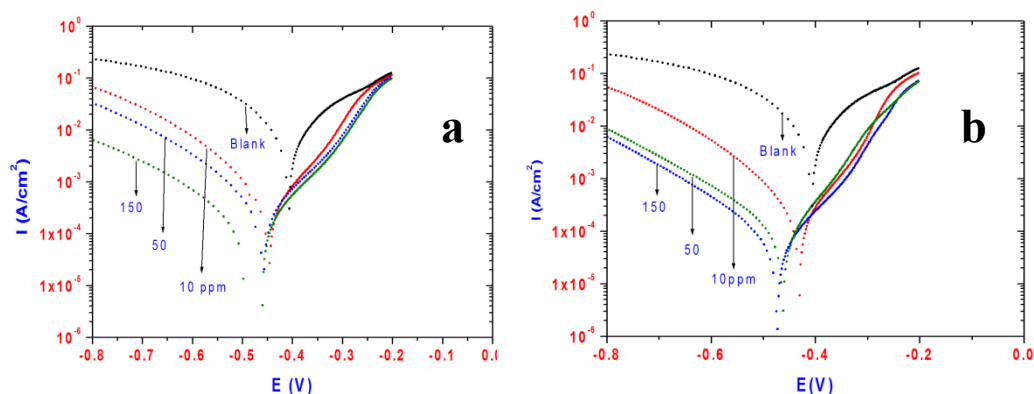
Fig. 8a: Polarization curves for steel in 1M HCl solution containing different inhibitor concentrations (RPEG600). 8b: Polarization curves for steel in 1M HCl solution containing different inhibitor concentrations (RLA- PEG600).

The decrease in the cathodic current densities may be attributed to the cathodic sites blockage by the inhibitors. In addition, RPEG600 and RLA- PEG600 are preferentially adsorbed at anodic sites on the steel surface by forming protective films, which give rise to more protection against corrosion. The inhibition efficiency (IE%) was calculated using the equation:

$$IE\% = 1 - i_{corr} / i_{corr}* \qquad (2)$$

Where $i_{corr}*$ and i_{corr} are the corrosion current density values without and with inhibitor, respectively. The values of IE% were calculated and given in Table 1and 2 for RPEG600 and RLA- PEG600, respectively. It is clear that the corrosion current densities (i_{corr}) decrease with increasing inhibitor concentration. The effect was maximal for the concentration 150ppm, which is the optimum concentration of inhibitor required to achieve the efficiency (92%). As expected, both the anodic and cathodic corrosion reactions are inhibited remarkably in presence of RPEG600 and RLA- PEG600 molecules. It is clear from the data presented in Table 1 and 2 that the values of IE% in presence of RLA- PEG600 is higher that experienced by RPEG600. The results can be attributed to the different in the molecular structure of both inhibitors. RLA- PEG600 is characterized by the presence of more reactive centers through, which enhances the adsorption of the RLA- PEG600 on steel surface and increase the IE%. In addition, the higher molecular weight of RLA- PEG600 compared with RPEG600 may increase the physical adsorption of these molecules on the steel surface, which in turn increase the area of the steel covered by RLA- PEG600 molecule. The above electrochemical polarizations data together with the EIS results indicated the formation of an inhibitive film, which can be attributed to the adsorption of RPEG600 and RLA- PEG600 on the steel surface. It can be concluded that the inhibition efficiency found from polarization curves and electrochemical impedance spectroscopy measurements are in good agreement

4. Conclusions

New Diels Alder adduct between rosin and LA were reacted with PEG 600 to produce water soluble nonionic surfactant.

The adsorption of RLA-PEG 600 at the interface increases with incorporation of LA in its chemical structure. This can be attributed to the interaction between the two head oxyethylene groups decreases coiling of oxyethylene located at the end of the RLA-PEG 600 molecules. Consequently, RLA-PEG 600 is easily packed at the air–water interface and highly adsorbed.

RPEG600 and RALA- PEG600 molecules inhibit the corrosion of steel in 1 M HCl and the corrosion inhibition largely depends on the molecular structure and concentration of the inhibitors.

A good correlation was observed between the EIS data and the results of polarization measurements.

Electrochemical data show that   RPEG600 and RLA- PEG600 suppressed the anodic and the cathodic reaction and   act essentially as a mixed-type inhibitor. The inhibition efficiency experienced by RLA- PEG600 molecule was much higher than that of RPEG600 molecules.

Acknowledgment

References

[1] S.V.Fulzele, P.M.Satturwar, A.K.Dorle, Int. J. Pharm.**249**, 175 (2002).

[2] S.V.Fulzele, P.M.Satturwar, A.K.Dorle,Eur. J. Pharm. Sci. **20**, 53 (2003).

[3] P.M.Mandaogade, P.M.Satturwar, S.V.Fulzele, B.B.Gogte, A.K.Dorle,Reactive & Functional Polymers **50**, 233 (2002)..

[4] C-M. Lee, S. L.Gwang-Yun Kim, Dong-Woon Kim, J. H. Rhee, K-Y. Lee, Biotechnology Letters **27**, 1487 (2005).

[5] A. M. Atta, R. Mansour, M.I. Abdou, A. M. Sayed. Polymers for Advanced Technologies **15**, 514 (2004).

[6] A. M. Atta, R. Mansour, (et al.) Journal of Polymer Research, **12**, 127 (2005).

[7] A. M. Atta, S. M. El-Saeed, R. K. Farag, Reactive and Functional Polymers, **66**, 1596 (2006).

[8] A. M. Atta, H. M. Bedawy, I.F.Nassar,   Reactive and functional polymers, **67**, 617 (2007).

[9] A.M. Atta, A. M. Elsaeed, R.K. Farag, S. M. El-Saeed, Reactive and functional polymers **67**, 549 (2007).

[10] I.Bicu, F.ˇ Mustata,Macromol. Mater. Eng., **280/281**, 47 (2000).

[11] F.Mustata, I.Bicu, European Polymer Journal **46,** 1316 (2010).

[12] N. J. Halbrook, J.. Wells, R. V. Lawrence, JACS, august, **26**, 2641 (1961).

[13] N. J. Halbrook, J.. Wells, R. V. Lawrence, ACS, **29**, 1017-1021 (1964).

[14] I. Bicu, F.Mustata, Journal of Polymer Science: Part A: Polymer Chemistry, **45**, 5979 (2007).

[15] S.Maiti, S.Sinharay, A. K. Kundu, Prog. Polym. Sci., **14**, 297 (1989).

[16] P.S. Piispanen, B. Hedman, T. Norin, Journal of surfactants and detergents, **5**, 165 (2002).

[17] A. M. Atta, A.M. Ramadan, K. A. El-Shafay, A. M. Mohamed, N. S. Ragab, M.Fekry,journal of dispersion science and technology, **30**, 1100 (2009).

[18] A. M. Atta, A. F. El-Kafrawy, M. E. Abdel-Rauf, N. E. Maysour, A. K. Gafer, Journal of dispersion science and technology, **31**, 567 (2010).

[19] A.M. Atta, M. E. Abdel-Rauf, N. E. Maysour, A.K. Gafer,Journal of dispersion science and technology **31,** 583 (2010).

[20] A.M. Atta, A. M. Elsaeed, Journal Applied Polymer Science **122**(1), 183 (2011).

[21] A.M Atta, G.A. El-Mahdy, H. S. Ismail, H. A. Al-Lohedan Int. J. Electrochem. Sci., **7**, 11834 (2012).

[22] A. M Atta, G.A. El-Mahdy, A. A. Al-Azhary, H.A. Al-Lohedan, Int. J. Electrochem. Sci., **8**, 1295 (2013).

[23] G. A. El-Mahdy, Ayman M Atta and Hamad A. Al-Lohedan, Int. J. Electrochem. Sci**., 8**, 5052 (2013) .

[24] A. M. Atta, G. A. El-Mahdy, A.K.F. Dyab,H. Allohedan, Int. J. Electrochem. Sci., **8**   9629 (2013).

[25] Y. Sun, F.S.Yin,Z.Q. Song, in new surfactants, chemical industry press, 2003, p5.

1058

[26] G. F.Whitfield J. Chem. Soc. C, 1781 (1968).

[27] G. Cardinale, J. A. M. Laan, J. P. Ward,Recueil des TravauxChimiques des Pays-Bas
106(2), 62 (1987).

[28] P. D. Nichols, P. M. Shaw, R.B. Johns, Journal of Microbiological Methods,
3(5–6), 311 (1985).

[29] L. Li, E. Coppola, J.Rine, J. L. Miller, D. Walker, Energy Fuels, **24**, 1305 (2010).

[30] A. Behr, M.Fiene, F.Naendrup,K.Schürmann,Eur. J. Lipid Sci. Technol., 342 (2000).

[31] W.Oppolzer, Intermolecular Diels-Alder Reactions, in: ComprehensiveOrganic Synthesis,
Vol. 5, Eds. Trost, B. M., and I.Fleming, Pergamon Press 1991, p. 315.

[32] W.Carruthers,: Cycloaddition Reactions in Organic Synthesis,Tetrahedron Organic Chemistry
Series Vol. 8, Pergamon Press,Oxford, New York, 1990.

[33] H. Baumann, M. Bühler, H. Fochem, F. Hirsinger, H. Zoebelein,and J. Falbe, NatürlicheFette
und Öle, Angew. Chem. **100,** 41 (1988).

[33] G. A. El-Mahdy, A.M. Atta, H. A. Al-Lohedan, Molecules, **19**, 1713 (2014).

[34] D. Asefi, M.Arami, A.A. Sarabi, N.M. Mahmoodi, Corros. Sci., **51**, 1817 (2009).

[35] Rosen, M.J. Surfactants and Interfacial Phenomena; John Wiley: New York, NY, USA,
1985; pp. 15.

[36] A M. Atta, A.K. F. Dyab,H. A. Al-Lohedan, JSurfactDeterg, **16**, 343 (2013.

[37] X.J.Xu, H.L.Goh, K.S.Siow, L.M.Gan,Langmuir **17**, 6077 (2001).

[38] H. Ma, S. Chen, L. Niu, S. Zhao, S. Li, D. Li, J. Appl. Electrochem. **32**, 65 (2002).

[39] M. Hosseini, H. Tavakoli, T. Shahrabi, J. Appl. Electrochem. **38**, 1629 (2008).

[40] M. Lebrini, M. Lagrenee, H. Vezin, L. Gengembre, F. Bentiss, Corros. Sci. **47,** 485 (2005).

[41] F.S. de Souza, A. Spinelli, Corros. Sci. **51**, 642 (2009).

[42] M.A. Amin, S.S. Abd El-Rehim, E.E.F. El-Sherbini, R.S. Bayoumi, Electrochim. Acta
52, 3588 (2007).

[43] E. McCafferty, N. Hackerman, J. Electrochem. Soc. **119**, 146 (1972).

[44] S.-L. Li, Y.-G. Wang, S.-H.Chen, R. Yu, S.-B.Lei, H.-Y.Ma, D.-X. Lin, Corros. Sci.
41, 1769 (1999).