



Synthesis of ethylolammonium salts of diethylolamido phosphate surfactant based on the flaxseed oil and their corrosion inhibitor properties

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ABSTRACT

Diethylolamide of flaxseed oil has been synthesized and modified with H_3PO_4 . The obtained compound was neutralized by monoethanolamine, diethanolamine and triethanolamine. The progress of the reactions was monitored and confirmed by FTIR, 1H NMR and ^{13}C NMR. The physical properties of the synthesized surfactants were studied. The surface properties such as the critical micelle concentration (CMC), the effectiveness of surface tension reduction (Γ_{CMC}), surface excess concentration (Γ_{max}) and surface area per molecule (A_{min}) have been determined by means of interface tension measurements. They were tested as corrosion inhibitors for carbon steel in H_2S medium. It was found that the corrosion inhibition efficiency depends on both concentration and molecular structure of the inhibitors.

Indexing terms/Keywords

Surfactants; Surface properties; Adsorption; Corrosion inhibitors; H_2S environment

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1. INTRODUCTION

Carbon steel as a relatively cheap material having very high mechanical characteristics is widely used in practically all fields. Regrettably, this alloy undergoes corrosion in practice under the action of such aggressive components as hydrochloric and hydrosulphuric acids, carbon dioxide and many others [1]. Hydrochloric acid is very effective for dissolving calcium carbonate scale inside the pipelines and finds a large application with this goal. There are several ways for decreasing the rate of metals corrosion. One of them is an introduction of inhibitors into acidic systems. The most preferable inhibitors for protection of metals against corrosion are of organic nature and contain such heteroatoms as nitrogen, oxygen, phosphorus and sulphur as well as aromatic rings and multiple bonds. Among various groups of inhibitors surface-active inhibitors are characterized by high levels of inhibition efficiency, cheapness, relative harmlessness and easiness of production. Inhibition was reported to be realized as a result of adsorption of the surfactant molecules, with an aid of their functional groups, to the metal surface [2–5].

Presence of such heteroatoms as nitrogen, sulfur and oxygen, because of their tendency to be adsorbed at the metal/media interface with formation of protective layer, is very important [6-8].

Inhibition of iron corrosion by surfactants may occur via two phenomena consisting in blocking and hydrophobing effects [9].

As is known, inhibitors are considered to be optimal if they are based on relatively cheap and non-toxic initial components and contain the above-shown heteroatoms and fragments. From this standpoint vegetable oils are very convenient raw materials as they are restorable and ecologically clean [10-13].

In the present study weight loss measurements were performed to examine the H₂S acid corrosion inhibition process of carbon steel by some surfactants synthesized on the basis of flaxseed oil and such ethanolamines as monoethanolamine (MEA), diethanolamine (DEA) and triethanolamine (TEA) for the range of concentrations below the critical micelle concentration. Similar surfactants were synthesized and studied as chemicals for removing thin petroleum films from water surface [14]. Meanwhile, the values of interfacial tension at the water-kerosene border in the presence of the synthesized surfactants have been determined and respective colloidal-chemical parameters have been computed.

2. EXPERIMENTAL PROCEDURES

2.1 INSTRUMENTS AND MATERIALS

¹H NMR and ¹³C NMR spectra were recorded on Bruker Avance II+300 (UltraShield™ Magnet) 300.13 MHz and 75.46 MHz spectrometer using CCl₃D as solvents. Infrared spectra (4000–400 cm⁻¹) were recorded on a Vertex 70 (Bruker) instrument in KBr pellets.

Flaxseed oil was obtained from Schneekoppe GmbH & Co, Germany. MEA (purity > 99% Merck®, Germany), DEA (purity > 98.5% Merck®, Germany) and TEA (purity > 99% Merck®, Germany) were of analytical grade. Ortho-phosphoric acid (85% wt. solution) was from Moscow's "Component-Reactant" Joint Stock Company (Russia) production. Kerosene was purified from aromatic compounds by treatment with sulfuric acid up to a surface tension of 24 mN/m (20 °C).

2.2 Synthesis of diethylolamide

The reaction was carried out in a round bottom Pyrex glass reaction flask submerged in an oil bath. The reaction flask was equipped with a mechanical stirrer, thermometer and condenser. DEA was reacted with the flaxseed oil at a molar ratio of 3:1. The reaction was carried out at a temperature of 145-155 °C and the formation of the diethylolamide was monitored with FTIR. At the end of the reaction, the reaction mixture was allowed to cool and was later dissolved in diethyl ether in a separating funnel. The ether phase was washed with 5% aqueous hydrochloric acid. The ether layer was separated, washed with water and passed over sodium sulphate. The resulting ether layer was later concentrated using a rotary evaporator.

2.3 Synthesis of ethylolammonium salts of ethylolamide phosphate

Ortho-phosphoric acid (0.135 mol) was added to 400 mL of anhydrous benzene at 50 °C in a three-necked round-bottom flask equipped with a thermometer sensor and a magnetic stirrer. The diethylolamide (0.135 mol) was gradually introduced into the flask and allowed to react with the phosphoric acid until a complete conversion was achieved. About 250 mL of deionized water was poured into the reaction mixture and left for 3 h. The organic phase was extracted three times with diethyl ether, washed with HCl (1 mol dm⁻³) and deionized water until free of acid. The diethyl ether was evaporated under reduced pressure, and then poured in ethanolic solution of the respective ethanolamine (0.135 mol). The resulting ethanol layer was later concentrated using a rotary evaporator at a reduced pressure to give a brown liquid which was finally air dried.

Ethylamide phosphate-IR ν_{max} (cm⁻¹): 1098 (P-O), 1655 (C=O), 2927 (C-H), 3442 (O-H). ¹H-NMR (300.13 MHz, CCl₃D), δ (ppm): 0.85-0.88 (CH₃), 0.94-0.99 (CH₃), 1.11–1.31 (CH₂ chain), 1.60-1.64 (CH₂-CH₂-C(O)), 1.99-2.30 (CH₂-CH=CH), 2.74-2.81 (CH=CH-CH₂-CH=CH), 3.58-3.68 (N-CH₂-CH₂-OH), 3.8-4.1 (NH-CH₂-CH₂-O-P), 5.2-5.4 (CH=CH), 7.7 (P-OH) (Fig 1). ¹³C-NMR (75.46 MHz, CCl₃D), δ (ppm): 14.2–14.4 (CH₃), 20.7-34.2 (CH₂ chain), 61.7-77.4 (N-CH₂-CH₂-OH and N-CH₂-CH₂-O-P), 127.2-132.0 (CH=CH), 173.9-179.9 C(O)N.

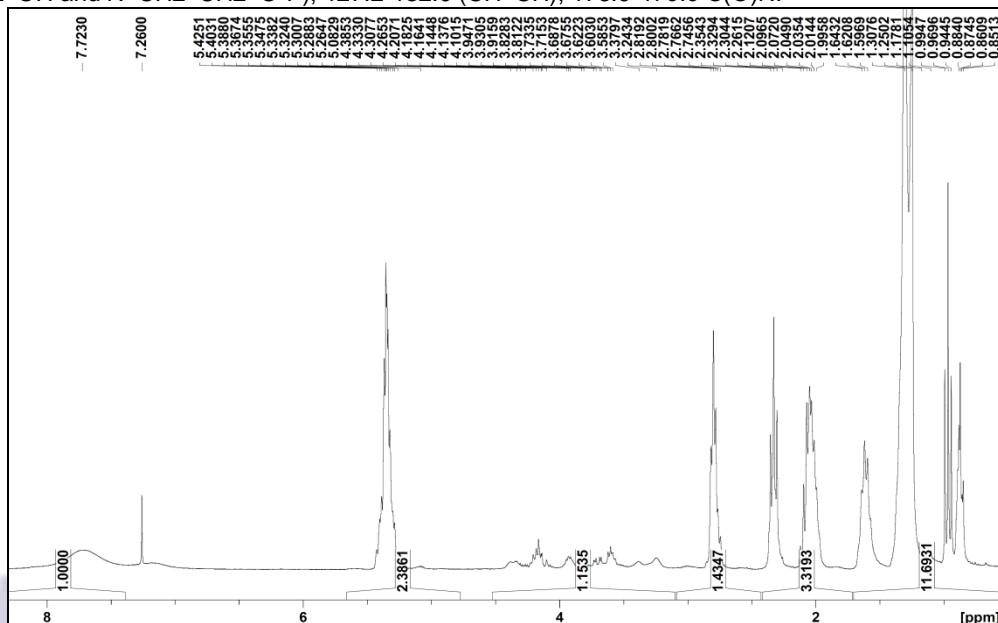


Fig 1. ¹H-NMR spectrum of flaxseed oil ethylamide phosphate

Monoethylammonium salt of ethylamide phosphate-IR ν_{max} (cm⁻¹): 1067 (P-O), 1654 (C=O), 2364 (N+H) 2927 (C-H), 3448 (O-H). ¹H-NMR (300.13 MHz, CCl₃D), δ (ppm): 0.87-0.99 (CH₃), 1.24–1.30 (CH₂ chain), 1.59-1.61 (CH₂-CH₂-C(O)), 1.99-2.34 (CH₂-CH=CH), 2.76-2.81 (CH=CH-CH₂-CH=CH), 3.58-3.62 (N-CH₂-CH₂-OH), 4.14-4.20 (NH-CH₂-CH₂-O-P), 5.28-5.40 (CH=CH) (Fig 2). ¹³C-NMR (75.46 MHz, CCl₃D), δ (ppm): 14.2–14.4 (CH₃), 20.7-34.4 (CH₂ chain), 61.7-77.4 (N-CH₂-CH₂-OH and N-CH₂-CH₂-O-P), 127.2-132.0 (CH=CH), 173.6-179.6 C(O)N.

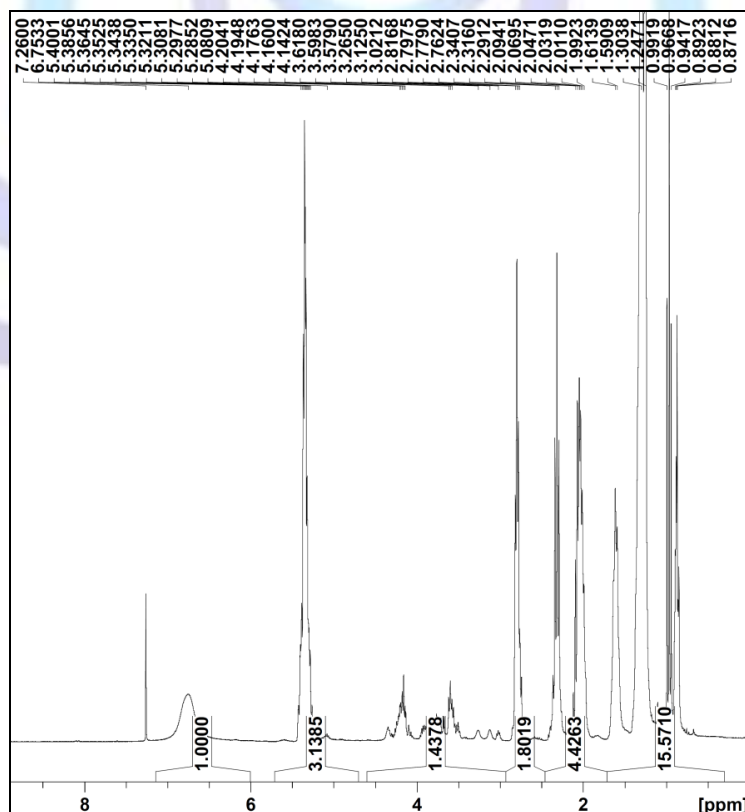


Fig 2. ¹H-NMR spectrum of monoethylammonium salt of flaxseed oil ethylamide phosphate

2.4 Interfacial tension measurements

All the interfacial tension measurements [15] were carried out using kerosene to make the solutions. The solutions kept at the desired temperature were measured 60 s after transfer to the thermostated measuring dishes. The actual temperature within the dishes was controlled prior to and after the measurement by means of a thermocouple. Deviations from the desired temperature were $\pm 0.2^\circ\text{C}$. The interfacial tension as a function of concentration was measured at 20°C using a drop volume Traube stalagmometer (Russian Federation). Interfacial tension values from the two measurements varying by no more than 0.2 mN m^{-1} were averaged and reported. The interfacial tension of pure kerosene at the border with water was 46.5 mN m^{-1} .

2.5 Weight Loss Measurements

The weight loss experiments were performed with carbon steel specimens having a composition of (wt%): 0.21-0.22 C, 0.15-0.30 Si, 0.40-0.65 Mn, <0.30 Ni, <0.05 S, <0.04 P, <0.3 Cr, <0.008 N, <0.3 Cu, <0.08 As and the remainder Fe.

The carbon steel sheets of $2 \times 4 \times 0.4\text{ cm}$ were abraded with a series of emery papers (grade 320, 500, 800 and 1,200) and then washed with acetone and distilled water. After weighing accurately, the specimens were immersed in a closed flask contained 250 mL of a solution of hydrosulfuric acid without and with the tested inhibitors I, II and III at different concentrations (10, 20, 50 and 100 ppm by weight) for 5 h at 20°C . Then, the specimens were taken out, washed, dried and weighed accurately. The test was performed for three specimens and the weight was the average of the three specimens. The coupons were polished with a hard plastic brush, first with hot water, then with ethanol to remove the corrosion products. The corrosion rate (R), the inhibition efficiency (IE %) and degree of surface coverage (θ) were calculated using Eqs. (1-3) [11,12]:

$$R = W / A \cdot \tau \quad (1)$$

$$IE\% = [(R_0 - R) / R_0] \times 100 \quad (2)$$

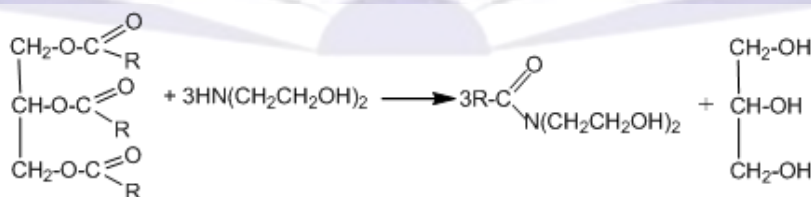
$$\theta = 1 - (R / R_0) \quad (3)$$

where W is the average weight loss of three parallel carbon steel sheets, A is the total surface area of the specimen, τ is immersion time, R_0 and R are the values of the corrosion rate without and with addition of the inhibitor, respectively.

3. Results and Discussion

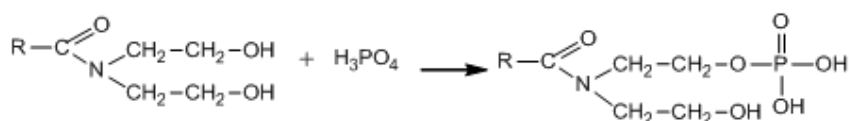
3.1 Synthesis of ethylolammonium salts

The reaction was carried out using flaxseed oil as the starting material. The oil was reacted with DEA at molar ratio of 1:3 (flaxseed oil:DEA) (Scheme 1):

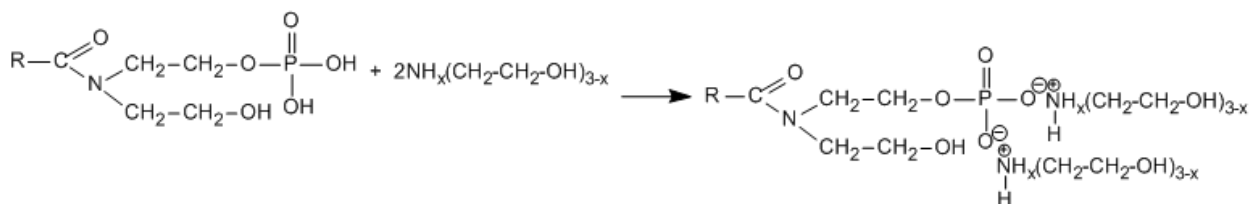


Glycerol was produced as the by-product of the reaction.

The synthesized diethylolamide was modified with ortho-phosphoric acid at the molar ratio 1:1. The reaction equation is shown in Scheme 2:



The obtained phosphate derivative was neutralized with MEA, DEA and TEA. The scheme of the neutralization reaction is as following:



where $x=0, 1$ or 2 .

3.2 Surface activity of the synthesized surfactants

The critical micelle concentrations (CMC) were determined by the surface balance method. The CMC values of the prepared ethylolammonium salts were determined at 293 K from the change in the slope of the plotted data of interfacial tension versus the natural logarithm of the solute concentration. Some representative plots (Fig. 3) were illustrated here for brevity. The obtained values of CMC for surfactants at 293 K temperature are tabulated in Table 1, together with values for the interfacial tension at CMC. Generally, the increasing in the number of ethylol groups in the head group of molecule decreases CMC values due to decreasing the solubility of the surfactants in kerosene. Such improved water-solubility lowers the tendency for the surfactant to form micelles.

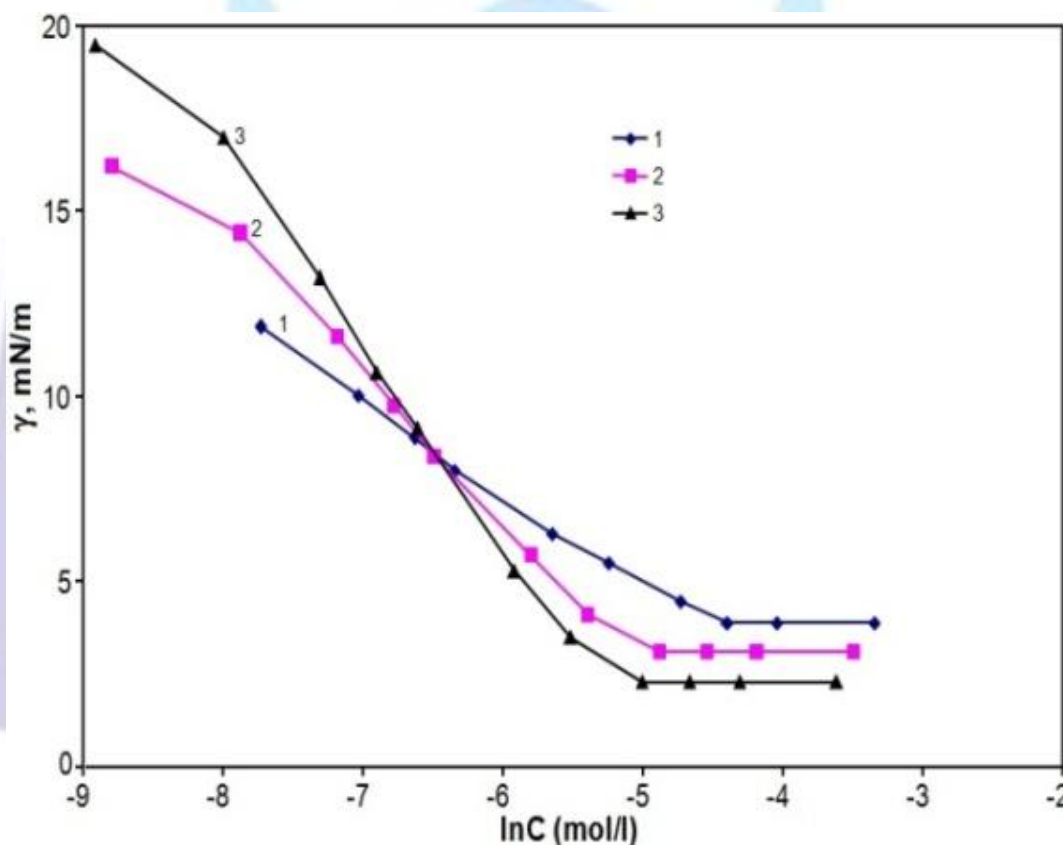


Fig 3. Interfacial tension at the border kerosene-water vs. \ln of the concentration of surfactants in kerosene solution (1-MEA salt, 2-DEA salt, 3-TEA salt) (20 °C)

Table 1. Interface properties of the ethylolammonium salts of diethylolamide phosphate surfactant based on flaxseed oil; 293 K temperature^a

Surfactants	$\text{CMC} \times 10^3, \text{mol} \cdot \text{dm}^{-3}$	$\gamma_{\text{CMC}}, \text{mN} \cdot \text{m}^{-1}$	$\Gamma_{\text{max}} \times 10^{10}, \text{mol} \cdot \text{cm}^{-2}$	$A_{\text{min}} \times 10^2, \text{nm}^2$	$\pi_{\text{CMC}}, \text{mN} \cdot \text{m}^{-1}$	$\Delta G_{\text{mic}}, \text{kJ} \cdot \text{mol}^{-1}$	$\Delta G_{\text{ad}}, \text{kJ} \cdot \text{mol}^{-1}$
MEA salt	12.3	3.9	0.49	336.1	42.6	-10.7	-19.3
DEA salt	7.5	3.1	0.86	193.8	43.4	-11.9	-17.0
TEA salt	6.7	2.3	1.13	147.2	44.2	-12.2	-16.1



^aCMC, critical micelle concentration; γ_{CMC} , equilibrium interface tension at the CMC; Γ_{max} , the maximum surface excess concentration at the kerosene solution/water interface; A_{min} , the minimum area per surfactant molecule at kerosene solution/water interface; π_{CMC} , effectiveness of interface tension reduction; ΔG_{mic} , change of standard free energy of micellization; ΔG_{ad} , change of standard free energy of adsorption.

As a result, a plot of interfacial tension as a function of equilibrium concentration of surfactant in one of the liquid phases, rather than an adsorption isotherm, is generally used to describe adsorption at this interface. The concentration of surfactant at the interface may therefore be calculated from interfacial tension data by using the following equation [16]:

$$\Gamma = -\frac{1}{RT} \left(\frac{\partial \gamma}{\partial \ln C} \right)_T \quad (1)$$

where $\left(\frac{\partial \gamma}{\partial \ln C} \right)_T$ is the slope of the plot of γ versus $\ln C$ at a constant temperature (T), and R is the gas constant in $\text{J}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$. The surface excess concentration at surface saturation (Γ_{max}) can be readily found and it is a useful measure of the effectiveness of adsorption of surfactant at the liquid-gas or liquid-liquid interface, since it is the maximum value to which adsorption can attain.

From the surface excess concentration, the area per molecule at interface is calculated using Equation (2)

$$A_{\text{min}} = \frac{10^{16}}{N\Gamma_{\text{max}}} \quad (2)$$

where N is Avogadro's number.

The effectiveness of interfacial tension reduction, $\pi_{\text{CMC}} = \gamma_0 - \gamma_{\text{CMC}}$, where γ_0 is the interfacial tension at the kerosene/water border and γ_{CMC} is the interfacial tension at the kerosene solution of surfactant/water border at CMC, was determined at 293 K temperature. The Γ_{max} , A_{min} and γ_{CMC} values were calculated and listed in Table 1. The data listed in Table 1 show that the minimum areas per molecule at the kerosene solution/water interface decrease with the increase of the number of ethylol units in the head group molecule. The data on A_{min} and Γ_{max} indicate the dependence of the effectiveness of adsorption at the kerosene solution/water interface from the structure of surfactants. It was found that increase in the number of hydroxyethylol groups in surfactant structure appears to have an unusual decrease in A_{min} at the interface. This can be attributed to the fact that TEA has a branched hydroxyethyl group, which makes coiling of hydrophobic chain with a consequent decrease in A_{min} [17].

The effectiveness of interfacial tension reduction in these compounds shows a steady rise with increase in the number of ethylol groups.

3.3 Standard free energies of micellization and adsorption at the kerosene solution/water interface

Standard free energies of micellization ΔG_{mic} , for the synthesized surfactants have been calculated by equation [16]

$$\Delta G_{\text{mic}} = RT \ln \text{CMC} \quad (3)$$

Standard free energies of adsorption ΔG_{ad} for these surfactants have been determined by using the relationship [6]

$$\Delta G_{\text{ad}} = RT \ln \text{CMC} - \pi_{\text{CMC}} \text{CMC} \quad (4)$$

The found values of ΔG_{mic} and ΔG_{ad} are listed in Table 1. From these data it may be concluded that micellization process has a spontaneous character ($\Delta G_{\text{mic}} < 0$). All values found for ΔG_{ad} are negative. Moreover, they are more negative than those of ΔG_{mic} , i.e. adsorption of the mentioned surfactants at the kerosene/water interface is associated with a larger decrease in free energy of the system. As the number of ethylol groups of head group rises, the values of ΔG_{mic} decrease, while the values of ΔG_{ad} increase. This indicates that the increase in the number of ethylol groups at N atom in these surfactants inhibit adsorption at the kerosene solution/water interface.

3.4 Effect of inhibitor concentration

It can be seen that the presence of inhibitors results in a high decrease in the rate of corrosion. In the case of these inhibitors, the corrosion rate decreases as the inhibitor concentration increases, getting maximum inhibition efficiency ranged between 97.0 and 99.5% at 100 ppm after 5 hours of exposure (Table 2). This trend may result from the fact that adsorption of these complex surfactants forms thin inhibitor films on the metal surface which relatively isolate the metal surface from the corrosive environment causing much reduced corrosion rates. Inhibition efficiency of these films depends on various factors including but not limited to corrosiveness of the environment, concentration of the surfactant, any synergetic effects with other molecules present in the environment and/or flow/ shear effects.

**Table 2. Corrosion rate, degree of surface coverage and inhibitor efficiency at different concentrations of surfactants in H₂S solution at 293 K (according to weight loss measurements)**

Inhibitors	Concentration (ppm)	Rate of corrosion, g/(m ² ·hour)	Surface coverage, θ	The inhibition efficiency, IE%
Blank	-	2.9	-	-
MEA salt	10	1.10	0.620	62.0
	20	0.46	0.840	84.0
	50	0.05	0.980	98.0
	100	0.01	0.995	99.5
DEA salt	10	1.01	0.650	65.0
	20	0.69	0.760	76.0
	50	0.14	0.950	95.0
	100	0.08	0.970	97.0
TEA salt	10	1.01	0.650	65.0
	20	0.46	0.840	84.0
	50	0.14	0.950	95.0
	100	0.04	0.983	98.3

3.5 Adsorption isotherm and thermodynamic considerations

The adsorption isotherms can provide basic information on the interaction of inhibitor and metal surface. In order to obtain adsorption isotherm, the surface coverage values (θ) for different concentrations of the prepared surfactants in H₂S solution have been obtained from gravimetric measurements and tested graphically for fitting a suitable adsorption isotherm. The plot of C/θ versus C gave a straight line with correlation coefficient of 0.9998 and the slope closed to 1 providing that the adsorption of the prepared surfactants in solution of hydrosulfuric acid on the carbon steel surface obeys Langmuir adsorption isotherm, which is presented by Eq. (5).

$$\frac{C}{\theta} = \frac{1}{K_{ads}} + C \quad (5)$$

where C is the inhibitor concentration, θ is the degree of coverage on the metal surface and K_{ads} is the equilibrium constant for adsorption-desorption process (Table 3). The high values of the adsorption equilibrium constant (1.36×10⁵, 1.18×10⁵ and 1.34×10⁵ M⁻¹ for MEA, DEA and TEA, respectively, at 20 °C) reflect the high adsorption ability of this inhibitor on carbon steel surface. The free energy of adsorption of inhibitor on carbon steel surface can be evaluated with the following equation:

$$\Delta G_{ads} = -RT \ln(55.55K_{ads}) \quad (6)$$

where ΔG_{ads} is the free energy of adsorption of inhibitor molecules on metal surface, K_{ads} is the equilibrium constant for adsorption-desorption process, R is the gas constant, T is the absolute temperature and 55.55 is the molar concentration of water.

Table 3. Thermodynamic parameters for the adsorption of the studied surfactants on carbon steel in H₂S solution medium

Inhibitor	Slope	Regression coefficient, R ²	K _{ads} ×10 ⁻⁵ , M ⁻¹	ΔG _{ads} , kJ·mol ⁻¹
MEA salt	0.963	0.9999	1.36	-38.58
DEA salt	0.971	0.9998	1.18	-38.24
TEA salt	0.960	0.9999	1.34	-38.54



The negative values of ΔG_{ads} indicate that the inhibitors are spontaneously adsorbed on the carbon steel surface. It is generally accepted that in the cases of the values of ΔG_{ads} up to $-20 \text{ kJ}\cdot\text{mol}^{-1}$, the types of adsorption are regarded as physisorption, where the inhibition acts due to the electrostatic interaction between the charged molecules and the charged metal, while the values around $-40 \text{ kJ}\cdot\text{mol}^{-1}$ or smaller, are seen as chemisorption, which is due to the charge sharing or a transfer from the inhibitor molecules to the metal surface to form a covalent bond. It is clear from Table 3 that the values of ΔG_{ads} in our measurements range from -38.24 to $38.58 \text{ kJ}\cdot\text{mol}^{-1}$. These results indicate that the adsorption mechanism of surfactants on carbon steel in H_2S saturated brine is typical chemisorption at the studied temperature.

4. CONCLUSIONS

1. Flaxseed oil-based diethylolamide phosphate and its surface-active ethylolammonium salts have been synthesized. Their colloidal-chemical properties have been studied.
2. The investigated surfactants act as effective corrosion inhibitors for carbon steel in oil well formation water under H_2S environment.
3. The adsorption of the synthesized surfactants molecules on the metal surface obeys Langmuir adsorption isotherm. The values of adsorption equilibrium constant suggest that the synthesized surfactants are strongly adsorbed on the carbon steel surface.

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