Investigation of Organic Complexes of Imidazolines Based on Synthetic Oxy- and Petroleum Acids as Corrosion Inhibitors

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ABSTRACT: *The mixture of Synthetic Petroleum Acids (SPA) and oxyacids (OSPA) have been synthesized on the basis of naphthenic-paraffinic hydrocarbons separated from 217-349°C fractions of Azerbaijan oils in the presence of the salts of Natural Petroleum Acids (NPA). The acid number of the obtained (SPA+OSPA) was 165 mgKOH/g, the yield was 40%. Imidazoline derivatives have been synthesized based on the mixture of SPA+OSPA and polyethylene polyamine (PEPA) and their complexes were prepared with CH_3COOH and HCOOH. The inhibition action of these complexes on steel corrosion in 1% NaCl solution saturated with CO_2 has been studied at 50°C. The results showed that all compounds are good inhibitors and the inhibition efficiencies in the presence of imidazoline derivatives based on SPA+OSPA were 93% and 97% at 25 and 50 ppm, respectively. The activation parameter study suggests the chemisorption for all inhibitors. The obtained values for Gibbs free energy show that the compounds are spontaneously adsorbed on the metal surface by chemisorptions. The image of the steel surface proved that the formed protective film on the electrode surface was stable. The adsorption of the studied compounds on steel surface follows the Langmuir adsorption isotherm.*

KEYWORDS: *Diesel fraction; Synthetic petroleum acids; oxy acids; CO_2 corrosion; Inhibition; Imidazoline derivatives.*

INTRODUCTION

Corrosion is the destructive attack of a material by reaction with its environment. Corrosion in the oil industry represents one of the major problems. The resistance of metals to the corrosion significantly depends on interaction with their medium. Due to the natural process of corrosion, it leads to the decreases of bond energy on metals. As a result of the corrosion process, metal atoms are oxidized by losing one or more electrons. Preparing

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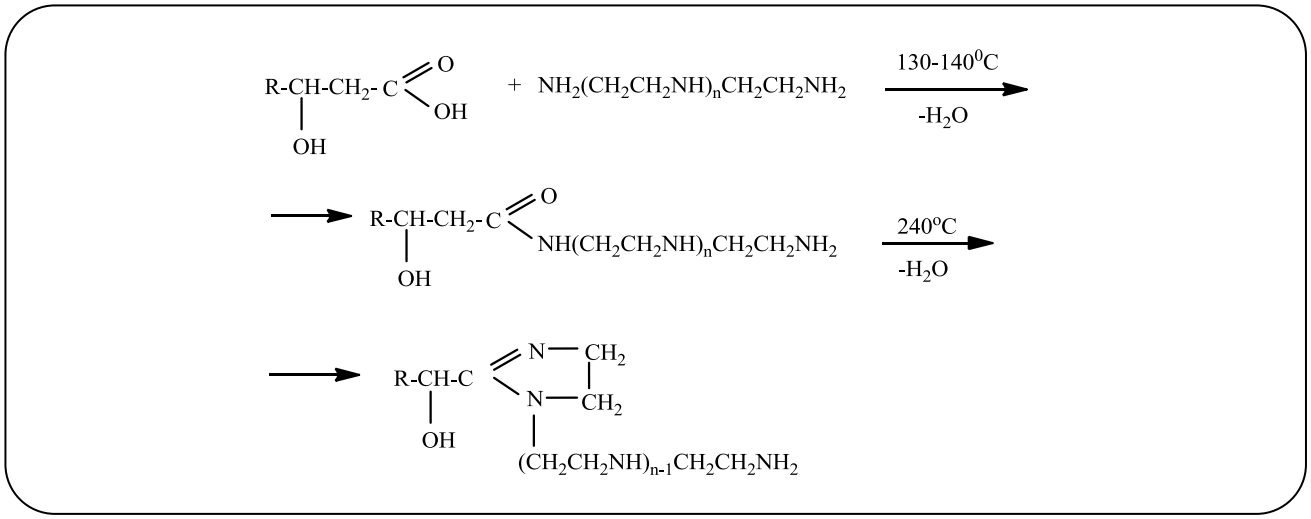


Scheme 1: General scheme for the synthetic procedure of imidazoline derivatives

the equipment by the corrosion-resistant materials cannot ensure their reliability and durability. It has been acknowledged that CO_2 corrosion is one of the major corrosion types resulting in oil well failure [1]. One of the main problems we have encountered in our industrialized society is metallic corrosion [2, 3]. One of the most common ways for the protection of metals from corrosion is the application of inhibitors [4]. Inhibitors often work by adsorbing themselves on the metallic surface, protecting the metallic surface by forming a film. Corrosion inhibitors are applied more widely in oil and oil-refining industry. Many organic compounds containing oxygen, nitrogen and sulphur atoms have been used as corrosion inhibitors for carbon steel in various aggressive environments [5]. Among the inhibitors nitrogen-base materials and their derivatives have the great importance. The amidoamine, imidazolines based on natural and synthetic petroleum acids particularly differ in corrosion inhibitors [6, 7]. This article is about the synthesis of imidazoline derivatives based on the mixture of synthetic petroleum and oxyacids and studies their protective effect on CO_2 corrosion. The aim of work - the advent of a new inhibitor that has to match up the above-mentioned requirement, describe the mechanism of inhibitors` action, main characteristics and the high efficiency on CO_2-corrosion.

EXPERIMENTAL SECTION

Naphthenic-paraffinic hydrocarbons separated from the diesel fraction of Azerbaijan oils were taken as the research object for the preparation of inhibitors. The fraction was purified from aromatic hydrocarbons by extraction method. As an extractant has been used N-Methyl-Pyrrolidone (NMP). It was defined that after dearomatization the process the number of aromatic hydrocarbons decreased from 16% to 1%. Naphthenic-paraffinic hydrocarbons were oxidized in the liquid phase with oxygen in the catalytic presence of the salts of natural petroleum acids, at 135-140°C temperature, within 6 hours in a barbotage reactor [8, 9]. In this case, the yield of the mixture of acids was 40%, acid number was 165 mg KOH/g. Synthesis imidazoline kept free amino on the basis of SPA+OSPA and polyethylene polyamine (PEPA) is taken by two stages. In the first stage was obtained amid compound on the basis of SPA + OSPA and PEPA, in the second stage imidazoline derivatives (Scheme 1).

Complexes were prepared from the imidazolines and CH_3COOH (S-10), HCOOH (S-11), in ratio 1:1. Complexes based on imidazoline derivatives and HX (X^-= CH_3COO^-, $HCOO^-$) were prepared in normal condition [10] (scheme 2).

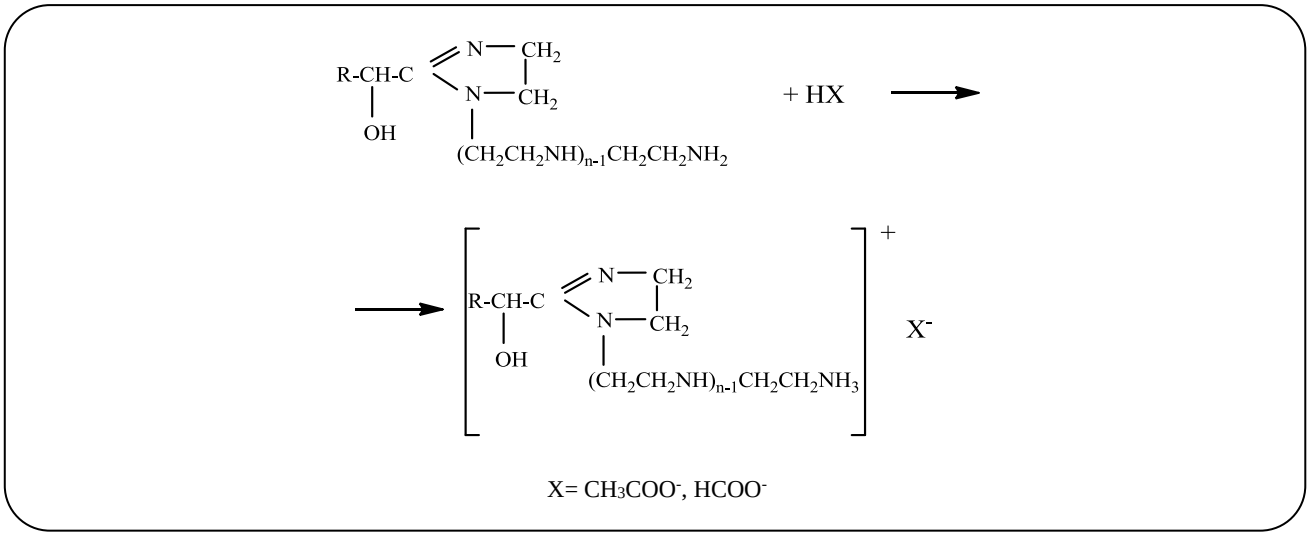
IR-spectrum of CH_3COOH complex of imidazoline derivatives was taken on universal IR-spectrometer "ALPHA" (company BRUKER, Germany) using KBr disks in the vibration range 4000-500 cm^{-1}. IR-spectrum of the complex is presented in Fig. 1.

Some physical-chemical indices of imidazoline derivatives were presented in Table 1.

As can be seen from Fig. 1, on 723 cm^{-1} vibrations of C-H bond of CH_2 group, on 1010 cm^{-1}, 1047 cm^{-1} C-O

Table 1: Physical-chemical indices of imidazoline derivatives

Ne	Indices	Amidoamine
1	Agregate state	Viscose liquid
2	Smell	Sharp
3	Colour	Dark brown
4	Molecular weight	524
5	Freezing temperature, °C	7
6	Density, g/cm^3 ; 20°C	1.1312



Scheme 2: General scheme for the synthetic procedure of Complexes based on imidazoline derivatives.

bond of alcohol; on 1335 cm^{-1} valence vibration of C-N bond; on 1642 cm^{-1} C=O bond of -C(=O)-NHR group of secondary amide; on 1455, 2854, 2923 cm^{-1} deformation and valence vibration of C-H bond of CH_2 and CH_3 groups, on 3078, 3271 cm^{-1} the N-H bond of secondary amide, on 2480, 2184 cm^{-1} NH_3^+ group of complex, on 1551 cm^{-1} N-H bond of NH group and CH_3COO^- anion.

The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO_2 were studied in ACM Gill AC potentiometer [11]. The potential of the working electrode was varied by a CoreRunning programme (Version 5.1.4.) through an ACM instrument Gill AC. The CoreRunning program converts a corrosion current in mA/cm^2 to a corrosion rate in mm/year. The electrodes are made of metal brand C1018 Grade Steel and have an area of 7.9 cm^2. The process was continued 20 hours at 50°C. The corrosion rate of electrodes without (blank) and with inhibitor (imidazoline complexes) was compared. 1% NaCl solution was prepared by dissolving of analytical grade NaCl in distilled water. The concentration range of the prepared surfactants was used 25, 50 ppm for corrosion measurements. The corrosion rate of the blank was 3.43 mm/year.

RESULTS AND DISCUSSION

The CH_3COOH, HCOOH complexes of imidazolines at concentrations 25 and 50 ppm for 20 hours have been investigated. The results of the protective effects of the imidazoline complexes were presented in Figs. 2 and 3.

Corrosion protection efficiency and thermodynamic parameters for the adsorption of all examples in 1% solution of NaCl, saturated with CO_2 are presented in Table 2.

The results obtained from Figs. 2, 3 and Table 2, such as corrosion rate and corrosion inhibition efficiency, which shows that on the addition of different concentrations

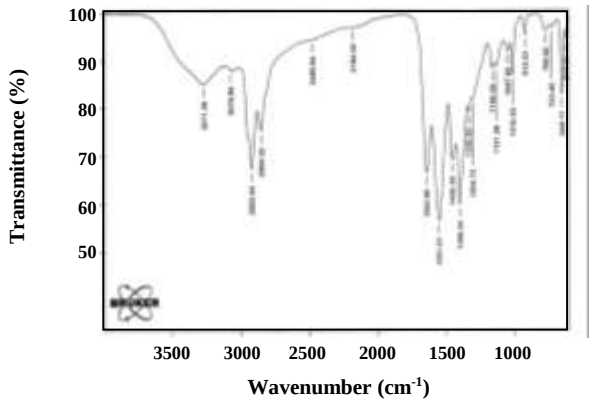


Fig. 1: IR spectrum of the CH_3COOH complex of imidazoline derivatives.

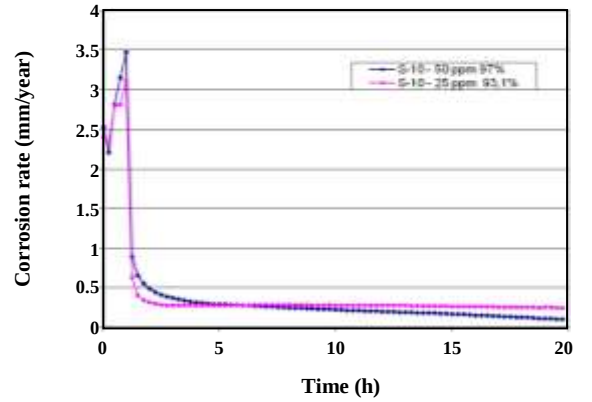


Fig. 2: Depending on the corrosion rate from time for mild steel in CO_2-saturated 1% NaCl solution containing different concentrations of CH_3COOH complex of imidazoline derivatives at 50 ^{0}C.

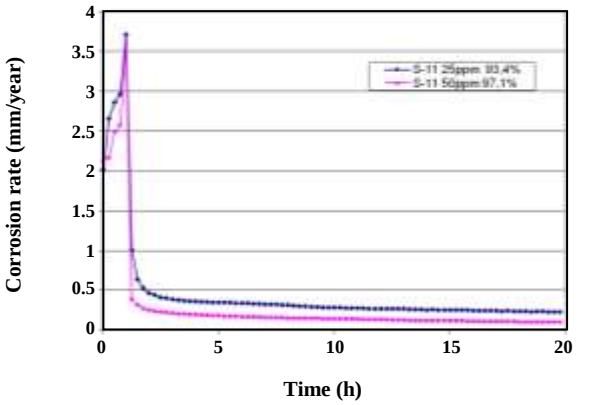


Fig. 3: Time dependence of the corrosion rate for mild steel in CO_2-saturated 1% NaCl solution containing different concentrations of HCOOH (S-11) complex of imidazoline derivatives at 50^{0}C.

of investigated inhibitors, the inhibition efficiency increases and the corrosion rate decreases. This indicates that the corrosion inhibition efficiency of the studied compounds is concentration dependent. As can be seen in medium without inhibitor the corrosion rate increased from 1.2 mg/year to 3.43 mm/year. When the content of the added complexes 25 ppm after 20 hours the corrosion rate reduced to 0.24 mm/year and 0.23 mm/year and the inhibition efficiency of 93.1% and 93.4%. With increasing concentration up to 50 ppm, to further reduce the corrosion rate of carbon steel is observed (97.0% and 97.1%). Increasing the concentration of inhibitor more than 50 ppm does not affect the corrosion rate, as well as significant changes, are not observed in the prices of the effect of corrosion protection.

The corrosion parameters were calculated on the basis of LPR corrosion rate test. The Protection Effect (PE, %) and surface coverage (θ) were calculated according to the following equations:

$$\mathrm{PE},\% \frac{\mathrm{CR}_0 - \mathrm{CR}_\mathrm{i}}{\mathrm{CR}_0} \times 100 \quad (1)$$

$$\text{Surface coverage} \quad \theta = 1 \frac{\mathrm{CR}_\mathrm{i}}{\mathrm{CR}_0} \quad (2)$$

Where CR_0 and CR_i are the corrosion rate without and with inhibitors, respectively. It can be seen that the presence of inhibitors results in a high decrease in the rate of corrosion. A general trend is observed in presence of the studied inhibitors, a decrease in the corrosion rate of carbon steel in presence of these complexes compared to the blank (inhibitor-free solution). By increasing the concentration of the complexes, a further decrease in the corrosion rate of carbon steel was observed. The maximum inhibition efficiency (IE,%) was obtained at 50 ppm of inhibitors. This trend may result from the fact that adsorption of these complexes forms thin inhibitor films on the metal surface which in order to relatively isolate the metal surface from the corrosive environment causing much-reduced corrosion rates. The effectiveness of studied complexes as corrosion inhibitors depends on their structures. Braking effect of reagents synthesized based on SPA + OSPA and PEPA may be due to the presence of O- and N-heteroatoms in the system, increasing the number of active centers, as well as the electron density and molecular size, accordingly,

Table 2: The calculated results of the protective effect against corrosion and thermodynamic parameters of S-7 və S-8 complexes in an aqueous solution of 1% NaCl saturated with CO_2.

The concentration of inhibitor, ppm	The braking effect, γ	Metal loss, mg	Protection effect, %	Corrosion rate, mm/year	K_{ads}, $M^{-1}\times10^4$	Surface coverage, θ	Gibbs energy, ΔG°_{ads} kJ/mol
Without inhibitor	-	0.005446	-	3.4342	-	-	-
S-10							
25	14.3	0.000945	93.1	0.241842	15.,3	0.929	-40
50	34.3	0.000876	97	0.101306	77	0.971	-44
S-11							
25	14.9	0.001042	93.4	0.227593	16	0.934	-40
50	34.3	0.000653	97.1	0.101925	74.3	0.970	-43.4

the intensity of precipitation of carbonates on the metal surface [12]. A solution of synthesized amidoamines due to free electron pairs of the nitrogen atoms in their composition exposed chemisorption by the surface of the metal. imidazoline molecule forms a complex with organic acids. In consequence NH_3^+ ions forms in the system. The acceleration of the anodic dissolution of iron takes place in the aerobic acidic environment containing NaCl. With the addition inhibitor chemisorption of NH_3^+ ion, complex occurs to these parts. The obtained film is more durable, thereby protection of corrosion is better.

The mechanism of corrosion inhibition may be explained on the basis of the adsorption behavior of the inhibitors [13]. The values of K_{ads} obtained from the Langmuir adsorption isotherm are listed in Table 2, together with the values of the Gibbs free energy of adsorption.

$$\frac{C_{inh}}{\theta} = C_{inh} + \frac{1}{K_{ads}} \quad (3)$$

$$K_{ads} = \frac{1}{C_{inh}} \times \frac{\theta}{1-\theta} \quad (4)$$

$$\Delta G_{ads} = -2.303RT \log(55.5\, K_{ads}) \quad (5)$$

where K_{ads} is the equilibrium constant of the inhibitor adsorption process and C_{inh} is the surfactant concentration; R is the universal gas constant, T is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [14].

It is known that values of ΔG^0_{ads} up to -20 kJ /mol are consistent with physisorption, while those around -40 kJ/mol or higher are associated with chemisorption as a result of the sharing or transfer of electrons from organic molecules to the metal surface to form a coordinate bond [15-18]. From Table 2, it was observed that the values of the ΔG^0_{ads} for studied inhibitors are ranged between -40 and -44 kJ/mol, which are more than -40 kJ/mol (Table 2). This proves that complexes form chemical adsorption with the metal surface.

So, the complexes of imidazoline derivates and organic acids have high inhibitor efficiency in the acid medium with high proportion CO_2 and after the research of these compounds as an industrial inhibitor, it can be recommended for the application.

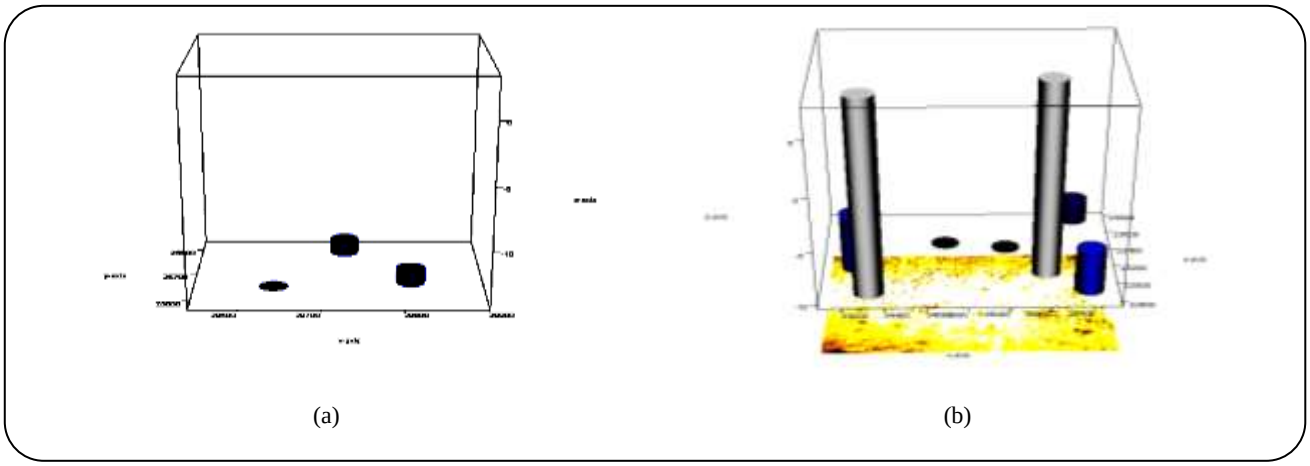
IR spectra of used electrodes before and after corrosion on S-10 and the image of their surface were taken on FT-IR microscopy LUMOS (company BRUKER, Germany) in the range of wave frequencies of 600-4000 cm^{-1}.

The image of the surface of the used electrode was selected 7 points and taken their IR spectra (Figs. 4 and 5).

Note: 1st point- blue, 2nd point – red, 3rd point – yellow, 4th point – grey, 5th point – black, 6th – green, 7th point – pink.

Analysis of IR-spectrum of points 2 and 7 show that this spectrum generally belongs to a complex of amine (1550, 1644, – N-H bond; 1108 cm^{-1} – O-H bond). Note that, IR-spectra of points 2 and 7 almost identical.

Comparing the IR- spectra of points 2 and 1, 3, 4, 5, 6 along with the absorption band on 1703 cm^{-1} appear several bands very weak intensity; on 1670-1800cm^{-1} is also characteristic of the C=O bond. The weak intensity of the absorption band of C=O bond confirmed that the corrosion process of the surface of electrode happened slightly (~3%).



(a) (b)

Fig. 4: The images of the surface of new (a) and the used electrode (b).

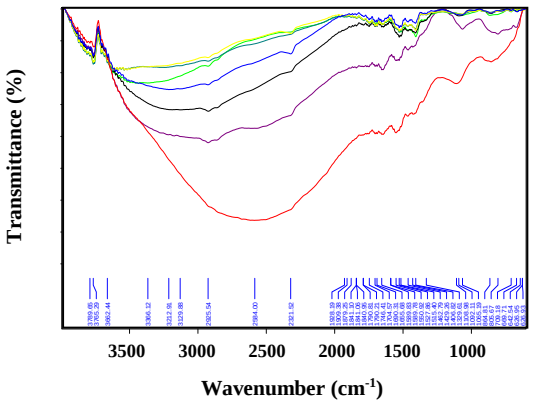


Fig. 5: IR spectra of the points of surface electrodes.

CONCLUSIONS

Imidazoline derivatives based on SPA+OSPA mixture and PEPA have been synthesized and their complexes were obtained with CH_3COOH and HCOOH. Corrosion of carbon steel in CO_2-saturated 1% NaCl solution and the inhibiting effect of the complexes of imidazoline derivatives have been studied. It has been found that all studied compounds act as effective inhibitors in the investigated medium. The results proved that for each example at 50 ppm concentration show the best inhibition performance – 97% (S-10) and 97.1% (S-11).

The Gibbs energy for studied compounds was ranged between -40 and -44 kJ/mol, confirmed that the adsorption process takes place spontaneously and was chemisorption.

Analysis of IR-spectra of points showed that this spectrum generally belongs to a complex of imidazoline derivatives. Thus, we can say that complexes in different concentrates easily exposed to adsorbed on a metal surface, confirming the stability of the protective film on the steel surface.

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REFERENCES

[1] Hany M Abd El-Lateef, Mohamed Ismael, Ibrahim Mohamed, Novel Schiff Base Amino Acid as Corrosion Inhibitors for Carbon Steel in CO_2-Saturated 3.5% NaCl Solution: Experimental and Computational Study**,** *Corrosion Reviews*. **33**: 77–97 (2015).

[2] Abd El-Lateef H. M., Abbasov V.M., Aliyeva L.I., Qasimov E.E., Ismayilov I.T., Inhibition of Carbon Steel Corrosion in CO_2-Saturated Brine Using Some Newly Surfactants Based on Palm Oil: Experimental and Theoretical Investigations, *Mater. Chem. Phys*, **142**: 502-512 (2013).

[3] Abd El-Lateef H. M., Abbasov V.M., Aliyeva L.I., Khalaf M. M., Novel Naphthenate Surfactants Based on Petroleum Acids and Nitrogenous Bases as Corrosion Inhibitors for C1018-Type Mild Steel in CO_2-Saturated Brine, *Egyptian Journal of Petroleum*, **24**: 175–182 (2015).

[4] Afandiyeva L.M., The Kinetic Effect of CO_2 Corrosion by Imidazoline Derivatives Based on Synthetic Oxy- and Petroleum Acids, *J. of Advances in chemistry*, **12**(1): 3944-3949 (2015).

[5] Farelas F., Ramirez A., Carbon Dioxide Corrosion Inhibition of Carbon Steels Through Bis-Imidazoline Compounds Studied by EIS, *Int. J. Electrochem. Sci*., **5**: 797-814 (2010).

[6] Shaker N.O., Badr E.E., Kandeel E.M., Adsorption and Inhibitive Properties of Fatty Imidazoline Surfactants on Mild Steel, *Pelagia Research Library Der Chemical Sinica*, **2**(4): 6-35 (2011).

[7] Abbasov V.M., Abd El-Lateef H.M., Aliyeva L.I., The CO_2 Corrosion Inhibition of Carbon Steel C1018 by Some Novel Complex Surfactants Based on Petroleum Acids and Nitrogen-Containing Ccompounds, *J. of Advances in Materials and Corrosion*, **2**: 26-32 (2013).

[8] Abbasov V.M., Mamedova T.A., Ismailov E.G., Askerova E.N., Teyubov Kh.Sh., Gasankhanova N.V., Alieva S.K., Catalytic Production of Olefins Using Natural Halloysite Nanotubes, *Catalysis in Industry*, **6** (3): 170-175 (2014).

[9] Aliyeva L.I., Afandiyeva L.M., Valiyeva F.M., Determination of Optimal Parameters for Obtaining Synthetic Oil Acids and Oxyacids Mixture from the Catalytic Oxidation of Naphthene-Paraffinic Hydrocarbons of Diesel Distillation, *International Journal of Scientific Engineering and Applied Science* (IJSEAS), **2**(3): 232-239 (2016).

[10] Abbasov V.M., Afandiyeva L.M., Agamaliyeva D.B., et all., Investigation Imidazoline Derivatives Obtained from Synthetic Petroleum Acids as Corrosion Inhibitor, *J. Advances in Chemistry*, **11**(1): 3372-3381 (2015).

[11] Song F.M., Kirk D.W., Graydon J.W., Cormack D.E., Predicting Carbon Dioxide Corrosion of bare Steel under an Aqueous Boundary Layer, *J. Corrosion*, **60** (8): 736-748 (2004).

[12] Taleb H.I. Zour M.A.: Corrosion Inhibition of Mild Steel Using Fig Leaves Extract in Hydrochloric Acid Solution, *Int. J. Electrochem. Sci*., **6**: 6442-6455 (2011).

[13] Abdel-Gaber A.M, Abd-El-Nabey B.A, Khamis E., Abd-El-Khalek D.E., A natural Extract as Scale and Corrosion Inhibitor for Steel Surface in Brine Solution, *J. Desalination*, **278** (1): 337-342 (2011).

[14] Flis J., Zakroczymski T., Impedance Study of Reinforcing Steel in Simulated Pore Solution with Tannin, *J. Electrochem.Soc*., **143**: 2458-2464 (1996)

[15] Szklarska-Smialowska Z., Mankowski J., Crevice Corrosion of Stainless Steels in Sodium Chloride Solution, *J. Corr. Sci.*, **18** (11): 953-960 (1978).

[16] Balaji J., Sethuraman M.G., Corrosion Protection of Copper with Hybrid Sol-Gel Containing 1H-1, 2, 4-triazole-3-thiol, *Iran. J. Chem. Chem. Eng. (IJCCE)*, **35**(4): 61-71 (2016).

[17] Hany M. Abd El-Lateef, Kamal A. Soliman, Ahmed H. Tantawy., Novel synthesized Schiff Base-based Cationic Gemini Surfactants: Electrochemical Investigation, Theoretical Modeling and Applicability as Biodegradable Inhibitors for Mild Steel Against Acidic Corrosion, *Journal of Molecular Liquids*, **232**: 478–498 (2017).

[18] Hany M. Abd El-Lateef, Ahmed H. Tantawy, Synthesis and Evaluation of Novel Series of Schiff Base Cationic Surfactants as Corrosion Inhibitors for Carbon Steel in Acidic/Chloride Media: Experimental and Theoretical Investigations, *RSC Adv*., **6**: 8681-8700 (2016).

[19] Hany M. Abd El-Lateef, Experimental and Computational Investigation on the Corrosion Inhibition Characteristics of Mild Steel by Some Novel Synthesized Imines in Hydrochloric Acid Solutions, *Corrosion Science*, **92**: 104–117 (2015).