



ISSN 2321-807X

## Investigation Imidazoline Derivatives Obtained from Synthetic Petroleum Acids as Corrosion Inhibitor

Abbasov V.M., Agamaliyeva D.B., Mursalov N.İ., Afandiyeva L.M., Jabrayilzadeh Sh.Z., Mammadova N.M., Seyidahmadova F.N., Tagizade Z.Y.

National Academy of Sciences of Azerbaijan The Y.H. Mamedaliyev Institute of Petrochemical Processes, AZ1025 Baku, Azerbaijan

Corresponding author: Lala Afandiyeva, E-mail: [efendiyevalm7@mail.ru](mailto:efendiyevalm7@mail.ru)

### ABSTRACT:

Imidazoline derivatives have been synthesized based on the synthetic petroleum acids (SPA) and diethylentriamine. Complexes were prepared from these compounds and HCl in ratio 1:1, 1:2, 1:3. 20% solution of the complexes were prepared in aqueous isopropyl alcohol. The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO<sub>2</sub> were studied ACM Gill AC potentiometer. It was found that, the imidazoline derivatives complexes based on the SPA and DETA with HCl in molar ratio 1:1 of 25 ppm concentration protection from corrosion is 83,5%, 100 ppm concentration – 97,1%; the proportion of 1:2 complex of 25 ppm – 82,8%, 100 ppm concentration – 97,3%, but in the case of the 1:3 complex shows the best result - 94 and 98,8%.

**KEYWORDS:** corrosion inhibitor; synthetic petroleum acids; oxidation; imidazoline; carbon steel



# Council for Innovative Research

Peer Review Research Publishing System

**Journal:** Journal of Advances in Chemistry

Vol. 11, No. 1

[editorjaonline@gmail.com](mailto:editorjaonline@gmail.com)

[www.cirjac.com](http://www.cirjac.com)



## INTRODUCTION

Corrosion of metal units damage to all over the sphere of national economy. Corrosion of the equipment of the oil and gas industry is caused greater losses. Therefore this related to being a high aggressive components and their work features in the sphere of the same equipment. On the other side, a result of corrosion in these spheres of industry is arisen shutdowns, that are not planned. As the result it damages economically to the oil and gas industry.

Preparing equipment from the materials of corrosion-resistant do not secure its reliable and durability. That's why in corrosion protection has to use other methods.

In corrosion protection using reduce aggression of corrosion sphere, and one of the widespread methods is in application inhibitors for to prevent corrosion of metals <sup>[1-5]</sup>.

The main requirements are consist of that: they must be obtained with simple technology, has to be a great raw material, multifunction effect and has to be a cheap. Among the inhibitors, that are suitable requirement above nitrogen-organic compounds, which are obtained on the basis of synthetic and natural petroleum acids have the great importance <sup>[6-10]</sup>. In this regard it is very important to use SPA, that obtained from the catalytic oxidation of naphthenic-paraffinic hydrocarbons in liquid-phase, that separated from Azerbaijan oil <sup>[11-15]</sup>. Thus for synthesis SPA was used fractional reservoirs that exist in our country. On the other side, unlike oil acids derivatives, derivatives of these acids solution in water, alcohol, aqueous alcohol is higher and their freezing temperature is very low.

This article is about the advent new inhibitors that has high effectivity in sphere of CO<sub>2</sub> and H<sub>2</sub>S, and they have to match up the above-mentioned requirement.

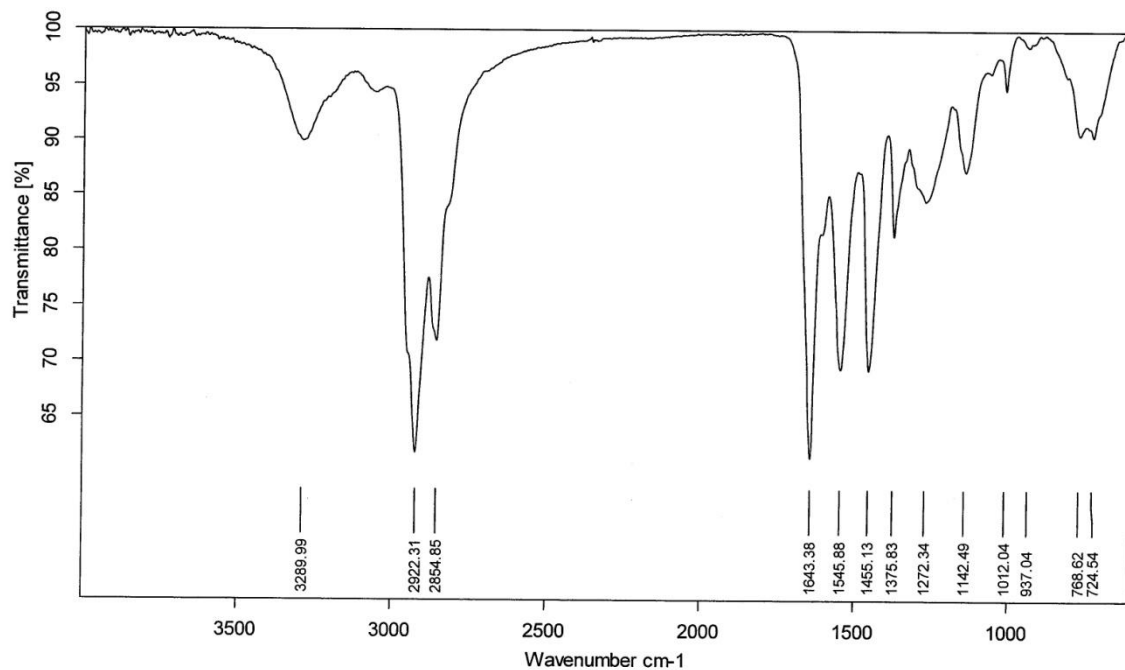
## MATERIAL AND METHODS

In the synthesis of a high efficient corrosion inhibitor was used SPA. For obtaining SPA as a object of research was taken boiling fraction 250-350<sup>o</sup>C of Azerbaijan oil which was dearomatized. The process of dearomatization was realized by sulfurization. The naphthenic-paraffinic hydrocarbons was oxidized in liquid-phase with oxygen of air, in the catalytic presence of salts of natural oil acids. The process is realized for 6 hours in the temperature of 135<sup>o</sup>C in a sparging reactor <sup>[16-18]</sup>. Some physical and chemical indices of obtained SPA is presented in table 1.

Table 1. Physical and chemical indices of SPA

Parameter	Value
Molecular weight	229
Density, 20 <sup>o</sup> C, g/sm <sup>3</sup> , $d_4^{20}$	0.9872
Refraction coefficient, $n_D^{20}$	1.4670
Boiling temperature, <sup>o</sup> C (6.65·10 <sup>-4</sup> mPa)	120-180
Acid number, mgKOH/g	245
Acid content, %	94

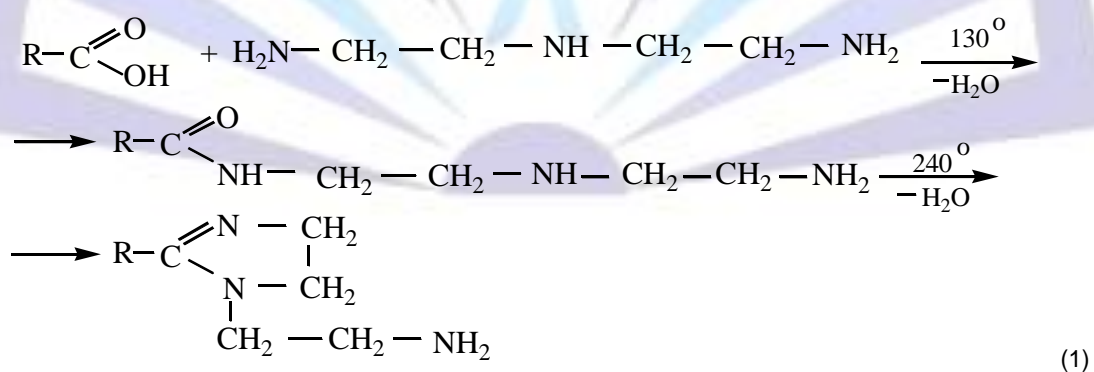
Spectrum of SPA is presented in figure 1.



**Fig. 1. IR-spectrum of SPA**

From the figure1 it is seemed that on  $724\text{ cm}^{-1}$  vibration of C-H bond of the  $\text{CH}_2$  group, on  $937\text{ cm}^{-1}$  valence vibration of C-H bond belongs to naphthene ring, on  $1242, 1272\text{ cm}^{-1}$  deformation vibration correspond to the C-O-C group, on  $1376\text{ cm}^{-1}$  the  $\text{CH}_3$  group, on  $1455\text{ cm}^{-1}$  deformation vibration of C-H bond on  $1455\text{ cm}^{-1}$  the deformation vibration of C-H bond belongs to  $\text{CH}_2$  group,  $2855, 2923, 2951\text{ cm}^{-1}$  valence vibration of C-H bond of the  $\text{CH}_2$  and  $\text{CH}_3$  groups, on  $1412\text{ cm}^{-1}$  deformation vibration, on  $3342\text{ cm}^{-1}$  valence vibration of the OH group of acid, on  $1702\text{ cm}^{-1}$  the group of  $\text{C}=\text{O}$  of acid, on  $2666, 2720\text{ cm}^{-1}$  valence vibration of the  $\text{COOH}$  group.

Synthesis imidazoline kept free amino on the basis of synthetic petroleum acids (SPA) and diethylenetriamine (DETA) are taken by two stages. In the first stage was obtained amid compound on the basis of SPA and DETA, in the second stage imidazoline derivatives:



Some physical and chemical indices of imidazoline derivatives are presented in the table 2.

Table 2. Physical and chemical indices of imidazoline derivatives.

No	Indicators	Imidazoline
1	Aggregate state	Viscous liquid
2	Smell	Sharp
3	Colour	Brown
4	Molecular weight	296
5	Freezing temperature, °C	10
6	Density, g/sm <sup>3</sup> ; 20°	1,0473
7	Refraction coefficient, n <sub>d</sub> <sup>20</sup>	1,5108

IR-spectrum of imidazoline derivatives is presented in figure 2.

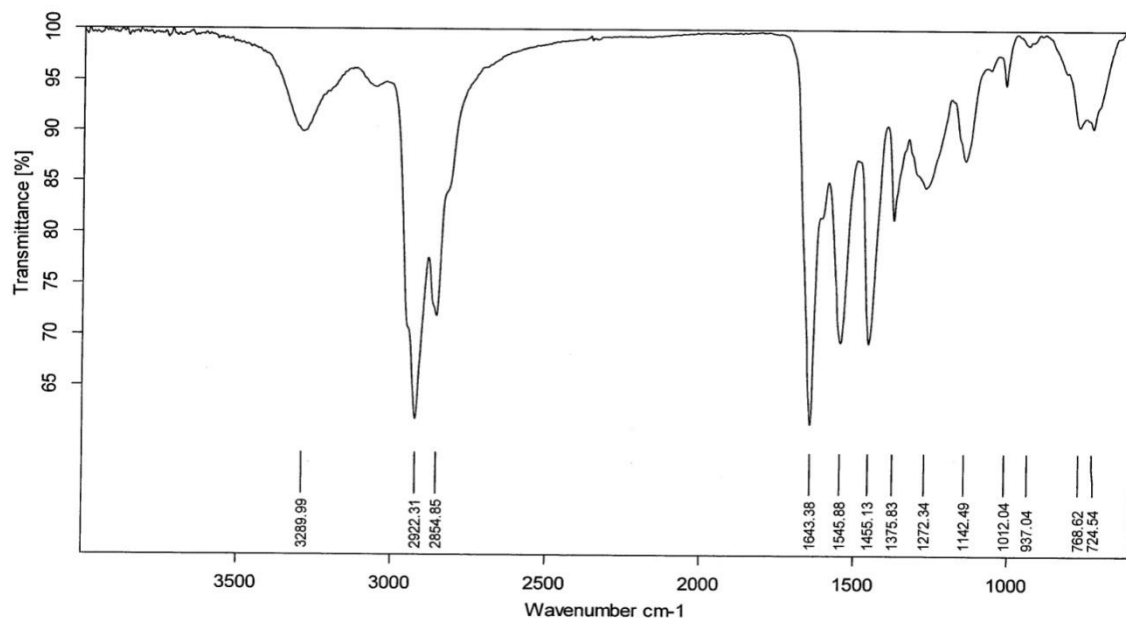
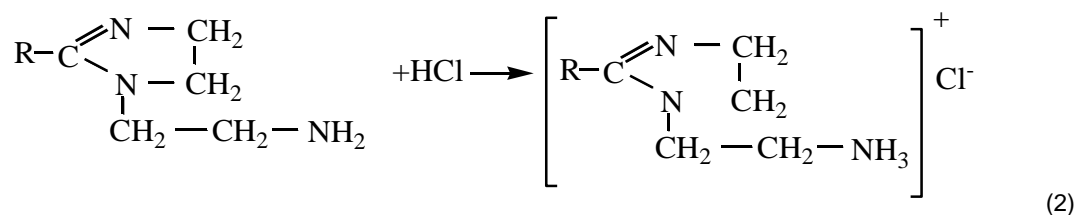


Fig. 2. IR-spectrum of imidazoline derivatives.

From the figure 2 it is seems that on 724 sm<sup>-1</sup> vibration C-H bond of CH<sub>2</sub> (n>4) group, on 768 sm<sup>-1</sup> vibration of C-H bond of CH<sub>2</sub> (n<4) group, on 1012, 1142, 1272 sm<sup>-1</sup> deformation vibration of C-N bond, 1455, 1375 sm<sup>-1</sup> and 2854, 2922 sm<sup>-1</sup> deformation and valence vibration of C-H bond of CH<sub>2</sub> and CH<sub>3</sub> group, 1643,1545 sm<sup>-1</sup> C=N bond of CN group and 3289 sm<sup>-1</sup> valence vibration of N-H bond of NH group.

Complexes based on the obtained imidazolines with HCl were synthesized in normal condition:



Complexes were prepared from these compounds and HCl in ratio 1:1 (example 1), 1:2 (example 2), 1:3 (example 3). 20% solution of the complexes were prepared in aqueous isopropyl alcohol.

Physical and chemical indices of the 20% solution of the HCl complexes on the basis of SNA and DETA are presented in the table 3.

**Table 3. Physical and chemical indices of the 20% solution of the HCl complexes on the basis of SNA and DETA**

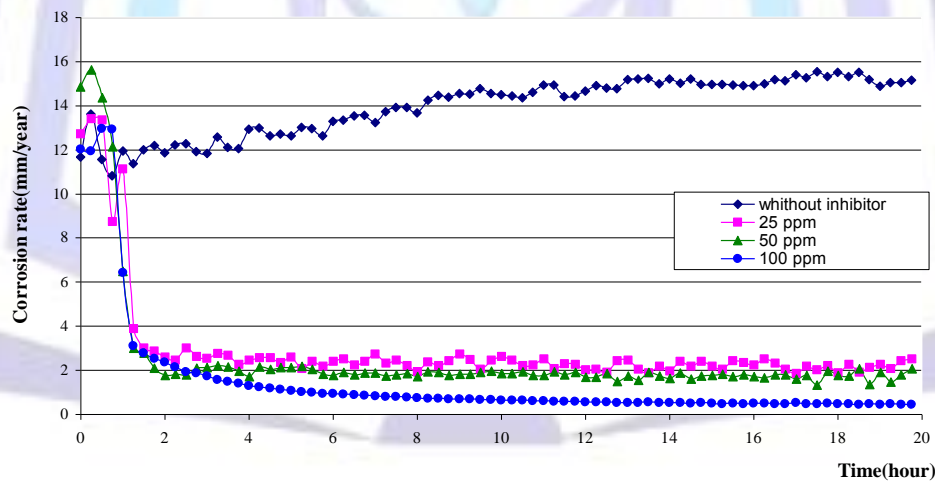
No	Solutions	Colour	Refraction coefficient $n_d^{20}$	Density, $\text{kg/sm}^3$ ; 20°	Freezing temperature, °C
<b>20% solution of the HCl complexes in ratio (1:1), (1:2) and (1:3)</b>					
1	example 1	brown	1,3820	924,6	-28
2	example 2	brown	1,3890	940,5	-33
3	example 3	brown	1,4060	952,3	-32

The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO<sub>2</sub> were studied ACM Gill AC potentiometer. The extrapolation of cathodic and anodic Tafel lines was carried out in a potential range ±100 mV with respect to corrosion potential ( $E_{corr}$ ) at scan rate of 1 mV/s. The potential of the working electrode was varied by a CoreRunning programme (Version 5.1.4.) through an ACM instrument Gill AC. The CoreRunning programme converts a corrosion current in mA/cm<sup>2</sup> to a corrosion rate in mm/year. A cylindrical carbon steel rod of the composition C1018 GRADE STEEL was used as a working electrode. Gill AC technology allows measure DC and AC

signals using standard Sequencer software. A small sweep from typically -10 mV to +10 mV at 10 mV/min around the rest potential is performed. The area of the electrode is 4,56 cm<sup>2</sup>.

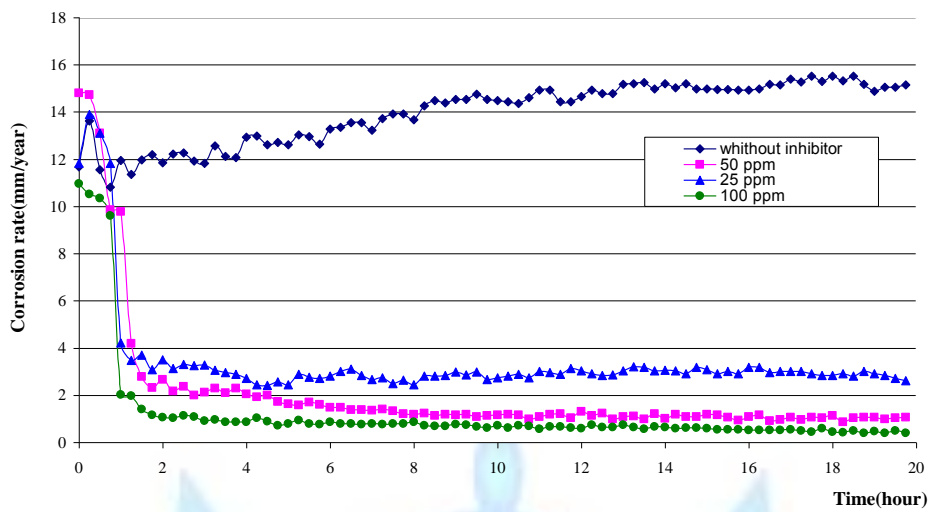
### RESULTS

Investigation was conduct in concentration 25, 50 and 100 ppm of complexes for 20 hours. In the same time corrosion of steel examples were learned without inhibitor sphere, too. The figure 3 shows the effect of example 1 on the corrosion rate of carbon steel in CO<sub>2</sub> saturated 1% NaCl solution from time at 50°C. From the graphic, it is seems that without inhibitor sphere depending corrosion ratefrom the time is increased. For the example 1 in 25 ppm concentration after 5 hours of research corrosion protection effect rose from 79,6% to 83,5% after 20 hours of research. In this example in 100 ppm concentration after 5 hours of research corrosion protection rose from 91,6% to 97,1% after 20 hours of research.



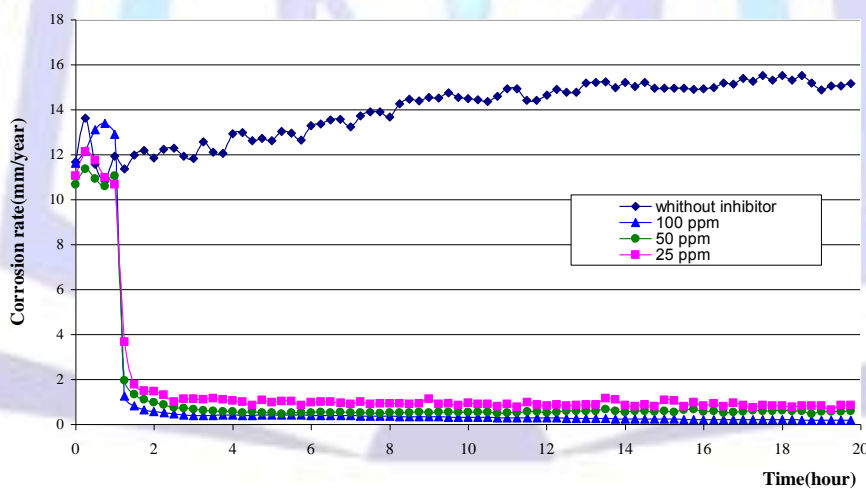
**Fig. 3. Depending corrosion rate from time for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations of example 1 at 50°C.**

In example 2 in 25 ppm concentration corrosion protection effect rose from 80,7% to 82,8% after 20 hours of research. In this example in 100 ppm concentration after 5 hours of research corrosion protection increased from 93,8% to 97,3% after 20 hours of research. The figure 4 shows the effect of example 2 on the corrosion rate of carbon steel in CO<sub>2</sub> saturated 1% NaCl solution from time at 50°C.



**Fig.4. Depending corrosion rate from time for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations of example 2 at 50 °C.**

Corrosion protection effect of example 3 in different concentration in the sphere of CO<sub>2</sub> was researched. In example 3 in 25 ppm concentration after 5 hours of research corrosion protection effect rose from 92,3% to 94,3% after 20 hours of research; in 100 ppm concentration after 5 hours of research corrosion protection increased from 96,8% to 98,8% after 20 hours of research. The figure 5 shows the effect of example 3 on the corrosion rate of carbon steel in CO<sub>2</sub> saturated 1% NaCl solution from time at 50 °C.



**Fig.5. Depending corrosion rate from time for mild steel in CO<sub>2</sub>-saturated 1% NaCl solution containing different concentrations of example 3 at 50 °C.**

Results of complexes that synthesized as inhibitor efficiency in different concentration are given in table 4.

**Table 4. Results of complexes as corrosion inhibitors**

Concentration, C, ppm	Time, hour	Example -1			Example -2			Example -3		
		Corrosion rate, $\rho$ , mm/year	Protection effect, $Z_i$ , %	Braking effect, $\gamma$	Corrosion rate, $\rho$ , mm/year	Protection effect, $Z_i$ , %	Braking effect, $\gamma$	Corrosion rate, $\rho$ , mm/year	Protection effect, $Z_i$ , %	Braking effect, $\gamma$
Without inhibitor	5	12,611	-	-	12,611	-	-	12,611	-	-
	10	14,48	-	-	14,48	-	-	14,48	-	-
	20	15,148	-	-	15,148	-	-	15,148	-	-
25	5	2,570	79,6	4,90	2,43	80,7	5,18	0,974	92,3	12,94
	10	2,601	82,0	5,56	2,65	81,7	5,46	0,947	91,2	15,29
	20	2,500	83,5	6,05	2,61	82,8	5,80	0,857	94,3	17,67
50	5	2,123	83,2	5,94	1,618	87,2	7,83	0,517	95,9	24,39
	10	1,825	87,4	7,93	1,154	92,0	12,54	0,538	96,3	26,91
	20	2,04	86,5	7,42	1,064	93,0	14,23	0,588	96,1	25,76
100	5	1,065	91,6	11,84	0,788	93,8	16,0	0,408	96,8	30,9
	10	0,617	95,7	23,46	0,721	95,0	20,08	0,313	97,8	46,26
	20	0,440	97,1	34,42	0,405	97,3	37,40	0,179	98,8	84,62

## DISCUSSION

Thus the complexes based on imidazoline and HCl in different mole ratio in low concentration protection effects rising when relative HCl is maximum. So protection effect of example 1 in 50 ppm concentration after 20 hours of research was 86,5%, for example 2 – 93%, for example 3 was 96,1%. But corrosion protection effects of examples in 100 ppm concentration after 20 hours of researching had little difference.

The mechanism of corrosion inhibition may be explained on the basis of the adsorption behaviour of the inhibitors<sup>[19]</sup>. The degree of surface coverage ( $\theta$ ) for different inhibitor concentrations was evaluated from polarization measurements by following equation:

$$\theta = \frac{I_{uninh} - I_{inh}}{I_{uninh}} \quad (3)$$

The best correlation between the experimental results and isotherm functions was obtained at high inhibitor concentrations using the Langmuir adsorption isotherm. The Langmuir isotherm is given by the following equation<sup>[20]</sup>:

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

where  $K_{ads}$  is the equilibrium constant of the inhibitor adsorption process and  $C_{inh}$  is the surfactant concentration.

The values of  $K_{ads}$  obtained from the Langmuir adsorption isotherm are listed in Table 4, together with the values of the Gibbs free energy of adsorption

( $\Delta G_{ads}^0$ ) calculated from [1].

$$K_{ads} = \frac{1}{C_{inh}} \times \frac{\theta}{1 - \theta} \quad (5)$$

$$\Delta G_{ads} = - 2.303RT \log(55.5K_{ads}) \quad (6)$$



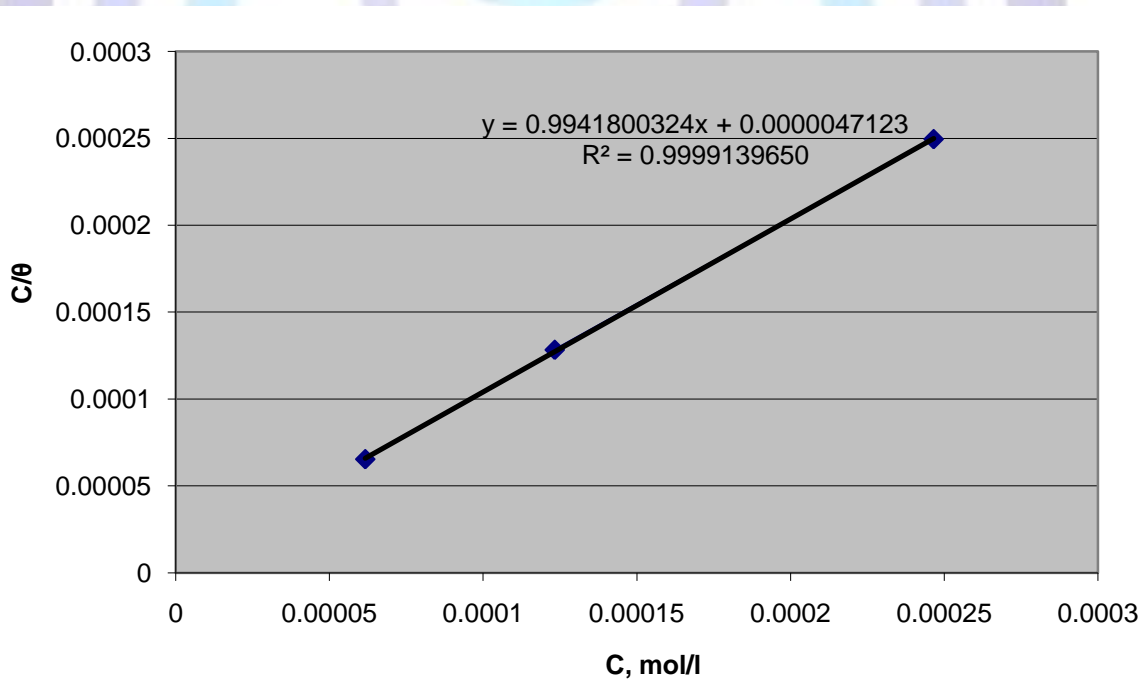
Where  $R$  is the universal gas constant,  $T$  is the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution. Thermodynamic parameters for the adsorption of the studied inhibitors (based on SPA and DETA) on mild steel electrode in  $\text{CO}_2$ -saturated 1% NaCl solution are presented in the table 5.

**Table 5. Thermodynamic parameters for the adsorption of the studied inhibitors (based on SPA and DETA) on mild steel electrode in  $\text{CO}_2$ -saturated 1% NaCl solution**

Inhibitors	Molecular weight, $M_r$	Concentration, $C$ , (mol/l)	Regression coefficients, $R^2$	$K_{ads}, M^{-1} \times 10^4$	$c/\theta$	Surface coverage, $\theta$	$\Delta G_{ads}^0$ kJ/mol $^{-1}$
Example -1	332,5	0,0003	0,9971	12,5	0,000308	0,970	-39,0
Example -2	369,0	0,00024	0,9999	14,2	0,000278	0,973	-39,3
Example -3	405,5	0,00027	0,9999	35,7	0,000249	0,988	-41,6

Generally, values of  $\Delta G_{ads}^0$  up to  $-20 \text{ kJ/mol}^{-1}$  are consistent with physisorption, while those around  $-40 \text{ kJ/mol}^{-1}$  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 [21]. In the present study, the values of  $\Delta G_{ads}^0$  obtained for studied surfactants on carbon steel in  $\text{CO}_2$ -saturated solution ranges between  $-39$  and  $-41,6 \text{ kJ/mol}^{-1}$ , which are around  $-40 \text{ kJ/mol}^{-1}$  (Table 5). These results indicate that the adsorption mechanism of complexes on carbon steel in  $\text{CO}_2$  saturated brine is typical chemisorption at the studied temperature. The high and negative values obtained for  $\Delta G_{ads}^0$  indicate that the adsorption process takes place spontaneously by strong interactions between the inhibitor and the steel surface, as was suggested by the obtained values of  $K_{ads}$ .

Langmuir adsorption isotherm ( $C_{inh}/\theta$  vs.  $C_{inh}$ ) fitting of the obtained from LPR corrosion rate data for mild steel in  $\text{CO}_2$  saturated brine containing various concentrations of the imidazoline derivatives complex based on the SPA and DETA with HCl in molar ratio 1:3 is presented in the figure 5.



**Figure 5. Langmuir adsorption isotherm ( $C_{inh}/\theta$  vs.  $C_{inh}$ ) fitting of the obtained from LPR corrosion rate data for mild steel in  $\text{CO}_2$  saturated brine containing various concentrations of the imidazoline derivatives complex based on the SPA and DETA with HCl in molar ratio 1:3.**





## CONCLUSIONS

The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO<sub>2</sub> of complexes based on imidazoline (obtained from SPA and DETA) and HCl were studied in different molar ration and the best result were shown in molar ration 1:3 (98,8% at 100 ppm). Complexes based on imidazoline and HCl in molar ration 1:3 in comparison with 1:1 and 1:2 molar ration easily exposed to chemisorption on metal surface, that's why protective film which is formed on the surface is stable. For this reason complex has a higher corrosion protection effect than others. Analysis of the obtained data show that, the inhibiting properties increase with inhibitor concentration. It was proved by Langmiur adsorption isotherm that the chemisorption process of inhibitor occur on the surface of metal. Calculated Gibbs free energy of adsorption confirm that the adsorption process takes place spontaneously.

## ACKNOWLEDGMENTS

The authors would like to thank the Institute of Petrochemical Processes of National Academy of Sciences of Azerbaijan and to the experts who have contributed towards development of the template.

## REFERENCES

- [1]. V.M.Abbasov, S.A.Mamedxanova, Hany M. Abd-El-Lateef et all. 2013. The CO<sub>2</sub> corrosion inhibition of carbon steel C1018 by some novel complex surfactants based on petroleum acids and nitrogen-containing compounds. *Advances in Materials and Corrosion*, №2, p. 26-32
- [2]. V.M. Abbasov, Hany M. Abd El-Lateef, L.I. Aliyeva et all. 2013. Evalution of new complex surfactants based on vegetable oils as corrosion inhibitors for mild steel in CO<sub>2</sub> – saturated 1.0% NaCl solutions. *Journal of materials Physics and Chemistry*, Vol. №2, p.19-26
- [3]. Fang H., Brown B.N. 2007. *NACE. Corrosion*, p. 6372
- [4]. Quraishi M.A., Khan S. 2005. "Thiadiazoles-A potential class of heterocyclic inhibitors for prevention of mild steel corrosion in hydrochloric acid solution". *Indian Journal of Chemical Technology*, v. 12, p. 576-581.
- [5]. Voloshin V.F., Skopenko V.S. Voloshin V.V. 2011. Inhibition of electrochemical corrosion of steel in environments containing hydrogen sulfide. *Visnyk of Pridneprovsk State Academy of Civil Eng. And Architecture*, № 1-2, P. 14-18
- [6]. Vagif M. Abbasov, Hany M. Abd El-Lateef, Leylufer I. Aliyeva et all. 2013. Inhibitive effect of some natural naphthenates as corrosion inhibitors on the corrosive performance of carbon steel in CO<sub>2</sub> – saturated brine. *International Journal of Scientific Research in Environmental Sciences (IJSRES)*, 1(8), p.166-178
- [7]. V.M. Abbasov, Hany M.Abd El-Lateef, L.I. Aliyeva et all. 2013. Applicability of novel anionic surfactant as a corrosion inhibitor of mild steel and for removing thin petroleum films from water surface. *American Journal of Materials Science and Engineering*. Vol.1, №2, p.18-23
- [8]. I.T. Ismayilov, Hany M.Abd El-Lateef, V.M. Abbasov et all. 2012. A novel sulfated fatty acid amides-based surfactants: synthesis and effect on the corrosion inhibition of carbon steel in CO<sub>2</sub> – saturated 1% NaCl solution. *Advances in Materials and Corrosion*, №1, p. 22-29
- [9]. V.M. Abbasov, L.H. Nuriyev, N.R. Abdullayeva, T.A. Ismayilov. (9-11 February, 2014). Prediction and Measurements of Corrosion Inhibition of Mild Steel C1018 Using Some Natural Naphthenate Surfactants in in CO<sub>2</sub>-Saturated NaCl Solution // *Egyptian Petroleum Research Institute EPRI «The 17<sup>th</sup> International Conference on Petroleum, Mineral Resources & Development»*, p.158
- [10]. V.M. Abbasov, L.I. Aliyeva, L.M. Efendiyeva. 2012. Efficiency of imidazolines on the basis of oil acids in the condition of acid corrosion of steel. *Journal "Practice Corrosion Protection"*, №2(64), p. 38-41
- [11]. Feizabadi H.S. 1997. Oxidation of Petroleum Hydrocarbon in Liquid Phase. 15<sup>th</sup> World Petroleum Congress, Beijing, China, Paper 29260
- [12]. Mal'kovskii P.A., Zainullov M.R., Minkhairov M.F. et al. 2003. Oxidation of naphthenic hydrocarbons of senomanion condensate. *Petroleum Chemistry*, 43 (1), p. 46-49
- [13]. Cirinnova V.S., Miljkovic D.A., Repic S. 1992. Synthesis of Petroleum Acids by the Catalytic Oxidation of Medium Distillates of Naphthenic Crude Oil. *Petroleum Chemistry*, 32 (6), p. 448-453
- [14]. Marei A., Fam S.A. 1969. Oxidation of Egiptian Petroleum Distillates to Naphthenic Acids. *Journal of Chemistry of the United Arab Republic*, 12 (1), p.129-136
- [15]. V.M. Abbasov, Shai-Ming Peng, L.M. Afandiyeva et all. 2009. Preparation of Naphthener Acids at Catalytic Participation of Pentanuclear Compex. *Processes of Petrochemistry and oil refining*, 10,3-4(39-40), p. 230-232
- [16]. V.M. Abbasov, L.M. Afandiyeva, L.H. Nuriyev. 2010. Oxidation of naphthenic hydrocarbons of Baku oils to Synthetic Naphthenic acids with various catalysts. *Azerbaijan Chemical Journal*, №2, p. 197-200



- [17]. Abbasov V.M., Zeynalov E.B., Afandiyeva L.M. et all. 2013. Selective Oxidation of Naphthenic-Iso-paraffinic Hydrocarbons of Diesel Fraction in the Presence of Cr-Mn Salts of Indigenous Petroleum Acids. *Processes of Petrochemistry and oil refining*, 14, №3(55), p. 183-190
- [18]. E.B. Zeynalov, V.M. Abbasov, L.M. Afandiyeva et all. 2011. Peculiarities of oxygen absorption kinetics at the oxidation of various hydrocarbons. *Reports National Academy of Sciences of Azerbaijan*, №3, p. 45-51
- [19]. Ashish Kumar Singh, Aditya Kumar Singh, Eno E. 2014. Inhibition Effect of Cefradine on Corrosion of Mild Steel in HCl Solution. *Int. J. Electrochem. Sci.*, 9 352 – 364
- [20]. W. Sun, and S. Nestic. 2008. Kinetics of Corrosion Layer Formation, Part 1. Iron Carbonate Layer in Carbon Dioxide Corrosion", *J. Corrosion*, 64, p. 334
- [21]. Z. Szklarska-Smialowska, J. Mankowski. 1978. Crevice corrosion of stainless steels in sodium chloride solution. *Corrosion Science*, Volume 18, Issue 11, p. 953-960

