



Investigation Imidazoline Derivatives Obtained from Synthetic Petroleum Acids as Corrosion Inhibitor

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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 CO₂ 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



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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 ^[1-5].

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 ^[6-10]. 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 ^[11-15]. 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 CO₂ and H₂S, 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 250-350⁰C 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 135⁰C in a sparging reactor ^[16-18]. 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 ⁰ C, g/sm ³ , d_4^{20}	0.9872
Refraction coefficient, n_D^{20}	1.4670
Boiling temperature, ⁰ C (6.65·10 ⁻⁴ mPa)	120-180
Acid number, mgKOH/g	245
Acid content, %	94

Spectrum of SPA is presented in figure 1.

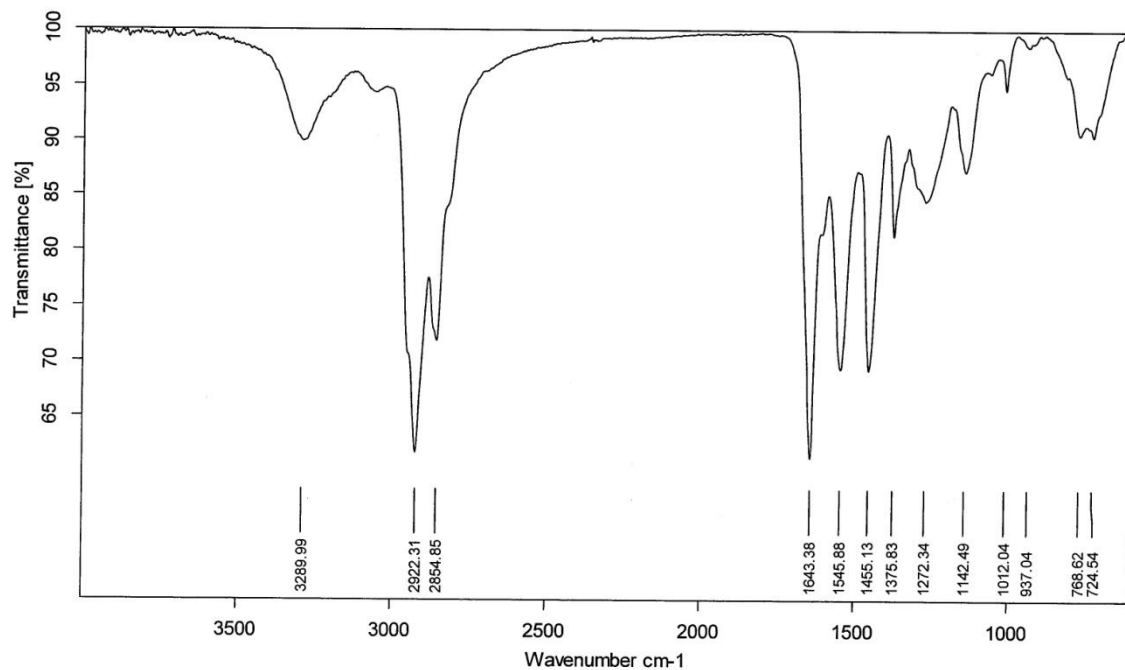
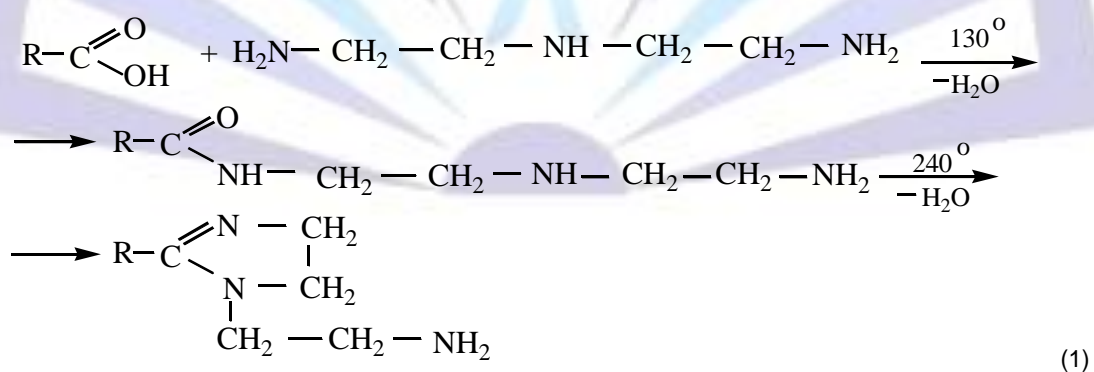


Fig. 1. IR-spectrum of SPA

From the figure1 it is seemed that on 724 cm^{-1} vibration of C-H bond of the CH_2 group, on 937 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 cm^{-1} the CH_3 group, on 1455 cm^{-1} deformation vibration of C-H bond on 1455 cm^{-1} the deformation vibration of C-H bond belongs to CH_2 group, $2855, 2923, 2951\text{ cm}^{-1}$ valence vibration of C-H bond of the CH_2 and CH_3 groups, on 1412 cm^{-1} deformation vibration, on 3342 cm^{-1} valence vibration of the OH group of acid, on 1702 cm^{-1} the group of $\text{C}=\text{O}$ of acid, on $2666, 2720\text{ cm}^{-1}$ valence vibration of the 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 ³ ; 20°	1,0473
7	Refraction coefficient, n _d ²⁰	1,5108

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

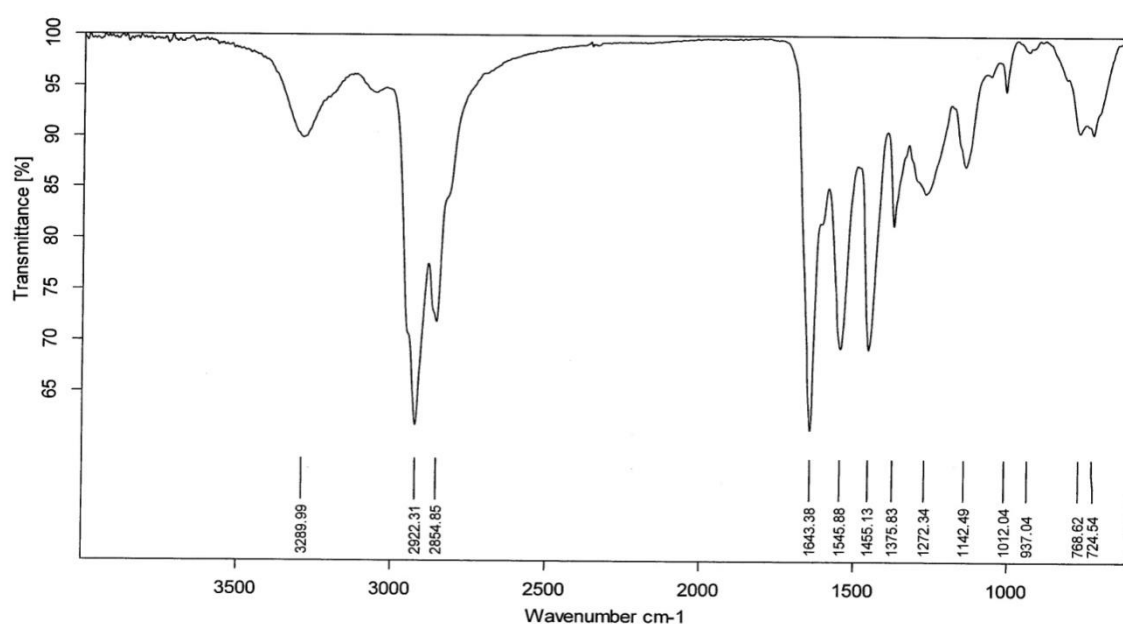
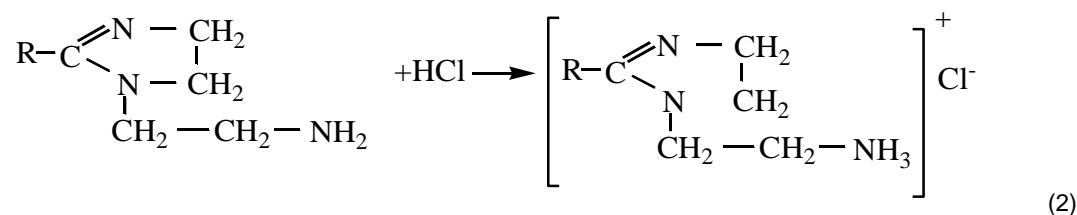


Fig. 2. IR-spectrum of imidazoline derivatives.

From the figure 2 it is seems that on 724 sm⁻¹ vibration C-H bond of CH₂ (n>4) group, on 768 sm⁻¹ vibration of C-H bond of CH₂ (n<4) group, on 1012, 1142, 1272 sm⁻¹ deformation vibration of C-N bond, 1455, 1375 sm⁻¹ and 2854, 2922 sm⁻¹ deformation and valence vibration of C-H bond of CH₂ and CH₃ group, 1643,1545 sm⁻¹ C=N bond of CN group and 3289 sm⁻¹ 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

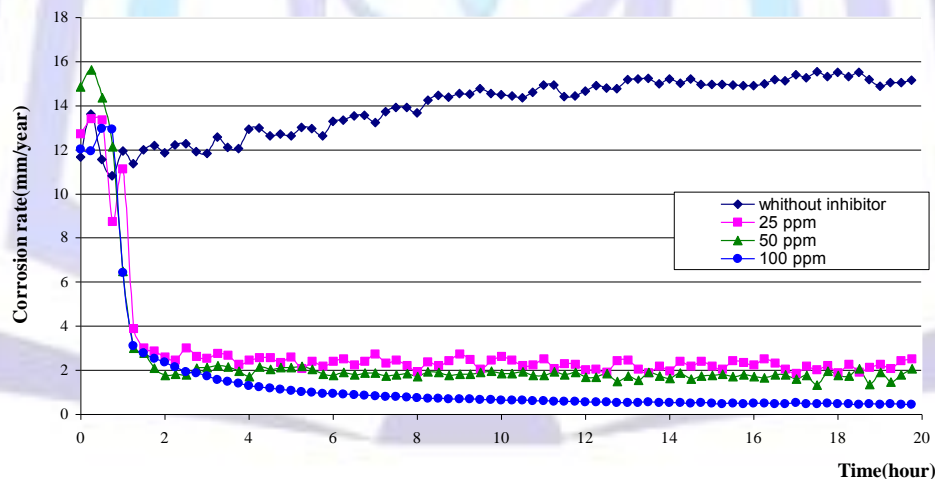
No	Solutions	Colour	Refraction coefficient n_d^{20}	Density, kg/sm^3 ; 20°	Freezing temperature, °C
20% solution of the HCl complexes in ratio (1:1), (1:2) and (1:3)					
1	example 1	brown	1,3820	924,6	-28
2	example 2	brown	1,3890	940,5	-33
3	example 3	brown	1,4060	952,3	-32

The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO_2 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^2 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 $4,56 \text{ cm}^2$.

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_2 saturated 1% NaCl solution from time at 50°C . From the graphic, it is seems that without inhibitor sphere depending corrosion rate from 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_2 -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_2 saturated 1% NaCl solution from time at 50°C .

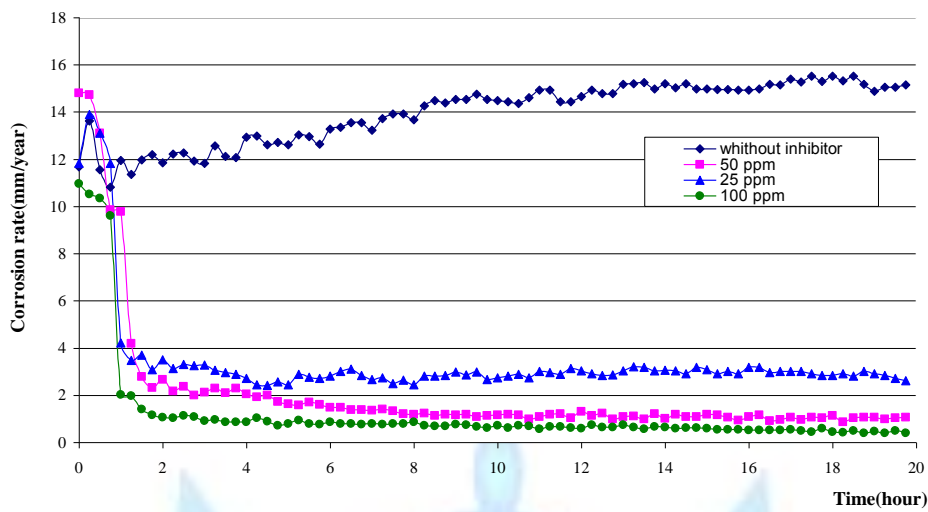


Fig.4. Depending corrosion rate from time for mild steel in CO₂-saturated 1% NaCl solution containing different concentrations of example 2 at 50 °C.

Corrosion protection effect of example 3 in different concentration in the sphere of CO₂ 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 CO₂ saturated 1% NaCl solution from time at 50 °C.

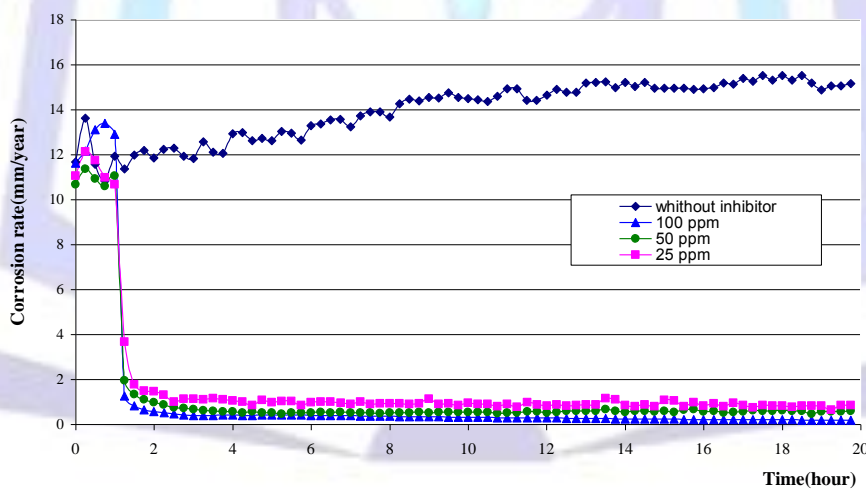


Fig.5. Depending corrosion rate from time for mild steel in CO₂-saturated 1% NaCl solution containing different concentrations of example 3 at 50 °C.

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, ρ , mm/year	Protection effect, Z_i , %	Braking effect, γ	Corrosion rate, ρ , mm/year	Protection effect, Z_i , %	Braking effect, γ	Corrosion rate, ρ , mm/year	Protection effect, Z_i , %	Braking effect, γ
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^[19]. The degree of surface coverage (θ) 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^[20]:

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

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

(ΔG_{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 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 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/θ	Surface coverage, θ	ΔG_{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 ΔG_{ads}^0 up to -20 kJ/mol^{-1} are consistent with physisorption, while those around -40 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 ΔG_{ads}^0 obtained for studied surfactants on carbon steel in CO_2 -saturated solution ranges between -39 and $-41,6 \text{ kJ/mol}^{-1}$, which are around -40 kJ/mol^{-1} (Table 5). These results indicate that the adsorption mechanism of complexes on carbon steel in CO_2 saturated brine is typical chemisorption at the studied temperature. The high and negative values obtained for ΔG_{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}/θ vs. C_{inh}) fitting of the obtained from LPR corrosion rate data for mild steel in 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.

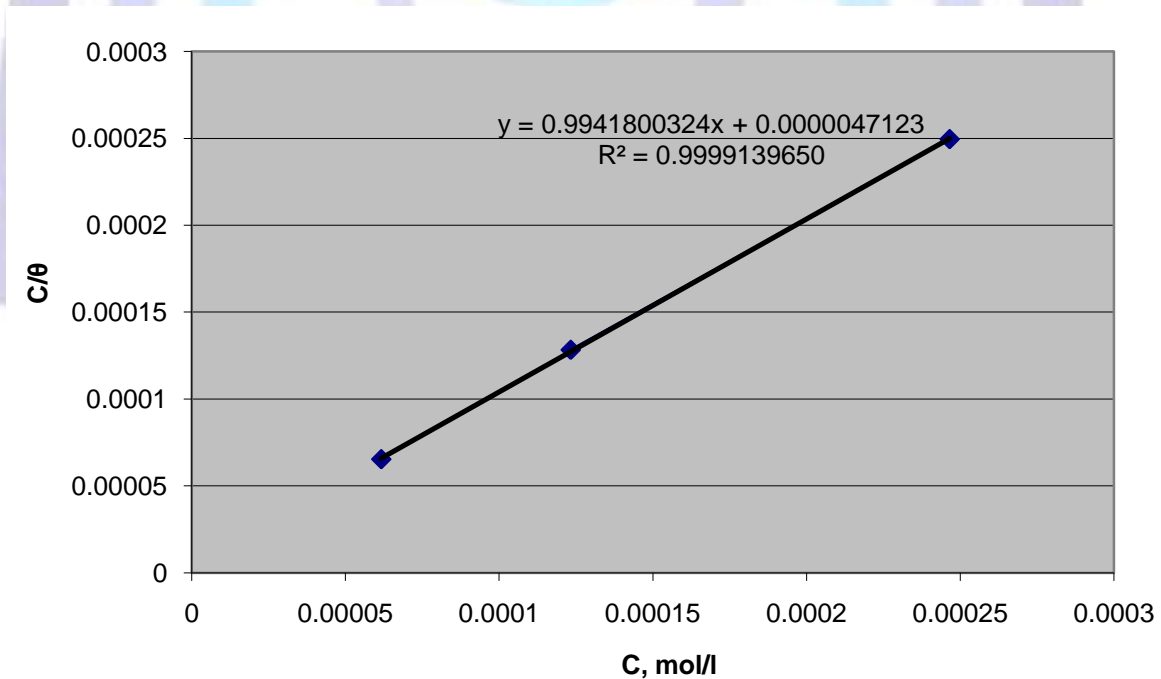


Figure 5. Langmuir adsorption isotherm (C_{inh}/θ vs. C_{inh}) fitting of the obtained from LPR corrosion rate data for mild steel in CO_2 saturated brine containing various concentrations of the imidazoline derivatives complex based on the SPA and DETA with HCl in molar ratio 1:3.



CONCLUSIONS

The kinetic effect of steel corrosion in 1% NaCl solution saturated with CO₂ 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.

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