# Investigation of the inhibitory-bactericidal effect of amidoamine-based inorganic complexes against microbiological and atmospheric corrosion

**Aghazada, Y.J.**[*], **Abbasov, V.M., Mursalov, N.I., Abdullayev, S.E., Yolchuyeva U.J.**

*Institute of Petrochemical Processes named after acad. Y.H. Mamedaliyev, Azerbaijan National Academy of Sciences, AZ1025, Khojali ave., 30 , Baku, Azerbaijan*
*[*]Corresponding author: yeqana.aqazade@mail.ru*

In the process, inorganic complexes of amidoamines obtained from the interaction of natural petroleum acid and oleic acids with diethylenetriamine have been developed and their effectiveness as inhibitor-bactericides has been investigated. The effect of the synthesized reagents on the kinetics of the corrosion process of steel and the activity of sulphate-reducing bacteria in 3% NaCl solution saturated with $CO_2$ and in the biphasic water–isopropyl alcohol medium with $H_2S$ dissolved has been analyzed. The thermodynamic and kinetic parameters of the corrosion process were calculated. The adsorption of the complexes was investigated using the Langmuir isotherm and the correlation constant was determined. State of the metal surface was investigated by SEM method in $CO_2$ and $H_2S$ media, with and without inhibitors, and the metal surface contact of complexes was studied by computer molecular simulation.

**Keywords:** corrosion, inhibitor, bactericide, adsorption, amidoamine.

## INTRODUCTION

In fact, corrosion control is an imperative concern in terms of application and it has been experienced that the use of the inhibitors is required, acting as a barrier to moderate the aggressiveness of the environments against the corrosion attack[1]. As it is known in the literature, the action mechanism of inhibitors in metal corrosion protection is explained by the theory of adsorption and coating on the metal surface[2]. According to this theory, the inhibitor first adsorbs onto the metal surface, then forms a chemical compound with the metal, and the resulting compound covers the protected metal surface in a thin layer[3, 4].

Compounds containing functional electronegative groups and triple or conjugated double-bond electrons are effectively used as corrosion inhibitors. The inhibitory ability of an organic inhibitor is enhanced by the presence of hetero-adsorption active centers in the molecule such as sulfur (S), nitrogen (N) and oxygen (O)[5, 6]. Inhibitor efficacy depends on factors such as molecule size, adsorption type, metal complex formation, and adsorption ability of the inhibitor on the metal surface[7, 8]. Previous studies show that adsorption on the surface of mild steel is mainly determined by physicochemical parameters such as the flatness of the inhibitor system, the presence of multiple active adsorption centers with unpaired or π orbital, the electron density of the donor atom and the molecule size. Therefore, the choice of an effective inhibitor is based on the structure of the inhibitor, its defense mechanism, and its ability of donating electron[9, 10].

Microbiological corrosion caused by sulphate-reducing bacteria (SRB) results in the loss of the quality of equipment used in oil fields. $H_2S$, formed as a result of the SRB bioactivity, contributes to the rapid corrosion process by dissolving in oil and produced water[11–13]. The main purpose of the study conducted against this problem is to investigate the inhibitory-bactericidal properties of the prepared complexes. To this end, amidoamines were obtained from the interaction of natural petroleum acids (NPA) and oleic acid with diethylenetriamine (DETA), the solutions of their inorganic complexes in solvent were prepared, and their anti-corrosive and anti-SRB inhibitory-bactericidal properties on mild steel sheets in $CO_2$ and $H_2S$ media have been investigated[14, 15]. Water–isopropyl alcohol (1:1) was selected for the complexes, with different solvents being tested, taking into account their economic efficiency and ability to dissolve.

The effect of the synthesized reagents on the kinetics of the corrosion process of mild steel in 3% NaCl solution saturated with $CO_2$ and in the biphasic water–isopropyl alcohol medium with $H_2S$ dissolved has been analyzed.

The dependence of bactericidal effects of complexes on the nature of inorganic anion, the relationship between their corrosion protection effects and their molecular structures has been established.

## EXPERIMENTAL PROCEDURE

### Preparation of materials

The experiments were carried out with DC01 (CR4) mild steel specimens. The main chemical composition (wt%) of mild steel is listed as follows: C%~0.07; Si%~0.01; Mn%~0.2–0.35; Ni%~0.06; S%~0.025; P%~0.02; Cr%~0.03; Al%~0.02-0.07; Cu%~0.06; Fe balance. The test sample size was 30 x 15 x 2mm. To have a clean surface state is essential, in terms of having a good reproducibility of measurements. The mild steel sheets were prepared, degreased and cleaned with deionized water and alcohol, then weighed by an analytical balance (0.0001 g)[16].

The complexes were tested on the "ACM Instruments GILL AC-1197" potentiometer equipped with the "ACM Instruments Version 5" software. Potentiometer's electrodes are made of 080A15 grade steel.

### Preparation of inhibitor

The present study was undertaken to assess the corrosion inhibition effect of, ICA (inorganic complexes of amidoamines) for mild steel in 3% NaCl solution using chemical and electrochemical techniques[17, 18].

In the synthesis of amidoamines, both oleic acid and –in NPA-based experiments–diethylenetriamine from polyamines were used. The NPA which is used in the

process has been obtained by the dearomatization of the Azerbaijan kerosene and diesel fractions with the boiling range of 220–340ºC. The dearomatization process has been operated with the extraction method. N-methyl pyrrolidone has been used as an extract. The physical and chemical properties of the fraction which is obtained from the extraction process were like this: $\rho_4^{20}$ = 0,8294 g/cm³; $n_d^{20}$ = 1,4677; $M_B$ = 187; freezing point = –51ºC; boiling point = 220–340n C, kinematic viscosity at 20 n C ~5.52 mm²/sec, total sulfur content~ 0,03%, the amount of aromatic hydrocarbos ~1%.

The reaction of obtaining amidoamine in a 1:1 ratio of NPA and diethylenetriamine was carried out at 140ºC with intensive stirring for 10.8 x 10³ – 126 x 10³ sec. To study the effect of organic cation and inorganic anion of complex on the bactericidal and inhibitory effects, hydrochloric (HCl), nitric ($HNO_3$) and phosphoric ($H_3PO_4$) acids were selected for the synthesis of inorganic complexes. The reaction of acid and amidoamine used in the preparation of inorganic complexes in a ratio of 1:1mol is exothermic, during the process the acids react with aminogroups in amidoamine at room temperature. The efficacy of the solutions of obtained complexes at different concentrations in the water–isopropyl alcohol (1:1) medium as inhibitor-bactericides was investigated[19–21]. Various substances were tested as solvents, and isopropyl alcohol was selected both for its ability to dissolve and its availability of industrial production in Azerbaijan.

The basic physicochemical parameters of the prepared solutions are given in Table 1.

The effect of corrosion kinetics of mild steel on 3% NaCl solution that contains ICA in $CO_2$ saturated water was investigated.

Inspection of hydrogen-sulfide corrosion protection was performed as follows. After 15 days of observation, the bactericidal effect of the reagents is determined based on the calculation of $H_2S$ amount produced. Distilled water is saturated with hydrogen sulfide up to 500 mg/l concentration. The water saturated with hydrogen sulfide is then mixed with kerosene in a ratio of 9:1 to create a two-phase system. An emulsion is obtained by continuous mixing of hydrogen-sulfide-water and kerosene mixture with a magnetic stirrer. Purified sheets are stored in $H_2S$ corrosion media for five hours by hanging with special hooks. The rate of corrosion is measured with the gravimetric method according to the loss in the mass of three sheets. First, the rate of corrosion in the hydrogen-sulfide medium without inhibitor addition is measured[22]. Subsequently, parallel experiments are performed with the inhibitor under the same conditions for comparison. In order to ensure the reproducibility, analyses are repeated three times.

**Weight loss measurements**

Before and after the experiment, sheets, cleaned from corrosion products are kept in a desiccator for twelve hours to obtain a constant mass. The sheets are then weighed and the metal loss is found. Corrosion rate (mg/cm² · min) based on the mass of the sheet is calculated by the following equation:

$$\vartheta = \frac{m_0 - m}{s \cdot t} \qquad (1)$$

Where m is the pre-experiment mass of the sheet, in mg; $m_1$ – mass of the sheet after the experiment, s – the surface area of the sheet, t – is the immersion time.

For the measurements of weight loss, triplicate experimentations were performed concurrently and the corrosion proportions were averaged[23].

Inhibitors affect the kinetics of electrochemical reactions by changing the rate of corrosion. To clarify the inhibitory effect, it is necessary to compare the corrosion rates of the metal in inhibitory and non-inhibitory media[24–26]. To estimate the effect of the inhibitor on the corrosion process rate at a certain concentration in the medium, value of the inhibitorization coefficient was designated (Eq. 3). Protection efficiency of inhibitor is determined by the following formula:

$$IE\% = \frac{\vartheta° - \vartheta}{\vartheta} 100 \qquad (2)$$

$$\gamma = \frac{\vartheta°}{\vartheta} \qquad (3)$$

Where *IE* is the protection efficiency of inhibitor, is the corrosion rate without inhibitor, is the corrosion rate with inhibitor, and γ is the inhibitorization coefficient.

Research with complexes is carried out at 50 ppm, 100 ppm, 150 ppm and 200 ppm.

**Effect of temperature and kinetic considerations**

Impact of electrolyte temperature on corrosion inhibition of ICA solution has also been evaluated and discussed. The correlated activation energy of corrosion, enthalpy of activation, entropy of activation, and thermodynamic parameters such as equilibrium constant, standard free energy of adsorption, and entropy of adsorption were calculated to enhance the corrosion inhibition mechanism[27–30]. Thermodynamic parameters are vital to further comprehend the adsorption process of inhibitor on steel solution interface[31]. The equilibrium adsorption constant, $K_{ads}$ is connected to the standard Gibbs free energy of adsorption ($\Delta G°_{ads}$) with the following equation:

$$K_{ads} = \frac{1}{55.5} \exp\left(-\frac{\Delta G^0_{ads}}{RT}\right) \qquad (4)$$

In the equation, $K_{ads}$ – adsorption constant, R – ideal gas constant (8.314 J · mol⁻¹K⁻¹), T – absolute temperature and $\Delta G^0_{ads}$ is the adsorption energy. The 55.5 value is the molar concentration of water in solution.

**Table 1.** Physicochemical properties of solutions of ICA

| № | Solutions of complexes | | Density of solution, gr/cm³ | Refractive index, $n_d^{20}$ | Freezing point, ºC |
|---|---|---|---|---|---|
| 1 | ICA-1 | Amidoamine (Oleic+DETA)+HCl | 1.0227 | 1.3110 | –23 |
| 2 | ICA-2 | Amidoamine (NPA+DETA)+HCl | 1.0132 | 1.3820 | –20 |
| 3 | ICA-3 | Amidoamine (NPA+DETA)+$HNO_3$ | 1.0050 | 1.3970 | –6 |
| 4 | ICA-4 | Amidoamine (NPA+DETA)+$H_3PO_4$ | 1.0350 | 1.3630 | –11 |

The effect of temperature on the corrosion behavior of mild steel in a 3% NaCl solution containing ICA was assessed in the 293–323 K temperature range. For the further illustration of the inhibitive properties of ICA and the reliance of the temperature on the corrosion rate, the activation energy-$E_a$, enthalpy of activation-$\Delta H^*$ and entropy of activation-$\Delta S^*$ were computed by Arrhenius equation and its alternative equation[32] shown as equations (5) and (6).

$$\vartheta = \frac{RT}{Nh}\exp\left(\frac{\Delta S^*}{R}\right)\exp\left(-\frac{\Delta H^*}{RT}\right) \tag{5}$$

$$\vartheta = A\exp(-E_a/RT) \tag{6}$$

where $\vartheta$ = corrosion rate, $N$ = Avogadro number, $h$ = Planck's constant, and $A$ – is the Arrhenius pre-exponential factor.

The appropriate plots for mild steel corrosion in 3% NaCl in the absence and presence of various concentrations of ICA at different temperatures are shown in Fig.1, accordingly. The calculated parameters are outlined in Table 2.

**Adsorption isotherm**

The type of the adsorption isotherm can provide further information about the features of the tested compounds. The Langmuir adsorption isotherm, commonly used in the modelling of inhibitors, was used to characterize the inhibitors' efficiency. According to this isotherm, the adsorption constant $K_{ads}$, is calculated by the following equation:

$$K_{ads}C = \frac{\theta}{1-\theta} \tag{7}$$

$$\theta = 1 - \frac{\vartheta}{\vartheta^\circ} \tag{8}$$

Here $K_{ads}$ is the adsorption constant, C is the concentration, $\theta$ is the degree of surface coverage.

To acquire the adsorption isotherm, the surface coverage degree ($\theta$) of the inhibitors should

be calculated with Langmuir adsorption isotherm. In this research, the degree of surface coverage values ($\theta$) for different concentrations of the inhibitor in 3% NaCl media have been examined from the measurements of weight loss.

**Determination of bactericidity.**

After investigating the bactericidal activity of the reagents, $S\%$ – the degree of reduction of SRB is calculated by the following formula:

$$S\% = \frac{(C - C_1)}{C} \tag{9}$$

$C$ – amount of $H_2S$ in the control test, ppm; $C_1$ – $H_2S$ content formed in reagent medium, ppm.

**Surface morphology**

The state of metal surface has been investigated by scanning electron microscopy (SEM: S-3400N HITACHI) in $CO_2$ and $H_2S$ media, both with and without inhibitors. After the corrosion of the steel was carried out in the $CO_2$ saturated medium for $72 \times 10^3$ sec at 50ºC with the presence of compounds studied, the metal surface state was magnified 100-fold[33].

Using molecular simulation (MS) and quantum modelling, a molecular model of oleic-based amidoamine has been created and its interaction with the metal surface has been studied. The modelling was done with the help of CambridgeSoft Corporation's Chem 3D Ultra and Chemcraft software[34].

**RESULTS AND DISCUSSION**

**Gravimetric method**

The inhibitive impact of the synthesized ICA for mild steel in 3% NaCl solution at 298 K was primarily explored with weight loss measurements. For $72 \times 10^3$ sec, the corrosion protection of the examined complexes in the metal sheets was tested at a temperature of 298 K and the calculated values of corrosion rate, inhibition efficacy, inhibitorization coefficient, adsorption constant and surface coverage are summarized in Table 2.

It can be seen from Table 2 that higher the value of adsorption constant ($2.92$–$3.94$ $M^{-1} \times 10^4$) the more easily is the inhibitor adsorbed on the metal surface, which means inhibitor has better inhibition performance. Apparently, the corrosion rate declined considerably with addition of these complexes compared to the blank, which could be associated with the robust adsorption of these complexes onto mild steel surface and creat-

**Table 2.** Results of $CO_2$ corrosion protection of ICA for mild steel in 3% NaCl solution at 298 K

| | C, ppm | WL, mg /cm² | $\vartheta$,(mg/ cm²min²) x 10⁻² | IE % | γ | $K_{ads}$ M⁻¹ x 10⁴ | θ |
|---|---|---|---|---|---|---|---|
| *Blank* | | 4.673 | 3.431 | – | – | | |
| ICA-1 | 50 | 2.264 | 1.822 | 46.8 | 1.9 | 3.25 | 0.468 |
| | 100 | 1.656 | 1.204 | 64.9 | 2.7 | 3.42 | 0.649 |
| | 150 | 0.982 | 0.446 | 86.9 | 7.7 | 3.81 | 0.869 |
| | 200 | 0.693 | 0.271 | 92.1 | 12.7 | 3.94 | 0.921 |
| ICA-2 | 50 | 2.322 | 1,876 | 45.4 | 1.78 | 3.19 | 0.745 |
| | 100 | 1.781 | 1,337 | 61.1 | 2.09 | 3.36 | 0.524 |
| | 150 | 1.131 | 0,661 | 74.6 | 8.9 | 3.54 | 0.807 |
| | 200 | 0.714 | 0,296 | 91.3 | 16.9 | 3.74 | 0.913 |
| ICA-3 | 50 | 2.341 | 1.923 | 43.9 | 1.78 | 2.64 | 0.439 |
| | 100 | 2.078 | 1.634 | 50.6 | 2.1 | 2.78 | 0.506 |
| | 150 | 0.811 | 0.385 | 88.7 | 8.9 | 2.89 | 0.887 |
| | 200 | 0.786 | 0.322 | 90.6 | 16.9 | 2.98 | 0.906 |
| ICA-4 | 50 | 2.395 | 1.951 | 43.1 | 1.7 | 2.29 | 0.431 |
| | 100 | 2.123 | 1.793 | 47.7 | 1.8 | 2.41 | 0.477 |
| | 150 | 0.971 | 0.585 | 82.9 | 5.9 | 2.63 | 0.829 |
| | 200 | 0.829 | 0.441 | 87.1 | 7.8 | 2.92 | 0.871 |

ing a defensive physical barrier to resist the aggressive corrosion attack[35]. It is obvious that with rising the inhibitor concentration, the efficiency of the inhibition also increased and the maximum values were found to be 87,1%, 90,6%, 91,3% and 92,1% for ICA solutions, correspondingly at 200 ppm, proposing that these inhibitors successfully inhibited the mild steel corrosion in 3% NaCl solution medium. This behavior could be ascribed to the rise in the area covered by adsorbed molecules on the mild steel surface that diminishes the direct interaction between steel and the corrosive environment. The changes in the inhibitory efficacy of ICA complexes depending on the concentration is shown in Fig. 1 for 50, 100, 150 and 200 ppm.
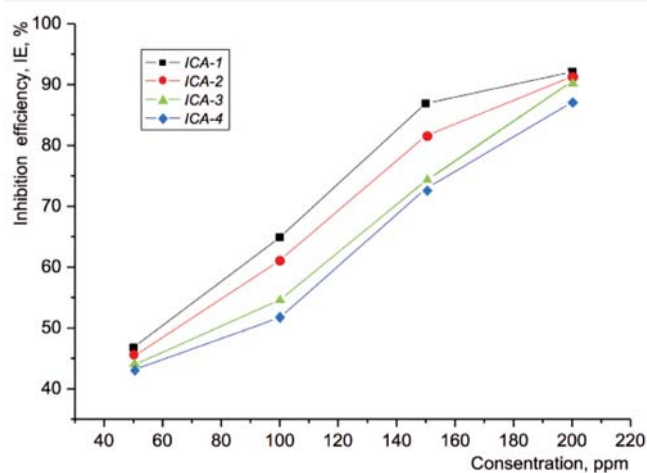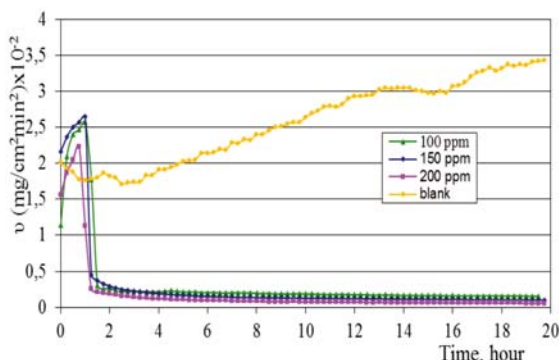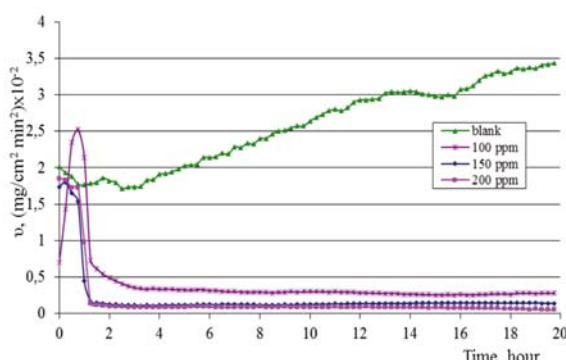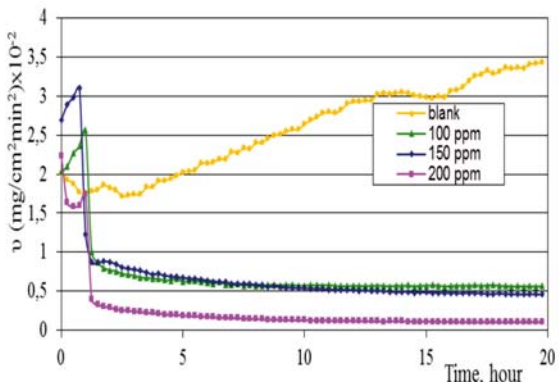


**Figure 1.** Dependence graph of the inhibitor efficiency of ICA complexes for mild steel in 3% NaCl solution at 298 K on concentration

Analysis of the results of $CO_2$ corrosion protection of various anion-containing aminoamine complexes suggests that $Cl^-$ anion containing solutions are more effective as inhibitors. Thus, ICA-2 solution at 50 ppm protects the metal sheets from corrosion at 45.4% and 91.3% at 200 ppm and ICA-1 solution, 92.1% at 200 ppm. Due to the value of inhibitorization coefficient being between 1.9–12.7, it can be concluded that these complexes are good corrosion inhibitors for mild steel in aggressive media.

The time dependence of the corrosion rate of the studied complexes for $72 \times 10^3$ sec in the corrosion protection of steel is shown in Fig. 2 (a–d).

As can be seen from the figures, the time dependence line of the corrosion rate of the studied complexes at a concentration of 100 ppm is higher. If we pay attention to the corrosion rates over time, it can be seen that the values obtained at the concentrations of 100 ppm, 150 ppm and 200 ppm are 0.2781 (mg/cm²min²) $\times 10^{-2}$, 0.1996 (mg/cm²min²) $\times 10^{-2}$ and 0.1763 (mg/cm²min²) $\times 10^{-2}$, respectively. It should be noted that during this time, the corrosion rate in an inhibitor-free environment was 2.13–3.51 (mg/cm²min²) $\times 10^{-2}$. As the concentration increases, the time dependence line of the corrosion rate lowers, indicating that the protective effect of the compounds is high.

As can be seen from the graphs analysis, all complexes have a high corrosion protection of steel sheets with regard to a non-inhibitory medium. In the course of the study, effects of the aggressive medium have not diminished the effectiveness of complexes as inhibitors over time.
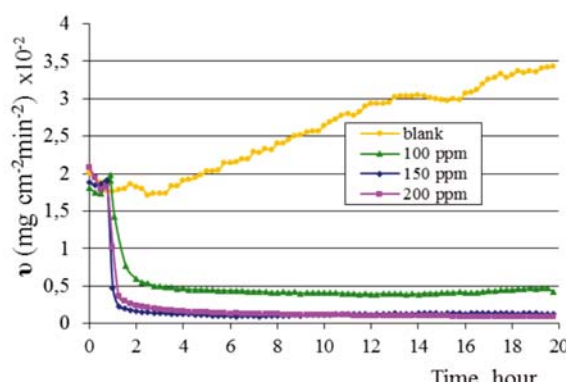


a) ICA-1 Amidoamine (Oleic+DETA) + HCl

b) ICA-2 Amidoamine (NPA+DETA) + HCl

c) ICA-3 Amidoamine (NPA+DETA) + HNO₃

d) ICA-4 Amidoamine (NPA+DETA) + H₃PO₄

**Figure 2.** Effect of ICA on the kinetics of steel corrosion in 3% NaCl solution with $CO_2$ saturated water in the absence and presence of different doses of inhibitors

## Effect of temperature

The corrosion reaction and the inhibition mechanism could be influenced by the temperature factor, so studying the effect of this parameter is crucial. In accordance with the experiments performed, the activation energy ($E_a$), enthalpy of activation ($\Delta H^0_{ads}$), entropy of activation ($\Delta S^0_{ads}$) and Gibbs energies ($\Delta G^0_{ads}$) of the complexes at 200 ppm concentrations in $CO_2$ medium were calculated. The results obtained are shown in Table 3.

Temperature impact is often used to determine physical or chemical adsorption of an inhibitor on a metal surface to inhibit corrosion. An improvement in inhibition effectiveness with increase in electrolyte temperature is often correlated with chemisorption phenomenon while the reverse implies physisorption[36–38]. To evaluate the effect of temperature on the corrosion inhibition of mild steel without and with ICA solution weight loss experiments were done at 293, 303, 313 and 323 K. Inspection of table 3 unveils that inhibition efficacies enhanced with rise in solution temperature, approving the ability of complexes to inhibit corrosion of mild steel in 3% NaCl solution at low and comparatively high temperatures and supports chemisorption that is more preferred at higher temperature for lesser kinetic energy barrier[39]. Moreover, at high temperatures, more desorption of water molecules from the surface of steel is observed, resulting in the larger surface zone available for the adsorption of ICA molecules. Also, a growth in the temperature of aqueous ICA solution raises the adsorption free energy, thus increasing the adsorption rate on the mild steel surface[40, 41].

To further obtain the thermodynamic and activation parameters, weight loss investigations were carried out at diverse temperatures ranging from 293–323 K. This phenomenon has been elucidated by the specific interaction between inhibitor molecule and mild steel. The evident activation energy ($E_a$) is computed by Arrhenius equation[42] (6).

The negative values of $\Delta G^0_{ads}$ reveals the spontaneity of the adsorption process for temperatures 293 and 323 K. The values of Gibbs energies in the range of $-20$ kJ · mol$^{-1}$ –$40$ kJ · mol$^{-1}$ are assigned for the physical mode of adsorption[43, 44]. Meantime, Gibbs energies $> -40$ kJ · mol$^{-1}$, this indicates that the adsorption agrees with the chemisorption. The negative values of $\Delta G^0_{ads}$ in the present investigation, range between $-35.61$ kJ mol$^{-1}$ to $-39.51$ kJ mol$^{-1}$, respectively, in the temperature range 293–323 K, indicating that the process of adsorption of ICA solution onto the mild steel surface involve mixed physisorption and chemisorption with predominantly chemisorption mechanism.

The negative sign of $\Delta H^0_{ads}$ exposes the exothermic process of the adsorption of complexes molecules that results in either chemisorption or physisorption while endothermic is qualified to chemisorption, The positive value of $\Delta H^0_{ads}$, displays the endothermic nature of the adsorption of the inhibitor molecules on the mild steel surface. This implies that the adsorption is chemisorption with the existence of electrostatic interaction forces between the molecules and the inhibitory mild steel surface oxidized impulsively. This mechanism occurs when the unshared electron pairs in analysed molecule interact with d-orbitals of Fe to provide protective chemisorbed film. The values of $\Delta S^0_{ads}$ in the existence of ICA solution are great and negative which agrees with an exothermic adsorption process[45]. On the other hand, the average difference value of the $E°_a–\Delta H°_a$ is 2.68 kJ · mol$^{-1}$, which is almost equal to the average value of RT (2.68 kJ · mol$^{-1}$) at the average temperature (323 K) of the domain examined. This result concurs that the corrosion process is a unimolecular reaction as illustrated by the known Eq. (10) of perfect gas:

$$E°_a - \Delta H°_a = RT \qquad (10)$$

Investigations have shown that amidoamine complexes protect the metal surface from corrosion by 43.1–92.1% at 50–200 ppm. The fact that the Gibbs energies of these compounds are at an interval of $-39.51$ to $-35.61$ kJ/mol$^{-1}$ signifies that they form a continuous coating with the surface because of chemical adsorption and the process is spontaneous[46].

The mechanism of corrosion protection of the synthesized complexes in $CO_2$ medium was investigated based on the Langmuir isotherm, and the values for the correlation constant ($R^2$) were determined (Fig. 3).

The fact that the correlation constants ($R^2$) calculated on the basis of isotherm are of values of 0.999 confirms that these substances form a layer on metal surface, and linearity of the isotherms indicates that each of the three complexes forms a monolayer.

**Table 3.** Kinetic and thermodynamic parameters of ICA

| Complexes | T (K) | $\Delta G^0_{ads}$ kJ mol$^{-1}$ | $E_a$ kJ mol$^{-1}$ | $\Delta H^0_{ads}$ kJ mol$^{-1}$ | $\Delta S^0_{ads}$ kJmol$^{-1}$K$^{-1}$ |
|---|---|---|---|---|---|
| ICA-1 | 293 | −38.06 | 5.31 | 2.88 | −0.1397 |
|  | 303 | −38.62 | 5.53 | 3.02 | −0.1374 |
|  | 313 | −39.19 | 5.72 | 3.12 | −0.1351 |
|  | 323 | −39.51 | 5.97 | 3.29 | −0.1325 |
| ICA-2 | 293 | −37.18 | 6.23 | 3.80 | −0.1398 |
|  | 303 | −37.43 | 6.47 | 3.96 | −0.1366 |
|  | 313 | −38.12 | 6.75 | 4.15 | −0.1353 |
|  | 323 | −38.47 | 7.01 | 4.33 | −0.1325 |
| ICA-3 | 293 | −36.08 | 7.71 | 5.28 | −0.1411 |
|  | 303 | −36.61 | 8.14 | 5.63 | −0.1394 |
|  | 313 | −36.98 | 8.34 | 5.74 | −0.1364 |
|  | 323 | −37.56 | 8.65 | 5.97 | −0.1347 |
| ICA-4 | 293 | −35.61 | 8.71 | 6.28 | −0.1429 |
|  | 303 | −35.93 | 8.92 | 6.41 | −0.1397 |
|  | 313 | −36.49 | 9.23 | 6.63 | −0.1377 |
|  | 323 | −37.21 | 9.44 | 6.76 | −0.1332 |
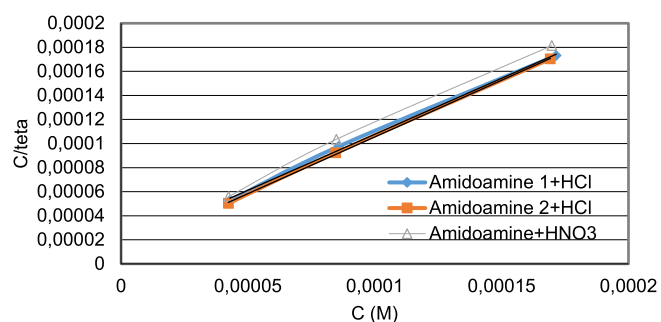
**Figure 3.** Langmuir isotherms of ICA

### 3.3. Determination of bactericidity

The bactericidal effects of solutions of the synthesized complexes in different solvents against SRB were studied[47, 48]. The extent to which the complexes prevent the activity of SRB at different concentrations is shown in Table 4.

When investigating the effects of low-concentration complexes on SRB activity in $H_2S$ medium, it was found that their biocide effects were also evident. The dependence of the corrosion rate on concentration, in 50, 100, 150, and 200 ppm and in accordance with the change in the SRB reduction rate is shown in Fig. 5.

The study of the graph shows that the solution of amidoamine(Oleic+DETA)+HCl complex at 200 ppm minimizes the bioactivity of SRB, which corresponds to the lowest corrosion rate.

Comparative analysis of the inhibitory and bactericidal properties of the solutions of complexes containing different inorganic anions in their molecules is given in Table 5.

Comparison of the results of the studies shows that while the composition of the complex molecule remains the same, the change of inorganic anion results in a change in the inhibitory-bactericidal effect. The solutions

**Table 4.** Bactericidal efficacy of complexes against SRB

| Reagents | The degree of inhibition of SRB activity in various concentrations (%) | | | |
|---|---|---|---|---|
| | 50 ppm | 100 ppm | 150 ppm | 200 ppm |
| 1. Amidoamine (Oleic+DETA)+HCl | 54.5 | 71.3 | 80.9 | 85.3 |
| 2. Amidoamine (NPA+DETA)+HCl | 55.2 | 73.5 | 78.3 | 82.9 |
| 3. Amidoamine (NPA+DETA)+HNO$_3$ | 52.7 | 69.7 | 75.1 | 80.7 |
| 4. Amidoamine (NPA+DETA)+H$_3$PO$_4$ | 49.4 | 63.6 | 70.4 | 74.8 |

It has been found that the solutions minimize the bioactivity of SRB at >75ppm. The dependence of the inhibitory-bactericidal effectiveness of amidoamine complexes against SRB in $H_2S$ medium on concentration is shown graphically below (Fig. 4):



**Figure 5.** Dependence of the inhibitory effect of corrosion protection on the concentration
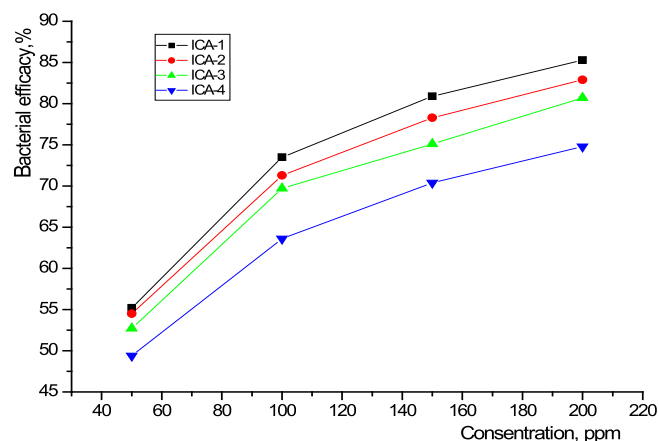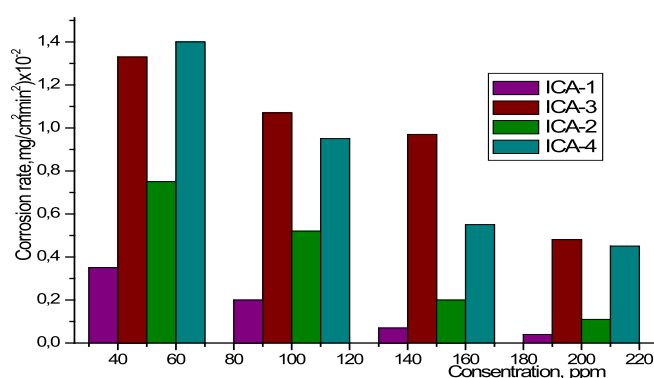


**Figure 4.** Dependence graph of the bactericidal effectiveness of ICA against SRB on concentration

As can be seen from the graph, increase in the concentration during the experiment results in increased bactericidal efficacy of complexes against SRB. Compared to other complexes, Amidoamine (Oleic+DETA)+HCl solution has been shown to be more effective as a biocide in all concentrations.

of amidoamine complexes that carry Cl$^-$ ions in their molecules display a high bactericidal character and also have effective $CO_2$ corrosion protection ability (>92.1%).

The surface state was captured by scanning electron microscopy (SEM) to study the protection mechanism of these complexes and the properties of the corrosion damage of the metal surface during corrosion processes. 100-fold magnified microphotos of metal samples were captured by SEM both with and without inhibitors (ICA-1), in $CO_2$ and $H_2S$ media, both before and after corrosion and studied. The images obtained are shown in Fig. 6 (a)–(f):

**Table 5.** Values for ICA as inhibitors and bactericides at the same concentration

| № | Name of complex solution | Concentration that provides corrosion protection, ppm | Corrosion protection effect, % | Reduction degree of SRB, % |
|---|---|---|---|---|
| 1 | Amidoamine (Oleic+DETA)+HCl | ≥200 | 92.1 | 85.3 |
| 2 | Amidoamine (NPA+DETA)+HCl | ≥ 200 | 91.3 | 82.9 |
| 3 | Amidoamine (NPA+DETA )+HNO$_3$ | ≥200 | 90.6 | 80.7 |
| 4 | Amidoamine (NPA+DETA)+H$_3$PO$_4$ | ≥200 | 87.1 | 74.8 |

a) *in the initial state*    b) *in H₂S medium, without inhibitors*    c) *in H₂S medium, with the presence of inhibitors*

d) *in the initial state*    e) *in CO₂ medium, without inhibitors*    f) *in CO₂ medium with the presence of inhibitors*
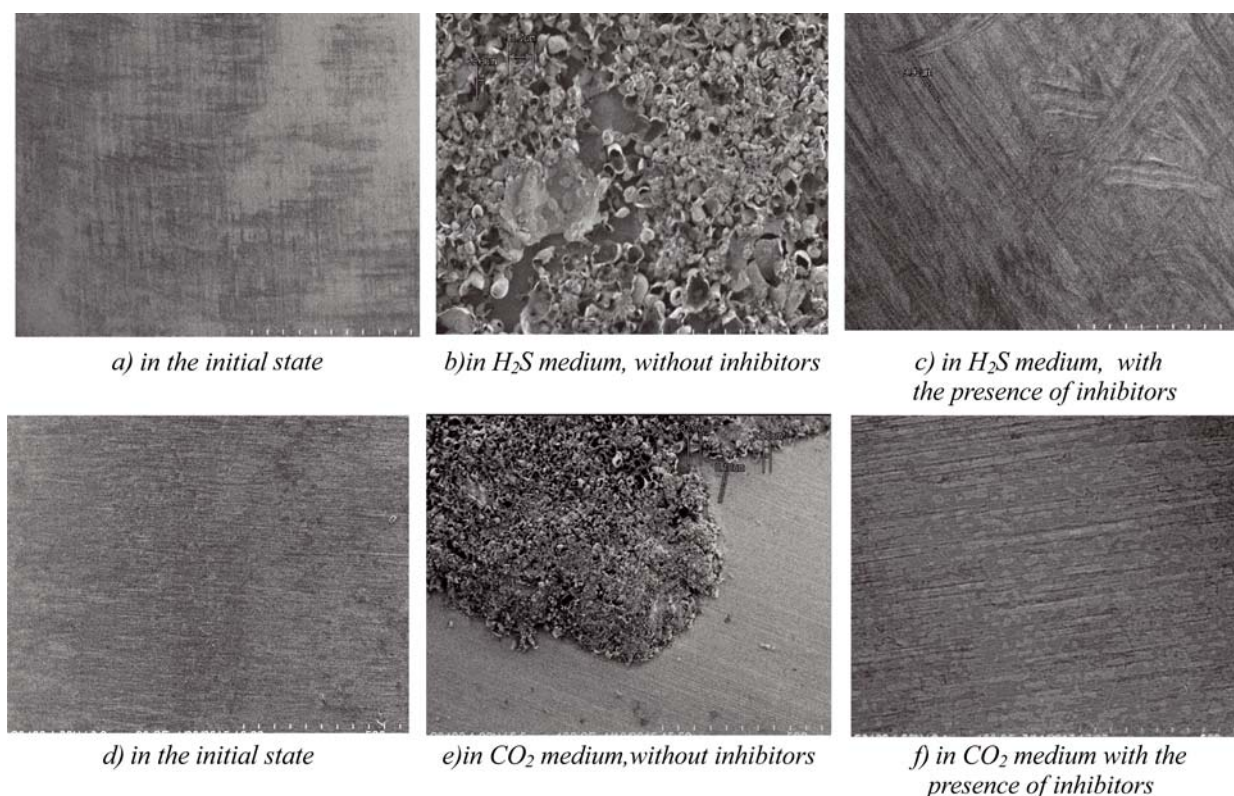
**Figure 6.** SEM Images of ICA specimens; before and after the immersion test

a) in the initial state, b) in $H_2S$ medium, after corrosion without inhibitors, and c) in $H_2S$ medium, after the experiment with the presence of inhibitors.

d) in the initial state, e) in $CO_2$ medium, after corrosion without inhibitors, and f) in $CO_2$ medium, after the experiment with the presence of inhibitors.

The image of the metal sample after corrosion without inhibitors in $H_2S$ medium reveals that the metal surface damage is local, with microphoto of the surface confirming the formation of micro-holes and wounds in the structure of coating. appearance of micro-holes and wounds in the structure of the coating. According to the image taken after the inhibitor was added to the corrosion medium, micro-holes and corrosion wounds are almost absent on the metal surface due to the application of the inhibitor to the medium.

The image of the metal sample after corrosion without inhibitors in $CO_2$ medium reveals that the carbonate layer forms unevenly and its morphology does not differ sharply at different points. On the surface of the layer, chaotically located iron carbonate crystals ranging in size from 5.76 to 19.6 microns have been formed. After corrosion of the steel was conducted in a $CO_2$ saturated medium for $72 \times 10^3$ sec with the presence of compounds studied at 50ºC, as can be seen, no corrosion traces on the metal surface are found. Thus, studies conducted by SEM prove the effectiveness of the inhibitory compounds developed.

A molecular model of one of the synthesized amidoamines (ICA-1) was created and its interaction with the metal surface was analyzed. In the oil and gas industry media, pH ranges between values of 4–6. It is known that in this interval, the stable oxide of Fe atom is $\alpha$-$Fe_2O_3$ (hematite). Therefore, the metal layer is coated with this oxide. During the analysis of

compounds with MS, it was assumed that the metal layer consisted of hematite.

By means of the program, the energy of each molecule was optimized with MM2 force field theory, and the structures of the molecules before and after contact with the iron surface are given:
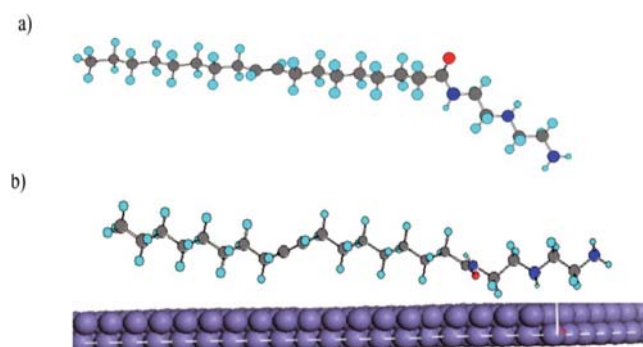


**Figure 7.** a) Modelled amidoamine molecule; b) Interaction of the amidoamine molecule with the metal surface. ○ – Hydrogen atom, ● – Carbon atom, ● – Oxygen atom, ● – Nitrogen atom

When examining the contact of the modelled molecules with the metal surface, the molecular simulation showed that the compounds approach the metal surface as in Fig.7 (b). Molecular simulation shows that in the adsorption of the molecules, owing to the double bonding of (-NH-, -NH₂) and (-C=C-), the oleic-based amidoamine compound is adsorbed onto the metal surface more horizontally, forming a layer which is able to cover more area on the metal surface. The results of the simulation corroborate the rationale that groups with double bond, π-orbital and electron pair enhance adsorption[49, 50].

## CONCLUSIONS

The following conclusions can be drawn:

– The results of the investigation show that, inorganic complexes of amidoamines are suitable as a bifunctional inhibitor-bactericide.

– The adsorption constant and the adsorption energy of the complexes were calculated and their chemisorption onto the metal surface was proved. The results of the investigation show that the inhibiting properties of the ICA depend on concentration and temperature.

– The adsorption of these inhibitors on mild steel surface was according to Langmuir adsorption isotherm. Thermodynamic parameters also revealed that the adsorption process is spontaneous.

– The results of theoretical calculation and SEM studies were found to be in good agreement with that of weight loss and electrochemical measurements. Using the molecular modelling, the structures of these compounds were investigated, and a dependence of their protective effects on their molecular structures was revealed.

– The solutions of ICA that carry $Cl^-$ ions in their molecules display a high bactericidal character (85,3%) and also have effective $CO_2$ corrosion protection ability (92.1%). Increase in the concentration during the experiment results in increased bactericidal efficacy of complexes against SRB.

– The thermodynamic parameters determined by gravimetric method, the results of SEM and MS, and the raw material base of the reagents used allow these complexes to be used as inhibitor-bactericides.

## ACKNOWLEDGMENT

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