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## **One-Pot Synthesis, Antibacterial Activity and Study the Inhibition Corrosion on Carbone Steel Alloy in Acid Media of 5-Phenyl-1,3,5- Dithiazinane & Cationic Surfactants.**

**Raneen. S. Al-Hilfi <sup>1</sup> \*, Najlaa. Z. Al-Ameri <sup>2</sup> , Mouhanad. J. Al-Asadi <sup>3</sup>**

<sup>1</sup> Chemistry department, Pure science education college, University of Basrah, Basra, Iraq. *[ranoosalim94@yahoo.com](mailto:ranoosalim94@yahoo.com)*

<sup>2</sup> Second party department, Basra oil company (BOC), Iraqi Ministry of Oil, Basra, Iraq. *[najlaa078@yahoo.com](mailto:najlaa078@yahoo.com)*

<sup>3</sup> Chemistry department, Pure science education college, University of Basrah, Basra, Iraq. *[dr.muhanned75@yahoo.com](mailto:dr.muhanned75@yahoo.com)*

## **الخالصة**

ْهَذَا البِحث عبارة عن تخليق المركبات الحلقية غير المتجانسة (5-Phenyl-1,3,5-dithiazinane) باستخدام طريقة وعاء واحد ومنشطات السطوح الكتأبونية كأملاح الأمونيوم الرباعية -5-phenyl-5) tetradecyl-1,3,5-dithiazinan-5-ium bromide and N-tetradecylbenzenaminium (bromide ، والتي تحتوي على الكبريت والنيتروجين وسلسلة هيدروكربونية في تركيب الجزيئةِ. تستخدم المر كبات المحضر ة كمثبط للتآكل مع انابيب النتر و ل المستخدمة في شر كة نفط النصر م

تم تشخيص المركبات (c ، b، a) بواسطة مطيافية GC – mass ،  $^1\mathrm{H}$  NMR ، FT - IR بواسطة مطيافية تقييم النشاط المضاد للبكتيريا للمركبات الحلقية غير المتجانسة والمنشطة للسطوح التي تم تحضير ها تجاه . Staphylococcus epidermisٔ Escherichia coli

تمت در اسة تأثير المركبات العطربة الحلقبة غير المتجانسة ومنشطات السطوح المحضرة كمثبطات للتآكل على الفو لاذ الكربوني (95 C) في حمض الهيدر وكلوريك (2 مو لار ي) يواسطة تقنية منحنيات تافل للاستقطاب. أظهرت النتائج أن كفاءة التثبيط (٪ IE) للمركبات المحصرة (c ، b، a) نزداد مع زيادة تر اكيز المثبط وكذلك مع انخفاض در جات الحر ار ة ٍ اُظهر ت منحنيات النافل تثبيطًا عالي الكفاءة للمركب (b) الذي يحتوي على حلقة غير متجانسة و ملح الأمونيوم الرباعي ، مما يتيح لهذا المركب ان يكون له تأثير مزدوجٍ مضباد للتآكل

## **Abstract**

 $\overline{\phantom{a}}$ 

 This research involves synthesis of heterocyclic compounds (5-Phenyl-1,3,5 dithiazinane) by using one-pot method and cationic surfactants as quaternary ammonium salts (5-phenyl-5-tetradecyl-1,3,5-dithiazinan-5-ium bromide and Ntetradecylbenzenaminium bromide), which contains structural sulfur, nitrogen, and hydrocarbon tail in the molecule. The synthesized compounds were used as an inhibitor of corrosion in petroleum pipelines were used by the Basra Oil Company.

The compounds (a, b, and c) were identified by  $FT - IR$  and  $^1H$  NMR spectroscopies, GC – mass spectrometry. The antibacterial activity of the heterocyclic and surfactants compounds that were prepared was been evaluated against Escherichia coli and Staphylococcus epidermis.

 The influence of heterocyclic aromatic and surfactants as corrosion inhibitors on Carbon steel (C 95) in 2 M hydrochloric acid was studied by Tafel polarization technique. The results showed that the inhibition efficiency (% IE) of the prepared compounds (a, b, c) increased with increasing inhibitor concentrations and also with a decrease in temperatures.

The Tafel curves showd the high-efficiency inhibition for compound (b) that has the heterocyclic part and quaternary ammonium salt which enables this compound have a double anti-corrosion effect.

**Keywords:** Cyclothiomethylation, formaldehyde, hydrogen sulfide, Tafel plot, Carbone steel alloy.

## **1. Introduction**

One-pot thiomethylation of amines with the  $CH_2O-H_2S$  system, offers a straightforward and economical synthetic method that takes place in a modest environment without polluting side products, is the most convenient and environmentally desirable method of synthesis of saturated N, S-containing heterocycles. Antibacterial, herbicidal, fungicidal, insecticidal, acaricidal, and antimicrobial activity have been discovered in several heterocycles that can be synthesized this way  $1-5$ .

In recent years, there has been a lot of interest in saturated sulfur- and nitrogencontaining heterocycles, which have a lot of unshared electron pairs on the heteroatoms and have a lot of complexing activity with metal cations, so they can be used as corrosion inhibitors in the industry  $6-9$ .

 The aime of this study is to discover the ideal conditions for synthesis using an example of cyclothiomethylation reactions and the effect of temperature, as well as the order in which the chemicals are added. To make this method more useful, researchers made more nitrogen-and sulfur-containing hetrocycles and compared their ability to stop corrosion and kill bacteria to that of derivatives of surfactants.

 As well as to study the influence of 5-Phenyl-1,3,5-Dithiazinane (a), 5-Phenyl-5-Tetradecyl-1,3,5-Dithiazinan-5-ium Bromide (b), and N-Tetra decyl Benzenaminium Bromide (c), as a corrosion inhibitor for carbon steel (C 95) in 2 M hydrochloric acid using Tafel polarization method. Further, the study also focuses on the effectiveness of the prepared compounds as antibacterial (Escherichia coli and Staphylococcus epidermis).

## **2. Experimental part**

## **2.1.Materials and Methods**

 All commercially available compounds involved in the synthesis have a purity of at least 97%: Aniline ( $C_6H_5NH_2$ , Sigma Aldrich), Acetone ((CH<sub>3</sub>)<sub>2</sub>CO, Scharlau), 37% Hydrochloric acid (HCl, B.D.H), 37% aqueous Formaldehyde solution (CH<sub>2</sub>O, Merck), 1-bromotetradecan (C<sub>14</sub>H<sub>29</sub>Br, Scharlau), Ethanol (C<sub>2</sub>H<sub>5</sub>OH, B.D.H), sodium sulfide (Na<sub>2</sub>S, Scharlau), Dichloromethane (CH<sub>2</sub>Cl<sub>2</sub>, B.D.H), Potassium hydroxide (KOH, B.D.H).

The reaction products were identified using  $H$  NMR spectra acquired on spectrometers (Bruker Avance 400 MHz), using internal standard TMS and DMSO-d6 a solvent. FT-IR spectra were recorded on a (Shimadzu - 84005 FT-IR spectrometer), in the range of  $400-4000$  cm<sup>-1</sup> by using KBr pellets. The corrosion rate was measured using the electrochemical method (Bank Eieiktronkik Intelligent Controls Type M lab 200(2007)). The melting point was determined by (Thermo scientific). GC- mass spectra were collected using a (5977 A MSD, Agilent 7890B GC) device (70 eV), Carrier gas helium and temperature program that increased: from 40 °C to 300 °C at a rate of 10 deg./min. Individuality and purity of synthesized compounds were controlled using TLC on Silufol UV-254 plates;  $I_2$ was used as a developer. Electrochemical measurements by Tafel polarization were carried out using (Bank Eieiktronkik Intelligent Controls/ Type MLab 200).

The Carbon steel C 95 cuts into  $5 \times 2 \times 0.3$  cm for length, width, and thickness respectively, SiC (grade 140, 320) was used to polish the carbon steel, which was then cleaned with distilled water, acetone, and ultimately dried in a desiccator.

## **Synthesis of 5-Phenyl-1,3,5-Dithiazinane (a)**

The synthesis was carried out in two steps:

**The First step:** In a three-neck flask were added formaldehyde (37 % aqueous solution, 0.3 mol, 24.3 mL) was added to ethanol (50 mL), then bubbled hydrogen sulfide (0.2 mole) with stirring for 30 min at room temperature  $1, 10, 11$ .

**The second step:** is to dissolve Aniline (0.1 moles, 9.1 mL) was dissolved in Ethanol (50 mL), then added it dropwise to a water solution of formaldehyde (37%) saturated with the hydrogen sulfide in the first step with stirring, the reagents ratio Aniline–H<sub>2</sub>S–CH<sub>2</sub>O (1:2:3), and finally reflux the mixture for 48 h at 75 °C. Then formed precipitate was filtered, recrystallized with hot Ethanol to give the target product **a**: Yield (40%, 1.8 g.) as a brown crystal, m.p. 150°C, as shown in (Scheme 1)<sup>2, 12, 13</sup>.

#### **Synthesis of 5-Phenyl-5-Tetradecyl-1,3,5-Dithiazinan-5-Ium Bromide (b)**

In a beaker was dissolved (0.02 mole, 4g.) of compound (a) was dissolved with (20 mL) ethanol, then added to it 1-Bromotetradecan (0.02 mole, 6mL). The mixture was stirrer on a magnetic at room temperature for 24 hours. Then a precipitate formed that was filtered, washed twice times with diisopropyl ether, and dried in the open air to give the target product **b**: yield (37%, 1.5 g) as a brown crystal, m.p.  $180^{\circ}$ C, as shown in (Scheme 1)<sup>13</sup>.

#### **Synthesis of N-Tetra Decyl Benzenaminium Bromide (c)**

In a beaker (0.005 moles, 4.6 mL) was dissolved in Aniline with (20 mL) ethanol, then added to it 1-Bromotetradecan (0.05 mole, 14.9 mL). The mixture was stirred on a magnetic stirrer at room temperature for 24 hours. Then the formed a precipitate that was filtered, washed twice with diisopropyl ether, and dried in the open air. to yield the target product **b**: yield (53%, 2.0 g) as a black liquid, (Scheme 1)  $^{13, 14}$ .



## **Scheme 1: schematic description for synthesis of compounds a,b and c**

#### **3. Results and Discussion**

#### **Characterization of the Synthesized Compounds (a, b, and c)**

**Compound (a):** FT-IR spectrum (v cm<sup>-1</sup>): (C-S) 636.51, (C=C)1616.35, (C-N) 1255.66, (C-H) Stretching aliphatic 2841.15 and 2902.87, (C-H) Stretching aromatic 3016.67. <sup>1</sup>H NMR spectrum (DMSO-*d*6), δ, ppm: 3.61 (s,2H, S-**CH2**-S); 4.08 (s,4H, N-CH<sub>2</sub>-S); 6.55 – 6.96(m, 5H, Ph-H). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 197.1  $[M]^{\dagger}$ ; 150.0  $[C_8H_8NS]^{\dagger}$ ; 136.0  $[C_7H_6NS]^{\dagger}$ ; 106.1  $[C_7H_8N]^{\dagger}$ ; 94.1  $[C_6H_8N]$ <sup>+</sup>; 77.1 [C<sub>6</sub>H<sub>5</sub>]<sup>+</sup> as shown in Figure 1<sup>2, 4, 8, 13</sup> 2, 4, 8, 13



#### **Figure 1: FTIR Spectrum of the Synthesized (a) Heterocyclic Compound.**

**Compound (b):** FT-IR spectrum (v cm<sup>-1</sup>): (C-S) 623.01; (C=C)1616.35; (C-N) 1255.66; (C-H) Stretching aliphatic 2924.09 and 2852.72; (C-H) Stretching aromatic 3234.62. <sup>1</sup>H NMR spectrum (DMSO-*d*6), δ, ppm: 0.86 (t, 3H, (CH2)12**CH3**); 1.25 (m, 24H, **(CH2)12**CH3); 3.35 (t, 2H, N-**CH2**(CH2)12CH3); 3.60 (s, 2H, S-**CH2**-S); 4.02 (s,4H, N-**CH2**-S); 6.83 – 6.90 (m, 5H, Ph-**H**). Mass spectrum,  $m/z$  ( $I_{rel}$ , %): 394.3 [M]<sup>+</sup>; 211.1 [C<sub>10</sub>H<sub>13</sub>NS<sub>2</sub>]<sup>+</sup>; 180.1 [C<sub>10</sub>H<sub>14</sub>NS]<sup>+</sup>; 106  $[C_7H_8N]^+$  as shown in Figure 2<sup>1, 2, 4, 11</sup>.



**Figure 2: FTIR Spectrum of the Synthesized (b) Heterocyclic Compound.**

*Compound (c)*: FT-IR spectrum ( $v$  cm<sup>-1</sup>): (N-H) bending 3415.93 and 3479.58, (C=C) 1616.35, (C-N) 1249.87, (C-H) Stretching aliphatic 2922.16 and 2852.72, (C-H) Stretching aromatic 3039.81. <sup>1</sup>H NMR spectrum (DMSO-*d*6), δ, ppm: 0.86 (t, 3H, (-CH2)12**CH3**); 1.24 (m, 24H, **(-CH2)12**CH3); 3.26 (t, 2H, -N-**CH2**); 3.52 (s, 2H, -**NH2**); 7.36 – 7.53 (m,5H, Ph-**H**). Mass spectrum, *m/z* (*I*rel, %): 289.3 [M]<sup>+</sup> ; 118.1  $\overline{[C_8H_8N]}$ <sup>+</sup>; 107.1  $\overline{[C_7H_9N]}$ <sup>+</sup>; 93.1  $\overline{[C_6H_7N]}$ <sup>+</sup> as shown in Figure 3<sup>14</sup>.



**Figure 3: FTIR Spectrum of the Synthesized (c) Heterocyclic Compound.**

#### **Anticorrosion studies of 5-Phenyl-1,3,5-Dithiazinane (a), 5-Phenyl-5- Tetradecyl-1,3,5-Dithiazinan-5-ium Bromide (b), and N-Tetra Decyl Benzenaminium Bromide (c):**

The properties of the prepared compounds (a, b, and c) as corrosion inhibitors were investigated using carbon steel alloy type C-95, which have the chemical composition shown in (Table 1).

## **Table 1. Components of the alloy (C -95)**



 The effectiveness of the prepared compounds (a, b, and c) as corrosion inhibitors for carbon steel was investigated using the Tafel extrapolation technique in an acidic condition of an aqueous solution of (2 M HCl) and at temperatures (298, 323 K) in the absence and presence of inhibitors, at concentrations of  $(1x10^{-1})$  $3, 5x10^{-3}, 1x10^{-4}, 5x10^{-4})$  M.

 Tafel curves gave values of different electrochemical parameters for corrosion current density ( $I_{\text{corr}}$ ), open circuit potential ( $E_{\text{corr}}$ ), cathodic ( $\beta$ c), and anodic ( $\beta$ a) Tafel slopes, the results are listed in Tables 2 and 3.

The value of the corrosion potential  $(E_{corr})$  of the utilized inhibitor compared to the value of the corrosion potential of the corrosive medium without the inhibitor helps explain the behaviour of the polarization curve and determine which one of the two reactions is dominant. When its value exceeds (80 mV), the inhibitor is either cathodic or anodic; However, when the amount of change in corrosion potential values is less than (50 mV), the inhibitors are of the mixed action type, which means when the inhibitor is added to the acidic solution, it slows down the anodic reaction and the release of hydrogen gas when the cathode reacts  $15-17$ .

 When different concentrations of inhibitors are added, the shape of the Tafel curve does not change much, as it tends to reduce the interaction on the anode and cathode electrodes almost equally. This indicates that the inhibitors are of the double type, as the inhibitors affect the anodic and cathodic interactions with almost the same effect as shown in Figures 1 to  $6^{16, 18}$ .

 The percentage of inhibition efficiency and the area of the part covered by the inhibitor ( $\Theta$ ) were calculated using the following "Eq. (1)" <sup>19</sup>.

$$
\% \text{ IE} = \left(\frac{\text{1}^{\circ} \text{corr}-\text{Icorr}}{\text{1}^{\circ} \text{corr}}\right) \times 100 \dots \dots (1)
$$

Where:  $(I_{\text{corr}})$ ,  $(I_{\text{corr}})$  Corrosion current density absences, and presences inhibitors respectively. using the following "Eq. $(2)$ ".

$$
\theta = \frac{\text{1}^{\circ}\text{corr}-\text{loor}}{\text{lcorr}} \dots \dots \dots (2)
$$

Tables 2 and 3 clearly show that the corrosion current density  $(I_{\text{corr}})$  for carbon steel was lower in the presence of inhibitors than in the absence of inhibitors and that adding inhibitors to an acidic solution in a range of concentrations reduces the corrosion current density. As shown in Fig. (1 to 6), the inhibition efficiency increases with it for each temperature, and in general, the inhibition efficiency reduces with increasing temperature for a similar concentration, probably due to desorption of the inhibitor molecule from the carbon steel surface, also due to increases in the melting of the hydrated iron (III) oxide layer (rust) when the temperature is increased from 298 K to 323 K.

 The corrosion rate (CR mpy) was calculated to a carbon steel alloy (C 95) in the acidic medium in the absence and presence of different concentrations of heterocyclic organic compounds as inhibitors and within the temperatures (298, 323 K), by the following "Eq.(3)"  $^{19}$ .

$$
CR = K \times \frac{\text{lcorr}}{\rho} \times EW \dots (3)
$$

Where **CR**: Corrosion Rate (mpy);**K**: a constant value equal to (0.1288 mpy/µA cm; I<sub>corr</sub>: Corrosion Current Density ( $\mu A/Cm^2$ ); **E.W**: Equivalent Weight (gm/mol);  $\rho$ : Alloy Density (g/cm<sup>3</sup>).

 The corrosion rate CR is rather high in the absence of inhibitors. However, rising temperatures produce an increase in the corrosion rate for one concentration of the inhibitor, as evidenced by the obtained results and displayed in Tables 2 and

 $3^{19, 20}$ . When comparing Tafel curves for corrosion of carbon steel alloy in an aqueous solution of hydrochloric acid without inhibitor and Tafel curves in the presence of inhibitors (a, b and c) in all concentrations, a decrease in corrosion current density and corrosion rate was observed, while corrosion potential increased, as a result, a positive shift happened. For the prepared compounds (a, b and c), the maximum inhibition efficiency was achieved at 298 K (67.2%, 86.8%, 66.6%) and 323 K (64.3%, 71.4%, 63.3%) in the concentration range (0.005M). From the results, compound b is more effective than a and c. The reason is that compound b combines the characteristics of compounds a and c, as it has a heterocyclic in addition to having a hydrocarbon tail, which makes it has two corrosion inhibitory properties that combine heterocyclic and surfactants, which makes it superior to the other a and  $c^{19-21}$ .

#### **4.Inhibition mechanism**

 The adsorption phenomenon can be used to explain the corrosion inhibition of various metals in acidic solutions. Because of their potential to generate both Van der Waals and covalent connections on the metal surface, the produced heterocycles compounds (a, b, and c) containing hetero rings N and S beside the hydrocarbon tails are promising corrosion inhibitors. Interaction between un protonated electron pairs of heteroatoms and vacant d- orbital of iron surface atoms. When molecules are adsorbed on the metal surface, a coordinate covalent bond may be formed by partial transference of electrons from polar atoms (N, and S) to d-orbitals of iron surface atoms. This process, called chemical adsorption (chemisorption), is slower than physical adsorption  $16, 19, 22$ .

 Furthermore, of the amphiphilic nature of surfactant molecules, the inhibitors can be adsorbed onto the carbon steel surface, obeying the Langmuir adsorption isotherm. The positive quaternary ammonium nitrogen interacts electro-statically with the bridging negatively charged (Br<sup>-</sup>) ions on the positively charged metal surface as outlined in Scheme 1, to form a protective layer that isolates the surface from contact with an aggressive medium so slowing down the steel corrosion  $14$ .

#### **Table 2. Tafel polarization parameters in the absence and presence of various concentrations of inhibitors for Carbon steel C95 in 2 M HCl, at 298 K**





## **Table 3. Tafel polarization parameters in the absence and presence of various concentrations of inhibitors for Carbon steel C95 in 2 M HCl, at 323 K**





**Figure 4: The Potentiodynamic polarization curve for C 95 alloy in (2 M HCl solution + Various concentrations of compound a) at 298 K.**



**Figure 5: The Potentiodynamic polarization curve for C 95 alloy in (2 M HCl solution + Various concentrations of compound a) at 323 K.**



**Figure 6: The Potentiodynamic polarization curve for C 95 alloy in (2 M HCl solution + Various concentrations of compound b) at 298 K.**



**Figure 7: The Potentiodynamic polarization curve for C 95 alloy in (2 M HCl solution + Various concentrations of compound b) at 323 K.**



**Figure 8: The Potentiodynamic polarization curve for C 95 alloy in (2 M HCl solution + Various concentrations of compound c) at 298 K.**





**5. Biological activity for the synthesized compounds**

 Heterocyclic compounds are biologically effective in inhibiting many different types of pathogenic bacteria, and the reason for this is the ability of their solutions to dissolve the outer cell wall, which leads to the exudation of cell fluids and causes their death  $23$ . The presence of unique functional groups within the composition of cyclic compounds such as groups  $(CS, CN, NH<sub>2</sub>)$  may lead to the formation of complexes with elements in the cell body such as copper, iron, and divalent cobalt ions needed by the bacterial cell, which leads to cell death due to its loss These items <sup>24</sup>.

 This type of corrosion is caused by bacteria present in the earth (in the formation water and crude oil) that convert some sulfur-containing oil compounds into  $(H_2S, SO_2, SO_3)$  and this, in turn, destroys metals by converting them in the presence of water to sulfurous acid, which is one of the causes corrosion  $25$ . Therefore, vigorous and continuous studies have been conducted in the field of inhibiting various types of bacteria, and because the heterocyclic compounds contain nitrogen and sulfur atoms that distinguish them for bonding with various elements, the orientation was to study the biological activity of some of the compounds prepared in this study and for two types of pathogenic bacteria, one of which is gram-negative for (Staphylococcus epidermis) and the second is Grampositive (Escherichia coli) as shown in Fig  $(10)$  and Fig.  $(11)^{24,26}$ .

 The results showed the biological effect of solutions of some compounds prepared from it at a concentration of (1000 ppm) with the bacteria under study. Compound (c) showed medium to good resistance to the growth of Escherichia coli at a concentration of (3000 μg/ml) and (9 mm) against Staphylococcus epidermis at the same concentration. The inhibitor molecules were found to pass through the cell wall of Staphylococcus epidermis through passive diffusion, whereas the presence of the peptidoglycan outer membrane in Escherichia coli may hinder the transport of chemicals into the cell. The chemical composition of the inhibitor, on the other hand, determined whether or not the inhibitor could pass through the outer membrane  $^{26}$ .

 These compounds, despite the sensitivity of the bacteria to them, do not appear to have a laboratory similar effect in the body of the organism, as what happens in the dishes is practically different in the body of the organism because the therapeutic process usually goes through complex metabolic reactions that are difficult to estimate despite the knowledge of the final results of treatment, whether negative or positive. There are factors Others interfere with the antibiotic treatment process<sup>27</sup>.



## **Figure 10: Images show effect of the synthesized compounds on growth Staphylococcus aureus**



## **Figure 11 :Images show effect of the synthesized compounds on growth Escherichia coli**

#### **6.Conclusions**

 The properties of inhibitory heterocyclic compounds on carbon steel type C95 in 2 M HCl were examined in this study. The following conclusions can be drawn from this investigation: Electrochemical measurements using Tafel polarization studies reveal that a concentration of 0.005 M offers the best efficiency to carbon steel immersed in a 2 M HCl solution, and the analyses of the results revealed that the inhibition efficiency increased as the inhibitor concentration, also it is observed that the inhibition efficiency decreases with increase in temperature in acidic medium.

 By managing both hydrogen evolution and metal dissolution, the produced compounds operate as possible inhibitors, operating as a mixed type of inhibitor. The produced inhibitor's adsorption isotherm on the metal surface follows Langmuir's adsorption isotherm.

 Furthermore, the Tafel curves show the high-efficiency inhibition was compound (b) that has the heterocyclic part and quaternary ammonium salt which makes the compound have a double anti-corrosion effect.

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## 7.References

1. Khafizova S. R, Akhmetova V. R, Kunakova R. V, Dzhemilev U. M.[2003]: Thiomethylation of aromatic amines: an efficient method for the synthesis of heterocyclic compounds, Russ Chem Bull. 52(8), p1817—1821.

2. Akhmetova V. R, Nadyrgulova G. R, Niatshina1 Z. T,.Dzhemilev U. M.[2009]: Cyclothiomethylation of primary amines with formaldehyde and hydrogen sulfide to nitrogen- and sulfur-containing heterocycles, Chem Heterocycl Compd (N Y).45(10), p1155—1176.

3. Akhmetova V. R, Niatshina Z. T, Starikova Z. A, Korzhova L. F,Ibragimov A. G.[2011] :Thiomethylation of heteroaromatic amines, Russian Journal of Organic Chemistry. 47(6), p 920–927.

4. Akhmetova V. R, Khabibullina G. R, Galimzyanova N. F, Ibragimov A. G.[2014]: One-Pot Synthesis and fungicidal activity of 2-(1,5,3-dithiazepan-3 yl) ethanol and n, n'-bis (2-hydroxyethyl) tetra thia diaza cycloalkanes, Russian Journal of Applied Chemistry. 87( 3), p294−298.

5. Bansal Raj K. [2009] : Six Membered Heterocyclic Compounds with Two Heteroatoms" in Heterocyclic Chemistry. 4th Edition.New Age International Publisher. New Delhi, India.

6. Akhmetova V. R, Khairullina R. R, Parfenova T. I, Sufiyarova, S. A,Bashkatov R. Sh, Kunakova R. V. [2011]: Synthesis and anti-inflammatory activity of 5-acyl-1,3,5-dithiazinanes. Pharmaceutical Chemistry Journal. 44(10), p534−535.

7. Akhmetova V. R, Anpilogova G. R, Khabibullina G. R, Akhmadiev N. S, Ibragimov A. G. [2014]: One-Pot synthesis of Bis-1,5,3-dithiazepanes and their sorption properties toward silver(i) and palladium (II). Russian Journal of Applied Chemistry. 87(5), p585−590.

8. Khabibullina G. R, Fedotova Е. S, Abdullin М. F, Tyumkina Т. V, Akhmetova V. R, Ibragimov A. G. [2017]: Efficient synthesis of ncarboxyalkyl-substituted dithiaza - and dioxadithiazacycloalkanes by cyclocondensation of amino acids with formaldehyde and  $\alpha$ ,ω-dithiols. Russian Journal of Organic Chemistry. 53(2), p277–281.

9. Gilchrist T. L.[1993]: Ring Synthesis" in Heterocyclic Chemistry. 2nd Edition. Pitman Publishing Ltd. London, UK.

10.Akhmetova V. R, Nadyrgulova G. R, Tyumkina T. V, Starikova Z. A, Antipin M. Yu, Kunakova R. V, Dzhemilev U. M. [2007]: Thiomethylation of amino alcohols using formaldehyde and hydrogen sulphide. Russian Journal of Organic Chemistry. 43(6), p918–925.

11.Rakhimova E. B, Ozden I. V, Ibragimov A. G. [2018]: Catalysis in the Synthesis of S, N-Heterocycles and O, N-, S, N-, and O, S, N-Macroheterocycles. Russian Journal of Organic Chemistry. 54(7), p961–986.

12. Akhmetova V. R, Khabibullina G. R, Ibragimov A. G.[2016]: Multicomponent cyclothiomethylation of phenylenediamines and 4,4' diaminodiphenyls with formaldehyde and 1,2-ethanedithiol. Russian Journal of General Chemistry. 86(7), p1130–1134.

13. Akhmetova V. R, Khairullina R. R, Nadyrgulova G. R, Kunakovab R. V, Dzhemilev U. M.[2011]: Multicomponent heterocyclization of carboxamides with H2S and CH2O. Russian Journal of Organic Chemistry. 44(2), p190−196.

14. Dingli W, Yongming L, Bo C, Lei Z.[2020]: Novel surfactants as green corrosion inhibitors for mild steel in 15% HCl: Experimental and theoretical studies. Chemical Engineering Journal. 402(12), p1−40.

15. Akhmetova V. R, Akhmadiev N. S, Zainullin R. A, Khayrullina V. R, Mescheryakova E. S, Glushkova N. A.[2020]: Synthesis, in vitro and in silico studies of inhibitory activity towards amylase of bis-azole scaffolds linked by an alkylsulfanyl chain. Can. J. Chem. 98(11), p725–735.

16. Al - Ameri N. Z. , Meften M. J.[2017]: Synthesis, characterization, and study of 5-benzyl-5-(4- benzyl-4- methylpiperazin-4-ium-l-yl) -1,3,5 dithiazinan- 5-ium as corrosion inhibitor, antibacterial, and antifungal. Ph.D dissertation. 2nd International Scientific Conference of Southern Technical University, Basra, Iraq.

17. Flitt H. J, Schweinsberg D. P. [2005]: Evaluation of corrosion rate from polarisation curves not exhibiting a Tafel region. Corrosion Science. 47(12), p3034–3052.

18. Markhali B, Naderi P, Mahdavian R, M, Sayebani M, Arman S.Y.[2013]: Electrochemical impedance spectroscopy and electrochemical noise measurements as tools to evaluate corrosion inhibition of azole compounds on stainless steel in acidic media. Corrosion Science. 75(10), p269–279.

19.Solomon M. M, Umoren S. A.[2015]: Electrochemical and gravimetric measurements of inhibition of aluminum corrosion by poly (methacrylic acid) in H2SO4 solution and synergistic effect of iodide ions. Measurement. 76(12), p104–116.

20. Liu Y, Liu Z, Xu A, Liu X. [2021]: Understanding pitting corrosion behavior of AZ91 alloy and its MAO coating in 3.5% NaCl solution by cyclic potentiodynamic polarization. Journal of Magnesium and Alloys.

21.Fouda A. S, Abd El-Maksoud S. A, El-Sayed E. H, Elbaz H. A, Abousalem A. S. [2021]: Effectiveness of some novel heterocyclic compounds as corrosion inhibitors for carbon steel in 1 M HCl using practical and theoretical methods. RSC Advances. 11(5), p19294–19309.

22. Meften M. J. [2014]: Synthesis of some new heterocyclic compounds through domino reaction, identification, and study of them as corrosion inhibitors for carbon steel alloy in acidic medium, and brine water. Ph.D. dissertation, Chemistry Department, Universityof Basra.

23. [Arabahmadi](https://chemistry-europe.onlinelibrary.wiley.com/action/doSearch?ContribAuthorRaw=Arabahmadi%2C+Raziyeh) R.[2019]: Cobalt (II) complexes derived from azo-azomethine ligands: synthesis, characterization, solvatochromic, fluorescence, thermal, electrochemical and antimicrobial properties.*Chemistry Select*. 4(17), p4883– 4891.

[24. Azam](https://pubmed.ncbi.nlm.nih.gov/?term=Azam+M&cauthor_id=29614828) M , [Al-Resayes](https://pubmed.ncbi.nlm.nih.gov/?term=Al-Resayes+SI&cauthor_id=29614828) S , [Wabaidur](https://pubmed.ncbi.nlm.nih.gov/?term=Wabaidur+SM&cauthor_id=29614828) S. M, [Altaf](https://pubmed.ncbi.nlm.nih.gov/?term=Altaf+M&cauthor_id=29614828) M , [Chaurasia](https://pubmed.ncbi.nlm.nih.gov/?term=Chaurasia+B&cauthor_id=29614828) B, [Alam](https://pubmed.ncbi.nlm.nih.gov/?term=Alam+M&cauthor_id=29614828) M , [Shukla](https://pubmed.ncbi.nlm.nih.gov/?term=Shukla+SN&cauthor_id=29614828) S. N , & [Gaur](https://pubmed.ncbi.nlm.nih.gov/?term=Gaur+P&cauthor_id=29614828) P, [Albaqami](https://pubmed.ncbi.nlm.nih.gov/?term=Albaqami+NTM&cauthor_id=29614828) N. T, [Islam](https://pubmed.ncbi.nlm.nih.gov/?term=Islam+MS&cauthor_id=29614828) M. S, [Park](https://pubmed.ncbi.nlm.nih.gov/?term=Park+S&cauthor_id=29614828) S. [2018]: Synthesis, structural characterization and antimicrobial activity of Cu (II) and Fe (III) complexes incorporating azo-azomethine ligand. *Molecules*. 4(23), p1- 13.

25. Fontana M. G, Staehle R. W. [1980]: Biological Corrosion" in *Advances in Corrosion Science and Technology*.1st Edition. New York, USA, Plenum Press.

26. [Jone Kirubavathy](https://www.sciencedirect.com/science/article/abs/pii/S002228601730950X#!) S, [Chitra](https://www.sciencedirect.com/science/article/abs/pii/S002228601730950X#!) S. [2017]: Structural, theoretical investigations and biological evaluation of Cu (II), Ni (II) and Co (II) complexes of mercaptopyrimidine Schiff bases. *[Journal of Molecular Structure](https://www.sciencedirect.com/science/journal/00222860)*.1147(11), p797–809.

27. Moghadamtousi S. Z, Kadir H. A, Hassandarvish P, Tajik H, Abubakar S, Zandi K. [2014]: A review on antibacterial, antiviral, and antifungal activity of curcumin. *BioMed Research International*. 2014(4), p1–12.