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Preparation of Heterocyclic Compounds and Their Use as Corrosion Inhibitors in the Cooling Towers of the North Refineries Company

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Abstract :

In this research, 7-Atom Heterogeneous Rings were prepared for oxazepine derivatives [M34, M38] by reacting a mole of phthalic anhydride with a mole of hydrazine and using ethanol as a solvent. The accuracy of the composition of the prepared maþterials was confirmed by measuring the physical properties, including melting point, molecular weight and color. Also, through spectroscopic measurements, including the proton nuclear magnetic resonance spectrum[1]HNMR, the carbon nuclear magnetic resonance spectrum C13-NMR, and the infrared spectrum IR, as well as types of corrosion inhibitors were prepared using Schiff bases. Corrosion inhibitors have been diagnosed by classical diagnostic methods such as checking the solubility and melting point of the reactants and then comparing them with the products.

Keywords: *Oxazepine, Schiff-Base, Corrosion Inhibitor, Cooling Water.*

تحضير المركبات الحلقية غير المتجانسة واستخدامها كمثبطات للتآكل في أبراج التبريد لشركة مصافي الشمال

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الخلاصة:

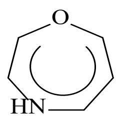
في هذا البحث، تم تحضير مركبات الاوكسابين السباعية الغير متجانسةعن طريق تفاعل مول من أنهيدريد الفثاليك مع مول من الهيدرازين واستخدام الإيثانول كمذيب. تمت دراسةقابلية المواد المحضرة للامتزاج بالماء والمذيبات الهيدروكربونية ، وتم استنتاج ان جميع هذه المواد المحضرة هي مادة ذات فعالية جيدة كمانع للتآكل.

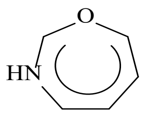
تم التأكد من دقة تركيب المواد المحضرة من خلال قياس الخواص الفيزيائية بما في ذلك درجة الانصهار والوزن الجزيئي واللون. وايضا من خلال القياسات الطيفية حيث استخدم طيف الرنين المغناطيسي النووي البروتوني وطيف الرنين المغناطيسي النووي الأشعة تحت الحمراء ، وكذلك أنواع مثبطات التآكل باستخدام قواعد شيف. تم تشخيص مثبطات التآكل من خلال طرق التشخيص التقليدية مثل التحقق من قابلية الذوبان ونقطة الانصهار للمواد المتفاعلة ثم مقارنتها مع المنتجات.

الكلمات المفتاحية: اوكسازبين ، قواعد شيف ، مانع التآكل ، مياه التبريد .

1. Introduction:

Oxazepine is heterocyclic unsaturated compounds containing five carbon atoms, one oxygen atom and one nitrogen atom [1,2]. There are three isomers of oxazepine 1,2,1,3 and 1,4-oxazepine, which determines the type of the compound. Its name in the ring is the location of the oxygen and nitrogen atoms in seven-ring and according to their location in atoms [3,4].


tetrahydro-1,4-oxazepine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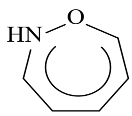
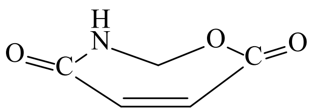
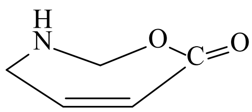

tetrahydro-1,2-oxazepine

The increase in the size of the ring makes it uneven when compared to the benzene ring [4]. As a result, the ring takes the form of a boat in the stereoscopic distribution of atoms, and this feature (uneven) was the reason for these compounds to be non-aromatic [5,6].


2,3-dihydro-1,-oxazepine-4,7-dione


3,4-dihydro-1,3-oxazepine-7-one

The seven-ring (Oxazepine) was prepared from it by direct addition of maleic anhydride or phthalic anhydride to the double bond (C=N) of hydrazone compounds to produce (1,3-oxazepine-4,7-diones) [7]. Oxazepine have very wide pharmacological applications [3], and among their chemical derivatives are heterogeneous polymers that have anti-cancer activity [8]. The compound (Amoxapine), which is a heterogeneous ring compound, contains three rings and is considered a medical drug against psychological depression, and it is a derivative of (dibenzoxazepine) [9]. Both compounds are considered (presynaptic reuptake) and (norepine phrine) inhibitors, and the metabolism of (7-hydroxy amoxapine) was found to be one of the drugs that affect the central nervous system (CNS) [10]. As for corrosion, it has an economic importance, which is to reduce material losses resulting from wasted breakdowns and sudden failure of pipes, tanks, and metal components of machinery, ships and structures [11]. It also preserves mineral resources whose supply to the world is limited, and the loss of them causes similar losses of energy and financial resources associated with the production and manufacture of metal structures [12]. The losses incurred by the industry by the army and by municipalities amount to millions of dollars annually [13].

2. Experimental:

2.1. Chemicals used: All chemicals used in this work were purchased from BDH, Aldrich and Fluka companies and were used without further purification.

2.2. Devices used: The melting points were measured using Electrothermal Melting Apparatus 9300. The FT-IR spectra were captured using a Shimadzu FT-IR 8400S spectrophotometer with a (400-4000) cm^{-1} by KBr disc. DMSO-d^6 as solvents were used to capture ^{1}H-NMR and ^{13}C-NMR spectra on Bruker instruments running at 400 MHZ.

2.3. Preparation of Oxazepine [M33-M35) [14,15]:

In a circular flask with a volume of 100 ml, (0.001mol) of hydrazone [M33-M38] is dissolved in 10 ml of ethanol, then (0.001mol) of phthalic anhydride is added to it, dissolved in (25ml) of ethanol, and the mixture reflex for (10) hours with Continuous stirring, the solutions are cooled in an ice bath, then the precipitate is separated by filtration and recrystallized from ethanol, and table (1) shows some physical properties of oxazepine [M34-53].

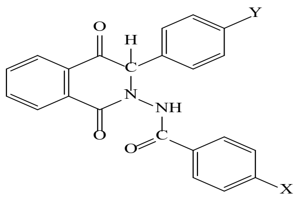


Table (1): Shows some physical properties of Oxazepine [M_{34}-$_{53}$].

Comp. No.	X	Molecular Formula	Color	M.P ^oC	Yield %
M_{34}	4-Cl	$C_{22}H_{15}ClN_2O_4$	brown	160-162	92
M_{35}	4-NH_2	$C_{22}H_{15}Cl_2N_3O_3$	yellow	168-170	93
M_{36}	2-NO_2	$C_{22}H_{14}N_3O_5$	light yellow	206-208	89
M_{37}	4-OH	$C_{22}H_{14}FN_3O_5$	light yellow	208-210	91
M_{38}	2-Cl	$C_{22}H_{15}ClN_2O_4$	orange	204-206	94

3. Results and Discussion:

Heterocyclic compounds have attracted the attention of many researchers due to their great importance from the chemical and biological aspects. As well as its use in the industrial and agricultural field. In the research, oxazepines were used as a nucleus for preparing a number of heterocyclic compounds that might have an expected biological importance, and then used as corrosion inhibitors [16,17].

3.1. Spectroscopic Interpretation (IR, ^{1}H-NMR, ^{13}C-NMR, UV, Mass) :

The IR spectrum showed a package at the frequency (1702-1705) cm^{-1} due to the stretching of the carbonyl group (C=O), and a package at the frequency (3034-3061) cm^{-1} due to (ArC-H) as well as the appearance of a package at the frequency (3551-3421) cm^{-1} belongs to the hydroxyl (OH) group [18], as in figure (1).

The ^{1}H-NMR spectrum of the compound (M37) showed a signal at the range (δ13.98ppm) belonging to the proton of hydroxyl group for carboxylic acid, as well as the signals of the aromatic protons in the range (δ7.49-8.68ppm), as in figure (2). As for the ^{13}C-NMR spectrum of the compound (M37), it showed a distinctive signal at 168ppm belonging to the carbonyl atom of the carboxylic acid, a signal at 120ppm belonging to carbon number 5, a signal at 123 ppm belonging to carbon number 9 and a signal at 126ppm belonging to carbon atom No. 6 and the appearance of multiple signals at 130 ppm belong to carbon atoms 16, 14, 12, and two signals at 138 ppm belong to carbon atoms [19], as in figure (3).

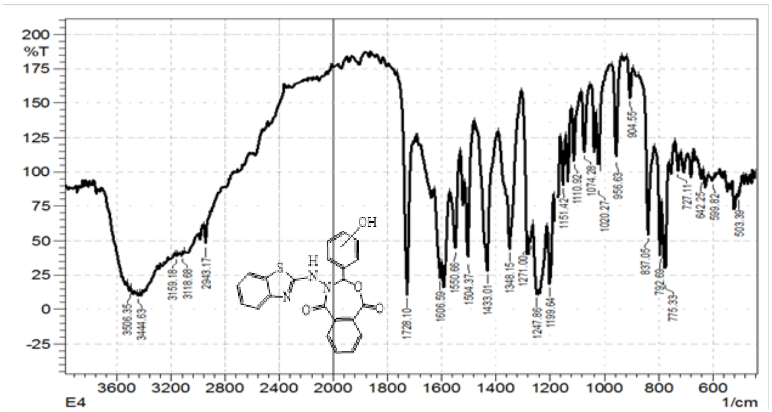


Figure 1: FTIR spectrum of M37

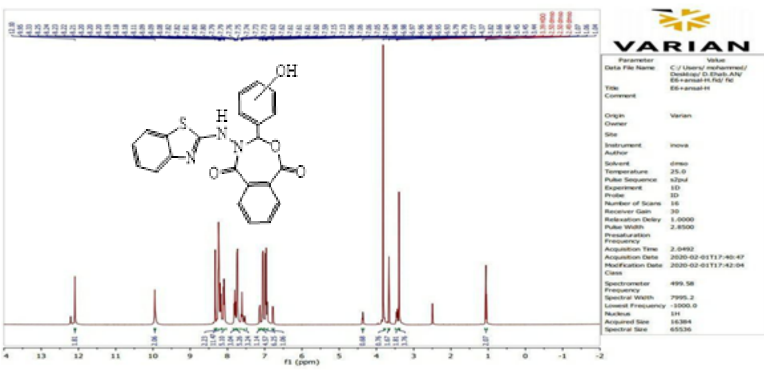


Figure 3: ^{1}H-NMR spectrum of M37

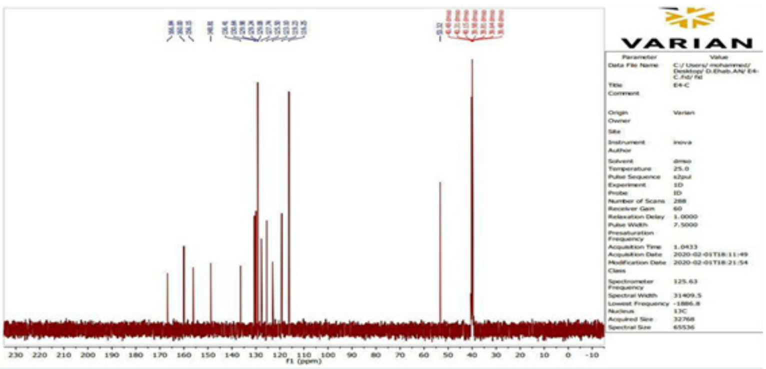


Figure 4: ^{13}C-NMR spectrum of M37

The first method: using the so-called "Potentiostat".

Tafel curves: They are the curves that are obtained to know the efficiency of inhibition after treatment, preceded by a reading to know the electrical potential difference E- a function of time and concentration for the studied oceans as a corrosive environment (acids, crude oils or salt water at a certain percentage) and with a certain PH. These curves define the corrosion rate as well as the inhibition affectivity after knowing the MPY through weight loss. This method relies on generating a voltage on the Coupon made of Low Carbon Steel by a cell consisting of three electrodes, a platinum electrode, a calumen working electrode and a reference electrode. The coupon is fixed at the working electrode and placed in a solution of 0.3N HCl with 0.2gm of corrosion inhibitor dissolved in a given volume of suitable solvent for half an hour at a temperature of 70°C. The data is processed by software via a computer connected to the device using the Tafel equation that relates voltage to current [20].

The second method: is called "weight loss".

It is by calculating weight loss, which is as follows:

- A piece of metal is taken from the same metal that we want to measure its erosion speed and we clean it of grease by washing it with acetone, then dry it well, weigh it and record the weight.
- The metal is exposed to the medium in which we want to measure the corrosion in the laboratory and given the same conditions for a long period of time.
- After a long period of exposure, we wash the piece with water and rub it with a rubber piece until the traces of corrosion disappear, then we dry it and weigh it, and this is the weight loss W [21]. Then we apply the equation: **r= 87.6*W/D*A*T**

r: Erosion velocity in mm/year, W: Weight lost in milligrams, D: Density in g/cm^3

A: The area subject to wear (the area of the whole piece if it is completely immersed) calculated in cm^2, T: Time in hours.

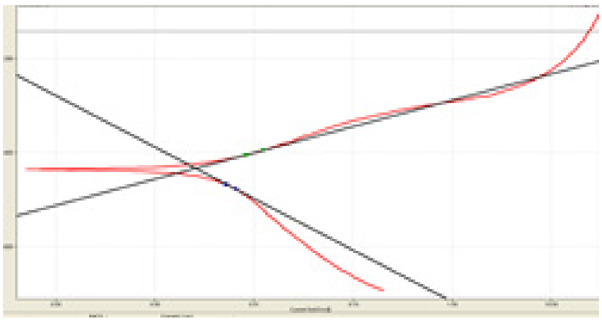
The value of (r) gives us an idea of the rate of corrosion of metals, if:

Less than 0.02 mm/year the metal is unaffected by corrosion in that medium.

- 0.02 - 0.1 mm/year the metal has excellent corrosion resistance.
- 0.1 - 0.5 mm/year the metal has good corrosion resistance.
- 0.5 - 1 mm/year the metal is of medium corrosion resistance.
- 1 - 5 mm/year the metal has poor corrosion resistance.
- 5 mm/year and above, metal never fit in that medium [22].

The results of the checkups are listed in the following two ways:

Scheme (1) : Corrosion rate of low carbon steel in (0.3% N HCl in inhibitor M_{35}) with solvent ethanol



Potential [mV]	Current [mA]	Potential [mV]	Current [mA]
-653.00	-1.08	-478.00	-10.80
-633.00	-615.00	-459.00	-2.10
-613.00	-384.00	-413.00	4.37
-599.00	-270.00	-373.00	1.72
-569.00	-133.00	-350.00	2.83
-533.00	-56.70	-338.00	6.10
-503.00	-26.20	-329.00	9.34
-493.00	-19.10	-313.00	1.90

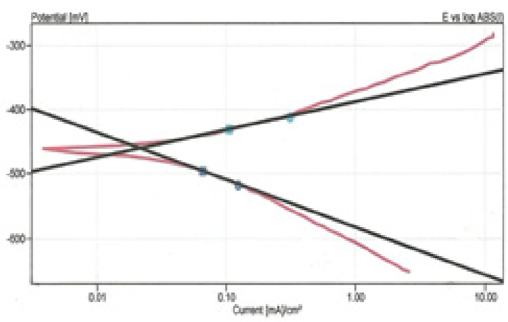
E_{corr} = -433 mv

I_{corr} = 2.58µA/cm^2

Wt loss rate = 27.084 MPY

Inhibition Efficiency % = 100x ($CR_{uninhibited}$ - $CR_{inhibited}$) / $CR_{uninhibited}$

Scheme (2): Corrosion rate of low carbon steel in (0.3% N HCl in inhibitor M_{37}) with solvent ethanol



Potential [mV]	Current [mA]	Potential [mV]	Current [mA]
-661.00	-2.77	-510.00	-6.20
-656.00	-2.37	-467.00	2.20
-651.00	-2.10	-447.00	3.45
-647.00	-1.87	-410.00	3.04
-641.00	-1.67	-321.00	4.14
-637.00	-1.50	-301.00	6.92
-631.00	-1.35	-290.00	8.47
-626.00	-1.22	-287.00	9.27
-621.00	-1.09	-282.00	10.09
-591.00	-5.62	-276.00	10.91
-567.00	-3.20		

E_{corr} = -437.3 mv

I_{corr} = µ 42.56A/cm^2

Wt loss rate = 71.196 MPY

Inhibition Efficiency % = 100 x ($CR_{uninhibited}$ - $CR_{inhibited}$) / $CR_{uninhibited}$

Inhibition Efficiency % = 100 x (92.25 - 42.56)/ 92.25 = 53.86%

Conclusions: All the prepared materials are miscible with water and hydrocarbon solvents, and this indicates that the prepared material is a material with good effectiveness as an anti-corrosion inhibitor. The melting degrees differed from the materials prepared from them, and when comparing the melting degrees of the reacting materials and the resulting materials with the standard melting tables installed in the sources, and this is one of the indications of the composition of the prepared materials. An evaluation of the anti-corrosion materials prepared by the internationally accepted standard evaluation methods has been carried out, which is the method of calculating the corrosion speed by drawing a curve between the voltage difference and the current, Tafel slopes using the Potentiostat device, and the other method is weight loss. The speed of weight loss is high, while the resulting materials gave high inhibition efficiency and low speed of weight loss. Five types of oxazepine were prepared that were used as corrosion inhibitors M34-38 three of them have demonstrated high inhibition efficacy and little weight loss, as follows: M36: It gave a percentage of inhibition (53.86%) and a weight loss of 71.196, which is a low percentage. M37: It gave an inhibition efficiency (81.30%) and a weight loss of 23.067, which is also a low percentage. M35: Proven high inhibition efficacy (97.56%) and weight loss of 27.084%. From tafel curves, it is possible to extract cyclic polarization, through which it has been proven that using the prepared inhibitors prevents the occurrence of foveal corrosion. Selection of high-efficiency inhibitors that have been prepared for use as local materials alternative to foreign materials.

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