Preparation Organometallic Compounds Containing Schiff Bases and Study their Electrical Properties

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Abstract:

The research includes preparation ligand from Schiff bases (DMAB) [2,3 - Dimethyl -1-phenyl-4-(benzledene)-3-pyrozoline-5–one] derived from condensation reaction of 4-aminoantipyrene with benzaldehyde .

Complexes of ligand with Fe(III) as symbol (M1) and Cr(III) as symbol (M2) , were prepared. The identity of prepared ligand has been characterized by spectral methods, infrared ray (IR) and measured melting point (m.p.) .

A study of molar conductivity of prepared complex solutions in absolute ethanol solvent at a concentration (1×10^{-3}M) and laboratory temperature, the complexity increased the conductivity significantly.

The corrosion rate for ligand and some complexes were measured by polarization curves resulting from readings of Tafel device by using tap water , and calculation the potential and corrosion current , the ligand has a small corrosion current, while the complexity increased of the corrosion current , and compare the results with similar compounds.

Key word: aminoantipyrene , benzaldehyde

الخلاصة :

تضمن البحث تحضير ليكاند (DMAB) [2,3 - Dimethyl -1-phenyl-4-(benzledene)-3-pyrozoline-5–one] من قواعد شف والذي يحضر من تفاعل تكثيفي 4– امينو انتي بايرين مع البنزلديهايد ، أستعمل هذا الليكاند في تحضير معقدات جديد لعنصر الحديد الثلاثي التكافؤ (III) ويرمز له اختصارا (M1) ، وعنصر الكروم الثلاثي التكافؤ(III) ويرمز له اختصارا (M2) ، تم تشخيص الليكاند المحضر بالطرائق الطيفية المتاحة وهي طيف الأشعة تحت ألحمراء وقياس درجة الانصهار ، وبينت دراسة التوصيلية المولارية لمحاليل المعقد المحضر في مذيب الايثانول وعند التركيز(1×10^{-3}) مولاري وبدرجة حرارة المختبر، أن التعقيد زاد من التوصيلية المولارية بشكل كبير ، قيس معدل التآكل للمادة الحرة وبعض معقداتها من خلال منحنيات الاستقطاب الناتجة من قراءات جهاز تافل Tafel Device باستخدام ماء الحنفية الاعتيادي، ومنها حساب جهد وتيار التآكل وكانت المادة الحرة ذات تيار تاكل قليل ، وان التعقيد زاده من تيار التآكل ، وقورنت النتائج مع مركبات شبيهة .

الكلمات المفتاحية : امينو انتي بايرين ، البنزلديهايد

Introduction:

Won the harmonizing chemistry in recent years a wide interest in chemistry, to develop rapidly in the practical part of preparation and diagnostic harmonizing complexes, these complexes used in the broad areas of medicine, industry and agriculture as well as in the field of pollution, The formation of complexes includes the transition elements and the represented elements, but they were observed, especially with the transition elements ions as it provides a blank orepettales and the energy of orepettales less of nonmetal atom orepettales embedded in the ligand structure who owns electron couples is not a common to bonding with metal ion, and among the large number of ligandes is Schiff bases, one of the most important organic ligand involved in the formation of many harmonizing complexes by giving electrons to the public elements and private transition [AL-Khafaji,2010].

Known corrosion that exists interaction between the matter and the Pacific, which leads to the dissolution of the material and influence in the mechanical and physical properties [Fontana , 1989], or known in some cases that failed to hit the metal, produced by chemical agents assisted

by factors mechanical available in the center, which employs metal [Scully , 1990].

One of the most popular economic methods for protection from corrosion in the cooling systems, is to add corrosion inhibitors which is a organic material or inorganic or metallic organic added small quantities to the corrosion ocean and lead to reduced speed of corrosion is significantly protect metals from corrosion. The function of inhibitors is by configuring a thin layer on the surface of the metal, or by interfering with the interaction anode, cathodic, or both [AL-Musawe, 2000].

Studied the researcher [Ala, 2005] behavior crystalline liquid and electrical properties of the new varieties of twins Schiff bases molecularly corresponding derived from albannzdin and it complexes, showing measurements of molar electrical conductivity that free liquid crystal ligandes, not conducted to the electric , while the impact of complexity evident in the improvement of electrical conductivity contineous and alternating to been in the range of organic semiconductors connectivity.

The researcher [Musa, 2010] prepared two compounds of the Schiff bases compounds and metallic complexes, and diagnosed these compound and complexes, were measured electrical properties of the all compounds, as shown measuring electrical conductivity of studied liquid crystal materials, is self semiconductors with low electrical conductivity, while the impact of complexity is improvement the electrical conductivity contineous and alternating current.

The aim of our study is to prepare organometallic compounds from Schiff bases, and measures the molar electrical conductivity, the corrosion current and voltage, for the large and growing importance of these compounds in the areas of applied and industrial.

Theoretical part:

Know the molar conductivity as conductivity (1 cm^3) of solution containing (1mole) of the solute matter.

Used molar electrical conductivity for solutions are widely used in harmonizing chemistry to learn ionic formulas of compounds in solution [Skoog, 1988] and in the solid state increased number of ions that would exonerate the complex in solution increased degree of electrical conductivity, and the complexes no ionized own low Electrical conductivity.

Don't use water as a solvent in chemistry harmonizing because of decomposition of complexes in which the ability or the difficulty of solubility, but often use organic solvents such as netrobenzen , dimethel formaed and ethanol. Etc., where the solvent is idle for the complexes with a high electrical insulation constant and a low viscosity [Feltham and Hayter ,1964].

The molar conductivity can be calculated by the following relations:

$$L_{complexes} = L_{solution} - L_{solvent} \quad \ldots\ldots\ldots\ldots\ldots\ldots(1)$$

$$E = L_{complexes} \times K_{cell} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$\Lambda_m = 1000\ E / C_m \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

$L_{complex}$ = conductivity complex (Ω^{-1}) , $L_{solution}$ = conductivity solution (Ω^{-1})
$L_{solvent}$ = conductivity solvent (Ω^{-1}) , E = specific Conductance(Ω .cm) $^{-1}$, K_{cell} = cell constant
C_m = Molara concentration of the solution ($mol.cm^{-3}$) , Λ_m = Molar Conductivity ($\Omega^{-1}.cm^2.mol^-$)
Electrochemical corrosion is a real chemical reaction between the center and metal or structure accompanied by the transfer of electrons between two sites on the surface, one with a higher electron density and other with low electron density, or between two points, one with large voltage and the other with a low voltage and the presence of ocean or electrolete solution is corrosive ocean. In this type of corrosion turns metal (M) to ions and dissolves in the ocean

(at the anode) according to the following reaction [AL-Musawe, 2000]:

$$M \rightarrow M^{+n} + ne^{-} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Move the resulting electrons (ne^{-}) to the cathode where gain metal ions (M^{+n}) or hydrogen ion accumulated electrons at the cathode, and it is reduced at surface, release hydrogen or deposited metals or reduced oxygen.

Cathodic or anode reaction rate must be equal according to the Faraday law and possible Guess by total flow-mediated to electron, which is called corrosion current, most of the corrosion reactions are electrochemical in nature [www .npi .co. ,2000].

Practical Part:

A - Preparation of Samples

The 4-amino antipyrine (2.03 g, 0.010 mol) dissolved with 4-dimethylamino benzaldehyde (1.06 g, 0.010 mol) in ethanol (20 ml). Five drops of glacial acetic acid added to the solution and the mixture was refluxed for (1.5hr). The Schiff base compound was isolated after the volume of the mixture was reduced to half using rotary evaporation, and the obtained product was collected by filtration, washed several times with ethanol and recrystilized from absolute ethanol. The result was (99.99 %).

Preparation of Schiff Base Complexes:

The prepared Schiff base (2.0 mmol) in 30 ml ethanol has been mixed with metal salts [$CrCl_3.6H_2O$(1.0 mmol), $FeCl_3$ (1.0 mmol)] respectively in the same amount and refluxed for two hours. The resulted complexes were collected by filtration and then washed several times with ethanol, dried and stored. All the prepared compounds have been characterized using infrared (IR) and ultraviolet and visible (UV-Vis) spectra.

B - The Method of Work :

Tafel completion method is used to measure the corrosion rate for the scientists Wagner and Traud to prove their theory, a mixed-potential Theory. This method is based on the readings that can be obtained from both polarization curves, anodic and cathodic [Fontana ,1989].

To draw the polarization curves in practice requires the construction of a electrical circuit involving the use of special equipment including a Potentiostate and Auxiliary Electrode , which is usually made of noble metal, for example as platinum and reference electrode of saturated calomel, in addition to working electrode is the sample you want to measure the rate of corrosion in the normal tap water, and pass the anodic or cathodic current through the electrode is called the assistant electrode .The effort working electrode measured for reference electrode , the accuracy of measuring the rate of corrosion to Tafel completion is often comparable to the way of traditional weight loss , although they prefer the way the loss of weight in that it enables us to measure the corrosion rates are very low in addition to localized corrosion, and the selections using this method are that it not be true only when the corrosion process includes one cathode reaction, as well as the wide range of voltage that must be shedding to get on Tafel region .

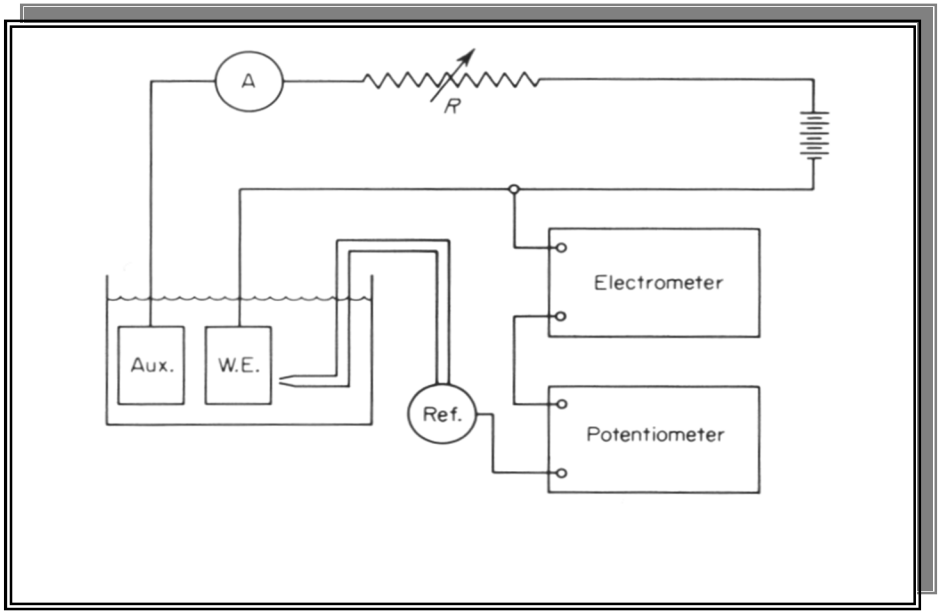

Figure (1): Diagram of electrical circuit to draw polarization curves using in studding corrosion

Results and Discussion:

The IR spectra provide valuable information regarding the nature of the functional group attached to the metal atom.[Heri and et. al. 2000] The spectrum of the free Schiff base ligand shows –C=N band in the region (1568 cm^{-1}), which is shifted to lower or upper frequencies in the spectra of all the complexes (1650–1564 cm^{-1}), indicating the involvement of the –C=N nitrogen in the coordination to the metal ion.[Sengupta and et. al. 2001] Coordination of the Schiff base to the metal through the nitrogen atom is expected to reduce the electron density in the azomethine link and lowers the ν C=N. All the complexes show bands in (1090–1100 cm^{-1}) and (700–750 cm^{-1}) regions and can be assigned to phenyl ring vibrations.[Nakamoto, 1997]. Assignment of the proposed coordination sites is further supported by the appearance of medium bands at (450–520 cm^{-1}), which could be attributed to ν M–N. [Howlader and Islam, 2007] [Thankamony and Mohanan, 2007].Table(1) spectral data and melting points of the compounds.

Table (1): Spectral data and melting points of the compounds units (cm^{-1})

No.	Compound	Symbol	(C=O) $\bar{\nu}$	Melting Point (°C)	(C=N) $\bar{\nu}$	(M-N) $\bar{\nu}$	(M-O) $\bar{\nu}$
1	$C_{18}H_{17}N_3O$	DMAB	1651.12	174	1568 .18	- -	- -
3	$[FeL_2Cl_2]Cl$	M1	1695.49	216	1599.04	515	440
4	$[CrL_2Cl_2]Cl$	M2	1651.12	198	1564.32	500	420

Known molar conductivity as connectivity ($1cm^3$) of solution containing the (1mol) of material, often used organic solvents in the preparation of solutions for measurements of conductivity molar, where the solvent is inert for the complexes with a electrical isolating

constant high and low viscosity, in this research measured conductivity molar to the solutions of complexes prepared in solvent ethanol absolute at the concentrations (1×10^{-3}) in the laboratory temperature (28°C) for determining electrolyte property, them being ionic or neutral , has been shown from measurements of molar conductivity, it is consistent with the formulas of synthetic complexes, as the bivalent copper complex (M1) behave neutral compound and is not conducted or very weak electrical conductivity in solution.

Either iron complex (M1) and trivalent chromium complex (M2), they behave neutral compounds and are of varying electrical conductivity, and Table (2) shows the values of molar conductivity of the prepared compounds.

Table (2):Molar conductivity at concentration (1×10^{-3}M) for the compounds at temperature (28°C)

No.	Compound	Color	Melting Point (°C)	Molar Conductivity ($Ohm^{-1}.cm^2.mol^{-1}$) $*10^{-6}$
1	DMAB	Yellow	174	3.3
3	M1	Read	216	81.4
4	M2	Green	198	50.9

That the values of conductivity electrical molar of the compounds prepared within the range of connectivity semiconductor and low electrical conductivity, while the impact of complexity and clear with the metal iron trichloride and chrome trichloride in improving electric conductivity, as the conductivity produced due to movement of charge carriers Interstate by bouncing, located inside the energy gap, which produces because of defects consisting of impurities during the preparation of materials and border granular materials multi-shape [Morrision ,1987], therefore, for the phenomenon of movement of the electrons charge through the elements shows the status of electricity conductivity for these compounds because they contain a variation in the electronic content to Orbatall (d).

corrosion current has been calculated of cathodic and the anode polarization curve resulting from your Tafel device , using ordinary tap water.

Forms (2), (3),and (4) describe the polarization curves of models(DMAB). (M1), (M2) are immersed in ordinary tap water , were obtained on the values of corrosion current by drawing masat for cathodic and anodic polarization curves , corrosion current and voltage values show in the table(3).

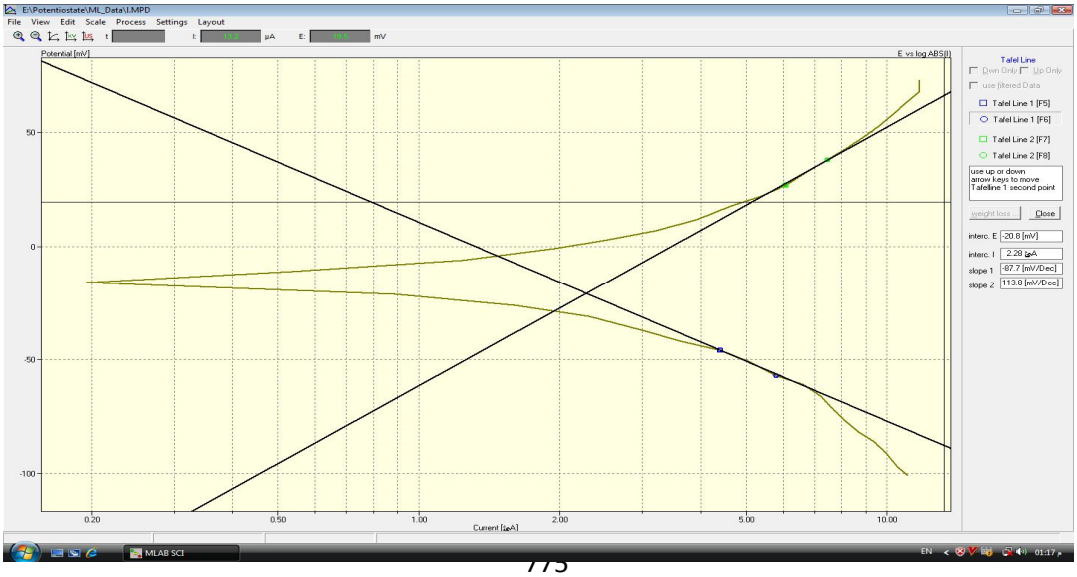

Figure (2): Polarization curve for sample (DMAB) in normal tap water

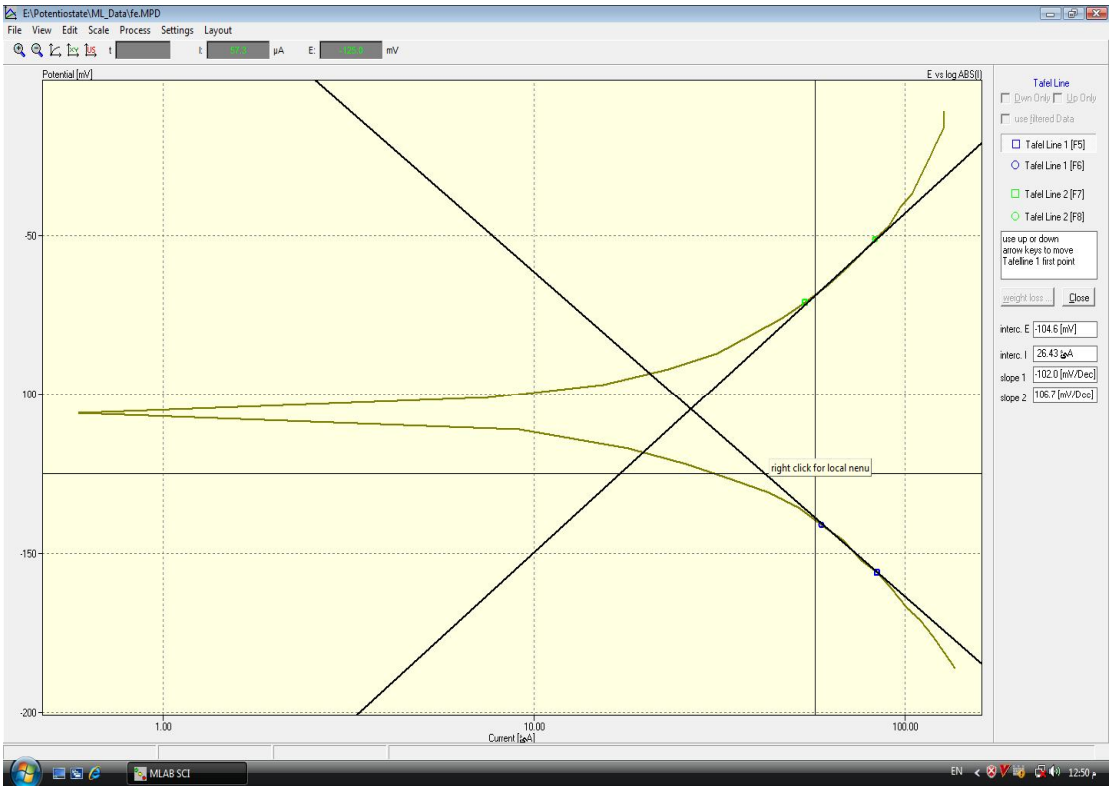

Figure (3): Polarization curve for sample (M1) in normal tap water

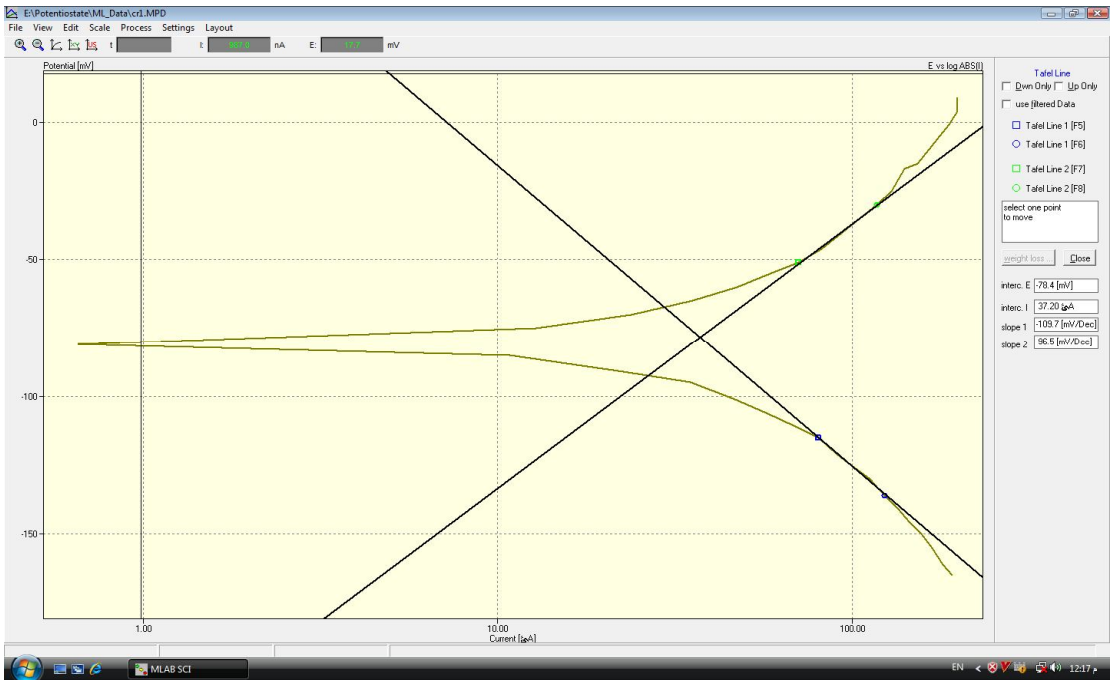

Figure (4): Polarization curve for sample (M2) in normal tap water

Table (3): Shows the values of voltage and current corrosion obtained from polarization curves of the compounds in ordinary tap water

Compounds	$I_{corr.}$ (μA) Corrosion current	Corrosion Voltage $E_{corr.}$ (mv)
(DMAB)	2.28	-20.8
(M1)	26.43	-104.6
(M2)	37.2	-78.4

Figures (2) , (3) and (4) describe the polarization curves resulting from a Tafel device , we note through the way that the curved bottom represents the cathodic current polarization current curve and the upper curve represent the anode current polarization curve , we note from the table (3) the values of corrosion current resulting from the Configures that the values of corrosion current of compounds irgement [I (DMAB) <I (M1) <I (M2)], where the normal water considerable possible harsh medium for many compounds due to the presence of dissolved gases and dissolved salts in addition to the presence solid components. Corrosion current is small and increased by complexed , and the reason the compound (DMAB) is an organic substance anti-corrosion [Ibrahim, 2007], and that the addition of inorganic materials (metals) When a complex has led to the emergence of qualities of inorganic materials and increased corrosion current.

Conclusions:

1 - The charge transfer phenomenon of electrons through the elements shows the status of electrical conductivity of these compounds because they contain a variation in the electronic content of the Orbital (d).

2 - The ligand be colored complexes with ions of copper(II), iron(III) and chrome (III).

3 - The results of molar conductivity, show that, prepared materials are semiconductors and low connectivity, complexity increased of the molar conductivity significantly, especially in the complex iron.

4 - The Tafel testing results, shows that the prepared materials have very little corrosion current, which can be used as an inhibitor. showing that complexity reduces of matters activity as an inhibitor.

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