



Schiff's bases and their metal complexes as corrosion inhibitors for aluminum alloys in corrosive media

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ABSTRACT

Due to the extensive use of aluminum in various fields, it is worthwhile to review the efforts done by researchers to protect aluminum from corrosive mediums and to investigate the corrosion inhibitors that support this goal. This review summarizes part of the contributions made to the literature in corrosion inhibitors of aluminum. © 2014 Trade Science Inc. - INDIA

KEYWORDS

Corrosion;
Inhibitors;
Schiff bases;
Metal complexes;
Aluminum.

INTRODUCTION

Aluminum is one of the world's most commonly used metals. Its lightness coupled with its strength, conductivity, barrier properties and its excellent corrosion resistance has all been its most important advantages and the main reasons for the continual growth in the usage of aluminum.

Untreated aluminum has very good corrosion resistance in most environments. This is primarily because aluminum forms a thin, but effective oxide layer that prevents further oxidation. However, low or high pH values (normally less than 4 and more than 9) lead to the oxide layer dissolving and consequently rapid corrosion of aluminum. Inorganic acids and strong alkaline solutions are thus very corrosive for aluminum. Acidic solutions are used for pickling, chemical and electrochemical etching of aluminium. Therefore, inhibition of aluminium corrosion in acidic media has a great importance^[1-3]. One of the most common methods to protect metals against acid

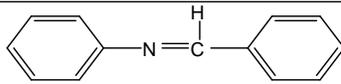
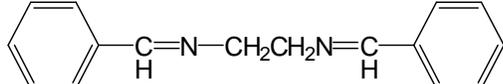
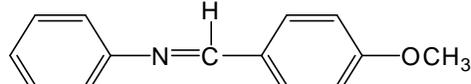
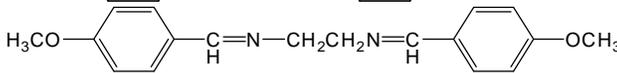
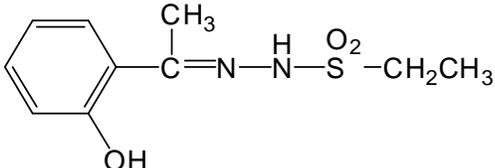
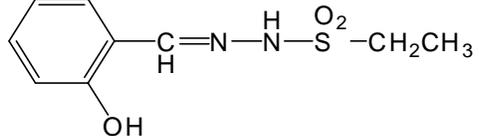
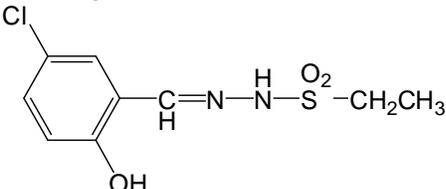
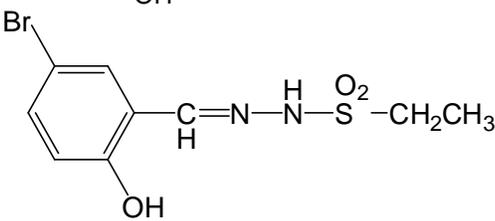
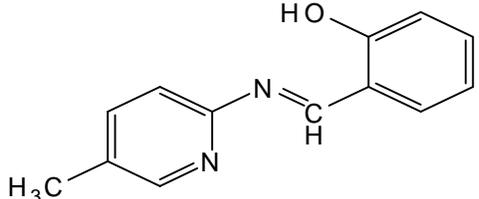
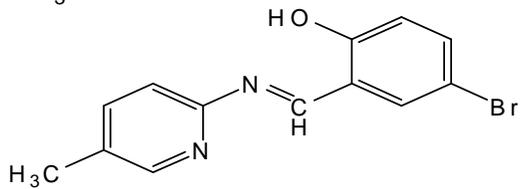
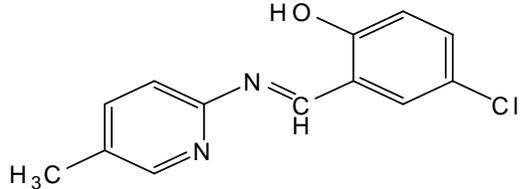
corrosion is the use of organic compounds containing functional groups, hetero atoms such as (P, S, N and O), and π electrons in their structure, as inhibitors^[5,33].

Schiff bases could be considered as good corrosion inhibitors because of the presence of the C=N-group, an electron cloud on the aromatic ring, and the electronegative nitrogen, oxygen and sulphur atoms that may be attached to the molecule^[34]. Increasing popularity of Schiff bases in the field of corrosion inhibition science based on the ease of synthesis from relatively inexpensive starting-materials and their eco-friendly or low toxic properties^[6,7]. These molecules normally form very thin and persistent adsorbed films that lead to a decrease in the corrosion rate due to the slowing down of anodic, cathodic reaction or both^[8]. The efficiency of the inhibitor depends on the environment, in which it acts, the nature of the metal surface, and the structure of inhibitor itself.

All chemical structures of the reviewed Schiff bases are summarized in TABLE 1.

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TABLE 1 : Schiff base corrosion inhibitors in hydrochloric acid solutions

Schiff base abbreviation	Molecular structure	Type of inhibitor	Type of aluminium metal	Reference
A		Cathodic	Aluminium	9
B		Cathodic	Aluminium	9
C		Cathodic	Aluminium	9
D		Cathodic	Aluminium	9
Afesh		-	AA3102 Aluminium alloy	13
Salesh		-	AA3102 aluminium alloy	13
Cl-Salesh		-	AA3102 aluminium alloy	13
Br-Salesh		-	AA3102 aluminium alloy	13
MP		Mixed	Alumimium	16
MBP		Mixed	Alumimium	16
MCP		Mixed	Alumimium	16

Schiff base abbreviation	Molecular structure	Type of inhibitor	Type of aluminium metal	Reference
E		Mixed	Aluminium	1
F		Mixed	Aluminium	1
G		Mixed	Aluminium	1
H		Mixed	Aluminium	1
SB		-	Aluminium (3RS)	21
SB-PEG Alkanoate		-	Aluminium (3RS)	21
	n = 9, 45 and 68 ethylene oxide units R = decanoate, hexadecanoate, octadecanoate, oleate			
TB		Cathodic	Aluminium	23
TC		Cathodic	Aluminium	23
D1		Cathodic	Aluminium	29
D2		Cathodic	Aluminium	29

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Schiff base abbreviation	Molecular structure	Type of inhibitor	Type of aluminium metal	Reference
D3		Cathodic	Aluminium	29
o-CANB		Mixed	Al-Pure	31
APh-Cl		Cathodic	Aluminium alloy	32
APh-OCH ₃		Cathodic	Aluminium alloy	32

SCHIFF BASES AS CORROSION INHIBITORS FOR ALUMINUM

Gamal K. Gomma and Mostafa H. Wahdan studied the inhibition efficiency of the Schiff bases A (aniline, N benzylidene) derived from benzaldehyde and aniline, a second compound B (ethylenediamine, N,N'-dibenzylidene) derived from benzaldehyde and ethylenediamine, a third C (aniline, N-(p-methoxybenzylidene) derived from anisaldehyde and aniline, and a fourth compound D (ethylenediamine, N,N-di-p-methoxybenzylidene) derived from anisaldehyde and ethylenediamine^[9] as corrosion inhibitors for aluminium in hydrochloric acid solution. Their results show that the efficiency of all the compounds increases with increasing inhibitor concentration. Addition of each compound shifts the corrosion potential in the negative direction; in which it has been more evident at higher concentrations. This means that the inhibitors used are considered to be cathodic inhibitors. The efficiencies of the compounds used were calculated from gravimetric data. Studies on the effect of temperature ranging from 30–50 °C reveal that the inhibition efficiencies of all the compounds were found

to increase with increasing temperature. Such inhibitors are of practical interest where retardation of corrosion at elevated temperatures is desired. According to Machu^[10], the kinetics of such corrosion process acquires the character of a diffusion process, in which at higher temperature the quantity of inhibitor present at the metal surface is greater than that at lower temperatures. It was suggested^[11] that the enhancement of the inhibition efficiency at higher temperatures may be due to the higher activation energy available for adsorption, and the higher rate of diffusion of inhibitor molecules.

Singh et al.^[12] consider that with increasing temperature some chemical changes occur in the inhibitor molecules, leading to an increment in the electron densities at the adsorption centers of the molecule, causing an improvement in the inhibitor efficiency.

Owing to the acidity of the medium, the basic compounds cannot remain in solution as free bases, and it may therefore be assumed that at least in the first few moments of contact between the metal and the solution, they exist at the interface in the cationic form, attached to the anodic points; it is also possible that the alkalinity produced at the cathodic sites favors the free base, which would then be generally adsorbed on the metal surface.

A. Aytae, U O Zeman and M. Kabasakaloglu introduced the Schiff bases 2-hydroxyacetophenone etansulphonyl hydrazone, Salicylaldehyde etansulphonyl hydrazone, 5-bromosalicylaldehyde-etansulphonylhydrazone and 5-chlorosalicylaldehyde-etansulphonylhydrazone as effective corrosion inhibitors for AA3102 aluminium in 0.1M HCl^[13]. The behavior of these compounds as corrosion inhibitors was investigated by hydrogen evolution and the impedance methods. The hydrogen evolution tests showed that the corrosion resistance was greatly enhanced in presence of inhibitors. These results were confirmed by the impedance measurements where it was observed that the effect of inhibitor addition appears by an increase in the resistance and, a decrease in the capacity of interface. It is suggested that their effects depend on their concentration and the molecular structures. The maximum inhibition efficiencies were obtained for the 5-bromosalicylaldehydetansulphonylhydrazon and 5-chlorosalicylaldehyde-etansulphonylhydrazone by both methods. Br-Salesh is the most efficient inhibitor and reduced the hydrogen evolution compared with other Schiff bases. It is also shown that the corrosion rates decrease with the addition of these inhibitors compared with standard solution and the corrosion rates decrease with increasing inhibitor concentration. With the exception of Afesh, the impedance diagrams show perfect semi-circles indicating a barrier layer formed on the surface and a charge transfer process mainly controlling the corrosion of aluminium for Salesh, Cl-Salesh and Br-Salesh at high frequency region and an inductive one at low frequency region. For Afesh, same circular Nyquistic diagram is obtained for high concentration. In fact the presence of these Schiff bases enhances the value of charge transfer resistance in 0.1M HCl solution.

Adsorption of these Schiff bases probably occur on bare surface with oxygen consumption since at the beginning of the hydrogen evolution measurement the volume of the corrosion system decrease at constant pressure. After the consumption of dissolved oxygen in the solution, the hydrogen evolution begins slowly. For maximum adsorption efficiency there must be optimum concentrations for Schiff bases and dissolved oxygen in acidic solution. According to the structures of these Schiff bases convenience of complex formation is in-

creased in the order of Afesh > Salesh > Cl-Salesh > Br-Salesh and is in the reverse order of inhibitor efficiency. In order to get a better understanding of the electrochemical process on the metal surface, adsorption characteristics at room temperature were also studied for Salesh, Afesh, Br-Salesh and Cl-Salesh. It is well known that this process is closely related to the adsorption of the inhibitors molecules and the adsorption depends on the molecular structure^[14,15].

The protection ability of these Schiff bases, is given in the order of Afesh < Salesh < Cl-Salesh < Br-Salesh. Cl-Salesh and Br-Salesh are the most effective ones, since they have electronegative atoms as chlorine and bromine as a para substituent on phenol ring.

When a phenol has chlorine and bromine substituents in para position, oxygen molecule as a radical is tied to the hydroxyl group of benzene ring and then Cl or Br phenolic radical is formed. Resonance in these adsorbed phenolic radicals makes stable radical structure and electron barrier against dissolution of aluminium atoms.

The most effective inhibitor is Br-Salesh since it has higher molecular weight than Cl-Salesh. Dispersion forces assist to adsorption in addition to other adsorption forces. Methyl group on Afesh makes steric hindrance on the adsorption of these molecules on the surface.

A. Yurt, S. Ulutas, H. Dal pioneered a research to investigate the electrochemical and theoretical aspects of three Schiff bases—2-[2-aza-2-(5-methyl(2-pyridly))vinyl]phenol (MP), 2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-bromophenol (MBP), and 2-[2-aza-2-(5-methyl(2-pyridly))vinyl]-4-chlorophenol (MCP)—on the corrosion of aluminium in 0.1 M HCl^[16]. The authors also used potentiodynamic and linear polarization methods. It was understood from polarization curves that the Schiff bases acts as a mixed-type inhibitors. It is also proposed that the variation in inhibition efficiency values depends on the type of functional groups substituted on benzene ring. It was found that the presence of bromine and chlorine atoms in the molecular structure of studied Schiff bases facilitate the adsorption of molecule on aluminium surface. The correlation between the inhibition efficiencies of the Schiff bases and their molecular structure has been investigated using quantum chemical parameters obtained by MNDO semi-

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empirical SCF-MO methods. These results indicate that adsorption of studied Schiff bases depends on the charge density of adsorption centers and dipole moments.

Results also suggest that all studied Schiff bases can be classified as mixed type inhibitors with a predominantly cathodic action. Inhibition efficiency values reveal that, inhibition efficiency increases with an increase in the concentration of additive. This suggests that the inhibitor molecules are adsorbed on the Al/solution interface where the adsorbed molecules mechanically screen the coated part of the metal surface from the action of the corrodent. The increase in inhibition efficiency observed at higher inhibitor concentration indicates that more inhibitor molecules are adsorbed on the metal surface, thus providing wider surface coverage and these compounds are acting as adsorption inhibitor. The inhibition efficiency values of the examined Schiff bases follow the order MCP > MBP > MP. Obtained results also show that addition of all of the examined Schiff bases causes increase in polarization resistance. Inhibition efficiency values calculated from potentiodynamic polarisation and linear polarisation methods were not equal but the trends are almost the same.

H. Ashassi-Sorkhabi, B. Shabani, B. Aligholipour, and D. Seifzadeh used polarization, electrochemical impedance spectroscopy (EIS) and weight loss measurements techniques to explore the effect of the Schiff bases benzylidene-(2-methoxy-phenyl)-amine (E), (2-methoxy-phenyl)-(4-methyl-benzylidene)-amine (F), (4-chloro-benzylidene)-(2-methoxy-phenyl)-amine (G) and (4-nitro-benzylidene)-(2-methoxy-phenyl)-amine (H) on the corrosion of aluminum in 1 M HCl^[1]. These synthetic compounds have attracted much attention because of their excellent inhibition efficiency. Maximum inhibition was obtained for 0.01 M Schiff base E. Results show that the inhibition efficiency increases with decreasing in temperature and increasing in concentration of Schiff base. Polarization curves reveal that the used inhibitors are mixed type inhibitors. The surface adsorption of the Schiff bases leads to a decrease of double layer capacitance as well as an increase of polarization resistance. The inhibitor performance depends strongly on the type of function groups substituted on benzene ring. The adsorption of used compounds on the aluminum surface obeys a Langmuir isotherm and

has a physical mechanism.

Some research works^[17] reveal that inhibition efficiency of Schiff base is much greater than corresponding amines and aldehydes. This may be due to the presence of a $-C=N-$ group in the molecules. The authors posited that the first stage of the underlying mechanism is the adsorption of the inhibitors onto the metal surface. The processes of adsorption of inhibitors are influenced by the nature and surface charge of the metal, the chemical structure of organic inhibitors, the distribution of charge in the molecule and the type of aggressive electrolyte. The chemisorptions are the principle types of interaction between organic inhibitors and the metal surface^[18,19]. Potentiodynamic polarization curves indicate that all used Schiff bases have effect on both cathodic and anodic reactions of corrosion process. Therefore, these compounds could be classified as mixed type (anodic/cathodic) inhibitors with a predominantly cathodic action. According to results, the inhibition efficiency increases with inhibitor concentration but decreases with temperature. Increasing of inhibition efficiency with the increase of inhibitor concentration indicates that, these compounds are acting as adsorption inhibitor. Decrease in inhibition efficiency with increase in temperature can be explain by desorption of inhibitor molecules on the metal surface. By substitution of the electron donating group such as CH_3- and $Cl-$ in the benzene ring of inhibitors, the inhibition efficiency decreases. This fact may be explained by the adsorption mechanism of these compounds on the aluminum surface. It appears that the physical adsorption plays a fundamental role in inhibition process. In acidic media Schiff base compounds exist in the form of protonated species. It is assumed that Cl^- anion is first adsorbed onto the positively charged metal surface by columbic attraction. Then the Schiff bases can be adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface^[20]. The presence of electro-donating group on the Schiff base structure decreases positive charge on the protonated molecule and decreases the adsorption of molecules on the metal surface. The adsorption of these compounds is spontaneous and has a physical mechanism because all ΔG_{ads} data are negative and less than 40 kJ/mole.

Non-ionic Schiff base amphiphiles of p-aminoben-

zoic acid was reported as inhibitors of aluminum (3RS) corrosion in 4N HCl by Nabel A. Negm, and Mohamed F. Zaki^[21]. The surface and corrosion inhibition activities were correlated to the chemical structures of the inhibitors.

The authors clarify that the inhibition efficiency increased by increasing the number of repeated methylene groups in the hydrophobic chains. Schiff base polyethylene glycol showed the maximum corrosion inhibition efficiency at 55.28%. Comparison between the corrosion rate of the different hydrophobic chains showed the following trend: oleate > stearate > palmitate > decanoate. This behavior could be attributed to two factors. First, the surface activity of these inhibitors at the interfaces. Second, the longer hydrophobic chains neighbored to each other can easily overlapped. That forms a condensed nonpolar layer consists of the alkyl chains. This layer faced the polar aggressive medium, hence good isolation occurred and the corrosion process stopped. The presence of coiling in these chains (in case of saturated chains) and/or unsaturation sites (in case of oleic acid derivative) enhances the mentioned overlapping. That effect appears obviously in the case of stearate and oleate derivatives (SB-2000-18 and SB-2000-oleate). Increasing the adsorption tendency (in terms of adsorption free energy), directing the inhibitor molecules towards the metal/corrosive medium interface where the inhibitor molecules act as a barrier; hence corrosion process steadily decreased. Since, the hydrogen evolution and weight loss techniques were used to assure the accuracy and the reproducibility of the results, the two techniques is highly comparable having very close values.

The mechanism of the inhibition processes of the corrosion inhibitors under consideration was thought to be the adsorption one. The process of adsorption is governed by different parameters depend almost on the chemical structure of these inhibitors. The adsorption process is occurred either physically or chemically. It is also pointed out that the inhibition efficiency increased by increasing the doses of the used inhibitors until the maximum values at 100 ppm. Then, the efficiency decreased gradually by increasing the inhibitor concentration to 200 or 400 ppm. That indicates the formation of neat layer of inhibitors at the metal/solution interface at the lower concentrations. The density of this layer

increases by increasing the dose to 100 ppm. The decrease in corrosion inhibition efficiency at higher doses indicates that the adsorption is not in successive layers due to the formation of the micelles at higher concentrations^[22]. It was concluded that longer hydrophobic chains and shorter polyethylene oxide chains increases the corrosion inhibition efficiencies of the corrosion inhibitors. Also, it can be said that the inhibition mechanism is a physical one and there is a critical concentration for the inhibitors to produce the maximum efficiency.

Aysel Yurt, and Ozlem Aykin studied the influence of diphenolic Schiff bases on the corrosion of Al in 0.1M HCl using potentiodynamic polarisation and electrochemical quartz crystal microbalance measurements^[23]. Results show that inhibition efficiencies increase with increase in inhibitor concentration. This reveals that the inhibition occurs through adsorption of the inhibitor molecules on the metal surface. Adsorption of these inhibitors follows Temkin adsorption isotherm. The correlation between the inhibitor performances and their molecular structures has been investigated using quantum chemical parameters obtained by MNDO (modified neglect of diatomic overlap) semi-empirical method. Calculated quantum chemical parameters indicate that Schiff bases adsorbed on aluminium surface by chemical mechanism.

Polarization studies indicate that investigated compounds can be classified as cathodic inhibitors^[24,25]. The corrosion current densities are dependent on the concentrations of the inhibiting agents, and current densities decrease as concentration of the Schiff base increases. This result may be related to the adsorption of the Schiff bases at the active sites of aluminium surface, retarding the corrosion reaction. The increase in inhibition efficiency observed at higher inhibitor concentration indicates that more inhibitor molecules are adsorbed on the metal surface thus providing wider surface coverage and these compounds are acting as adsorption inhibitor. In order to investigate the adsorption process of TC and TB on the aluminium surface, several adsorption isotherms were tested for the description of adsorption mechanism. The best fitted straight line was obtained for the plot of surface coverage versus natural logarithm of inhibitor concentration. This suggests that the adsorption of Schiff bases on electrode surface obeyed Temkin adsorption isotherm^[26,27].

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Thermodynamic adsorption parameter shows that the corrosion inhibition effect of the two tested inhibitors is due to their chemisorption onto the aluminium surface blocking the corrosion process. Schiff bases can be chemisorbed on the aluminium surface by the interaction of unshared electron pairs of N and O atoms with the metal and by the interaction of p-electrons with the metal. Consequently, the adsorption of inhibitors is the result of the formation a coordinate covalent bond between N atoms and metal, and/or is due to the p-electrons which are easily translated to d-orbital of metal atom along to p-system. Polarisation measurements indicate that inhibitor performance is affected by molecular structure of inhibitor. The variation in the inhibition efficiency of investigated Schiff bases depends on the presence of different electronegative substituents, such as Br and Cl atoms, in the molecular structure of TB and TC, respectively. This fact shows that adsorption ability of molecules onto the metal surface should be related with electronegativity values of substituents. According to the Pauling's scale, the electronegativity value of Cl (3.16) is higher than that of Br (2.96)^[28]. Therefore, the presence Cl atoms instead of Br atoms in the molecular structure of Schiff base leads to a greater change in the values of the charge density on imine ($-C=N-$) group, oxygen and also benzene ring that are responsible for adsorption. The frequency change of Al electrode in acidic test solution containing inhibitor immediately increased in the first minutes and remained approximately constant thereafter. This is an indication that Schiff bases were chemically adsorbed and remained on the aluminium surface. Addition of TB produces better protection, against corrosion of aluminium, than TC. This fact can be due to a different packing density of inhibitor onto the metal surface and also shows that inhibitor performance and inhibition mechanism are affected by molecular structure. More surface information was drawn from scanning electron micrographs. Aluminum specimens after immersion 24 h in 0.1 M HCl suffer severe corrosion due to the aggressive attack by HCl. The specimens immersed in the inhibitor solutions are in better conditions having smooth surfaces compared with that of surface immersed in 0.1 M HCl alone. This indicates that in presence of the inhibitor, the rate of corrosion was suppressed and that there was a good protective film adsorbed on speci-

mens' surface, which was responsible for the inhibition of corrosion. The variation in the protection action between TC and TB should be related with the slight morphological difference between the protective films formed from TB and from TC on the metal surface. protective adsorbed layer on aluminium surface obtained in the presence of TC is more porous than layer obtained in the presence of TB. Due to the porous structure of adsorbed TC layer, it may not provide sufficient protection against to the attack of aggressive ions to metal surface. This observation is in good agreement with the electrochemical measurements.

The authors eventually conclude that diphenolic Schiff bases behave as efficient cathodic inhibitors for the acidic corrosion of aluminium. Their inhibition efficiencies tend to increase with increasing inhibitor concentration. The inhibition action of the studied compounds is mainly due to their adsorption on the aluminium surface. Regarding the EQCM measurements, the decrease in the corrosion rate of aluminium in the presence of Schiff bases indicate that adsorbed protective layer formed on the aluminium surface is persistent in the 0.1 M HCl media. The values of standard free energy of adsorption and the relationship between the inhibition efficiency values and calculated quantum chemical parameters suggest that these Schiff bases can be adsorbed on aluminium surface by chemical mechanism. Chemisorption of Schiff bases involves sharing electrons between the N atoms and vacant p-orbitals of aluminium.

It was left to Serpil Safak, Berrin Duran, Aysel Yurt, and Gulsen Turkoglu to determine the inhibition efficiency of 1,5-bis[2-(2-hydroxybenzylideneamino) phenoxy]-3 oxopentane (D1), 1,5-bis[2-(5-chloro-2-hydroxybenzylideneamino) phenoxy]-3 oxopentane (D2) and 1,5-bis[2-(5-bromo-2-hydroxybenzylideneamino) phenoxy]-3-oxopentane (D3) on aluminium corrosion in 0.1 M HCl^[29]. The effect of these compounds against the corrosion of aluminium was expounded on the basis of electrochemical impedance spectroscopy, Tafel polarisation and scanning electron microscopy techniques. The study is closely related to that done by Aysel Yurt, and Ozlem Aykin on diphenolic Schiff bases described later, and established that the compounds exhibit inhibitor properties and adsorption of these compounds was found to accord with

Temkin adsorption isotherm. Polarisation curves indicated that the studied Schiff bases were cathodic inhibitors and the effectiveness of these inhibitors decreased in the order of D3 > D2 > D1. Quantum chemical calculations were performed to provide further insight into the inhibition efficiencies determined experimentally.

The impedance study indicates that the corrosion of aluminium in 0.1 M HCl solution is mainly controlled by charge transfer process and formation of a protective layer on the metal surface. Increase in inhibition efficiency with increasing inhibitor concentration indicates that, more inhibitor molecules are adsorbed on the metal surface providing wider surface coverage and these compounds act as adsorption inhibitors. The calculated values of free energy ΔG° point out that the adsorption of compounds occurs by chemisorption. SEM images obtained in the presence of inhibitors show that, the addition of these compounds modifies the features of the layer at the metal surface. The damage of metal surface has diminished in the presence of inhibitors and rough, corroded aluminium surface displaces to much smooth surfaces; especially D3 compound has the much smooth surface compared to the others.

On the other hand, there are much less and very small cracks on the surface of aluminium with D2 and D1 compounds than that of surface immersed in 0.1 M HCl alone. This may be due to protective film formation by adsorption of these compounds on the metal surface that the film is responsible for the inhibition of corrosion. As a result, the inhibitor molecules hinder the dissolution of aluminium by forming organic film on the metal surface and thereby suppress the rate of corrosion, as indicated by SEM images. Through the quantum chemical calculations it was shown that calculated parameters were correlated with the experimental results and it was found that inhibition efficiency increased with the higher energy HOMO and lower ΔE (LUMO – HOMO) values^[30]. Comparative study of these inhibitors shows that the inhibition efficiency follows the order: D3 > D2 > D1 and the order of protection effect is the same for both electrochemical and computational methods. The difference in the inhibition efficiencies of three compounds lies in their structure and electronegative bromine and chlorine atoms facilitate the adsorption of molecule on the aluminium surface.

In a recent scientific article, A.S. Patel and coworkers reported the potent inhibitory effect of *o*-Chloroaniline-*N*-benzylidene (*o*-CANB) toward the corrosion of Al-Pure in 1.0 M hydrochloric acid^[31]. Corrosion inhibition was studied by chemical method (weight loss) and electrochemical techniques including polarization method and electrochemical impedance spectroscopy (EIS). There was evidence that the inhibitor is good in acidic media and the inhibition efficiency up to >99% in 1.0 M HCl was attained. Polarization measurement revealed that the investigated inhibitor is a mixed type with a predominant action on cathode. Impedance measurement also showed that the charge transfer resistance increased and double layer capacitance decreased with an increase in the inhibitor's concentration. Obtained results about inhibition efficiency from weight loss, polarization study and EIS are in good agreement with each other. The adsorption of the inhibitor on the metal surface in the acid solution was found to obey Langmuir's adsorption isotherm.

The results demonstrated that the inhibitor inhibited the corrosion of Al-Pure in 1.0 M HCl at 35 ± 0.5 °C for an exposure period of 60 min. Increasing the concentration of *o*-CANB, increases in the inhibition efficiency (%IE) up to a maximum value of >99% at 0.5% inhibition concentration. Therefore, it could be concluded that the inhibition was found to depend on inhibitor's concentration. The inhibitory action of *o*-CANB against Al-Pure corrosion can be attributed to the adsorption of its molecules on Al-Pure surface, which limits the dissolution of the latter by blocking its corrosion sites and hence decreasing the weight loss, with increasing efficiency as the concentration increases. Also results reveal that the inhibition efficiency increases with inhibitor concentration but decreases with temperature. Increasing of inhibition efficiency with the increase of inhibitor concentration indicates that, this compound is acting as an adsorption inhibitor. But decrease in inhibition efficiency with increase in temperature can be explained by desorption of inhibitor molecules on the metal surface at higher temperatures. Activation parameters from Arrhenius-type plot suggest physical adsorption of the inhibitor molecules on the metal surface. Obtained results about inhibition efficiency from weight loss, polarization study and EIS are in good agreement with each other.

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SCHIFF BASE METAL COMPLEXES AS CORROSION INHIBITORS FOR ALUMINIUM

In contrast to Schiff bases, perusal of the literature show relatively very few articles that described the effect of Schiff base metal complexes as corrosion inhibitors for aluminium, and the area still deserves extra efforts and remains a promising field of research.

To investigate the relationship between corrosion inhibition and formation constants of -Cl and -OCH₃ substituted 2-aminophenol Schiff bases and their Cu(II), Co(II) and Ni(II) complexes, Nuresn Sari and Aylin Aytac conducted a research to probe the inhibition efficiency of these compounds by means of potentiodynamic polarization and impedance techniques^[32]. The inhibition efficiencies obtained from Tafel plots and EIS methods are in good agreement. The protonation constants of the Schiff bases and stability constants of the metal complexes have been determined potentiometrically in 1:1 methanol: water solution at 25 °C and 0.1 M KCl ionic strength. In this study, it seems that the Cu(II) complex has highest formation constants and is best inhibitor for Al alloy in 0.1 M HCl.

Polarization curve indicates that the Schiff bases and their metal complexes act as cathodic inhibitors. The variation in inhibitive efficiency mainly depends on the type and the coordination structures of the metal complexes and the substituents present in the ligands.

According to the structures of these metal complexes tendency of complex formation is increased in the order of Cu(II) > Ni(II) > Co(II) and the inhibitor efficiency is of the same order.

The difference in the inhibitive efficiencies of the (Aph-Cl) and (Aph-OCH₃) may be traced to the effect of the substituent groups in changing the electron activation of the aromatic ring, which may have better adsorptivity to the inhibitor. The conjugation pattern in the metal complexes may lead to higher efficiency. The results of inhibitor efficiency indicate that copper(II) complexes shows more efficiency than the other complexes due to conjugation.

CONCLUSION

Although the review is not completely surveyed all

the tremendous efforts put to investigate Schiff bases as corrosion inhibitors, the purpose of performing such a review is to highlight general clues about what different structures of Schiff bases can play in suppressing corrosion of aluminium in acid medium. It is clearly evident that:

- 1 The inhibition of the studied compounds depends mainly on their chemical structures and substituents associated with it. In general,
- 2 The presence of chlorine or bromine atoms facilitates the adsorption on aluminium surface and retard the corrosion process.
- 3 Not all compounds with similar chemical structure have the same inhibition action.
- 4 The most effective corrosion inhibitors are those compounds containing hetero atoms like nitrogen, oxygen and sulfur in addition to aromatic ring which can aid their adsorption onto metal surfaces.
- 5 Compounds of high molecular weights such as amphiphiles, are likely to effectively cover more surface area (due to adsorption) of the metal thus preventing corrosion from taking place.
- 6 Schiff base metal complexes are not yet fully tested for corrosion inhibition, and the area still is of vital importance.

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