Correlation in Between Inhibition Efficiencies and Stability Constants of The Schiff Bases and Their Metal Complexes

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To investigate the relationship between corrosion inhibition and formation constants of -Cl and -OCH$_3$ substituted 2-aminophenol Schiff bases and their Cu(II), Co(II) and Ni(II) complexes have been synthesized. Inhibitor effect of synthesized Schiff bases and their complexes, as corrosion inhibitors for aluminium in 0.1 M HCl, have been determined by potentiodynamic polarization and impedance techniques. The inhibition efficiencies obtained 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 ºC 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.

Key Words: Stability constants, Corrosion inhibitors, Schiff bases, Impedance studies, Metal complexes.

INTRODUCTION

Recently, researchers' attentions have focused on the inter-discipline areas. This has been partially the result of reports concerned with interaction of various chemicals including molecules and their properties[1,2]. These properties can be importance to understand some activities or efficiency on molecule structure. In the last decade, various hetero atom substances have been studied extensively, among them the study of a good number of Schiff bases[3]. Furthermore, nitrogen and oxygen containing ligands and their complexes have a number of potential technological applications in the areas of chemical transistors[4], including rechargeable batteries[5] and biochemical analyses[6-8]. The main results showed that some mechanical properties depends on the electronic and structural properties of the inhibitor molecule such as aromatic and functional groups, electron density on donor atoms and π orbital character of donor electrons[9,10].

This paper reports synthesis, characterization, inhibition effective of Al alloy in 0.1 M HCl solution, of -Cl and -OCH$_3$ substituted 2-aminophenol Schiff bases (Fig. 1) and their cobalt(II), nickel(II) and copper(II) complexes.

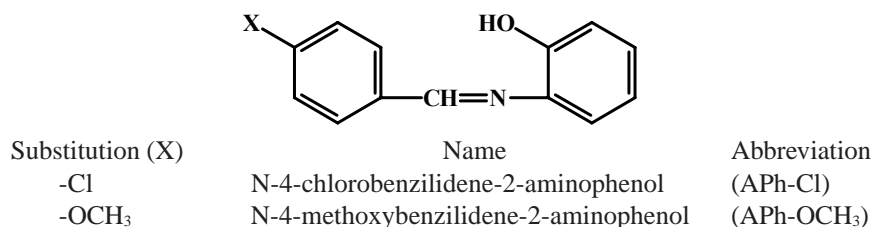| Substitution (X)	Name	Abbreviation
-Cl	N-4-chlorobenzilidene-2-aminophenol	(APh-Cl)
-OCH₃	N-4-methoxybenzilidene-2-aminophenol	(APh-OCH₃)

Fig. 1

In addition, the protonation constants of the Schiff bases and stability constants of their ML_2 type complexes with Cu(II), Co(II) and Ni(II) determined by the potentiometric titrations are also reported here. The present study is to examine the relationship between the corrosion inhibitor and stability constants of Schiff bases and their Cu(II), Co(II) and Ni(II) complexes.

EXPERIMENTAL

Preparation of the Schiff bases and complexes: A solution of 2-aminophenol (0.0941 g, 0.001 mol) in dioxane (25 mL) was added dropwise to a solution of aldehyde (0.001 mol) in dioxane (25 mL). The mixture was heated under reflux for 1 h. The reaction volumes were reduced to 10 mL by evaporation and then resulting yellow or deep-yellow precipitates were filtered, washed with diethyl ether and dried *in vacuo* at room temperature. Yields: 71-75 %. The compound was dissolved in THF, DMSO and DMF.

A sample of $MCl_2 \cdot nH_2O$ (1.25 mmol, M: Cu(II), Ni(II), Co(II)) was dissolved in methanol (25 mL). To the solution of metal chloride, Schiff bases (1.25 mmol) in methanol (25 mL) was added, immediately giving a colour solution. The resulting solution was stirred for *ca.* 1 h, filtered and allowed to stand for some time. On standing for further 2 h, the colour solid complexes formed was collected by filtration, washed with a small volume of ethanol and dioxane and then, dried in a desiccator over $CaCl_2$.

Physical measurements: Elemental analyses were carried out with a LECO-CHNS-9320 instrument. Metal contents were determined by a Philips PU 9285 atomic absorption instrument. ^1H and ^{13}C NMR spectra were recorded with a Bruker DPX-400 MHz using TMS as an internal standard and DMSO as a solvent. Mass spectra were recorded on a Micro Mass-UK Platform II mass spectrometer at Tubitak, Ankara, Turkey. Electronic spectra were recorded on an Unicam-UV2-100 spectrophotometer in MeOH. Infrared spectra were recorded on a Mattson-5000 FT-IR instrument in KBr pellets. Melting points were determined with a Gallenkamp melting pont apparatus. Magnetic measurements were carried out with a Sherwood Scientific magnetic susceptibility balance (Model No. MK 1) at 21 ºC with $Hg[Co(NCS)_4]$ as a calibration. Schiff bases and their complexes are soluble in methanol and other polar solvents.

Potentiometric reagents, solutions and measurements: 1:1 Ethanol:water solution was used as solvent. All metal salt solutions were prepared from their analytical grade chlorides and standardized by the atomic absorption spectroscopic method. A standard 0.052 M KOH solution (Merck) was used for titrations. KCl (Merck, extra pure) and concentrated HCl (Merck, extra pure) were used for preparation of 1.0 and 0.055 M HCl solutions. HCl solution was standardized against standard KOH solutions. Alkali solutions were stored under nitrogen atmosphere. The system used for potentiometric measurements and calculations was described previously pH meter readings in aqua-organic system were corrected[3].

Corrosion measurements: Aluminium specimens of size 2.00 cm × 0.45 cm × 0.2 cm (compositions: 0.42 % Fe, 0.21 % Mn, 0.07 % Si, 0.01 % Ti, 0.01 % V as ingredients) were used for electrochemical techniques. Prior to each experiment, the surface pre-treatment of aluminium specimens was performed by mechanical polishing (using a polishing machine) of the electrode surface with successive grades of emery papers down to 1200 grit up to a mirror finish. The electrodes was then rinsed with acetone, distilled water and dried at room temperature. The EIS measurements were carried out in a conventional three electrodes electrochemical cell. The counter and reference electrodes were platinum plate (2 cm^2) and silver/silver chloride electrode, respectively. The impedance measurements were carried out 5 mV (rsm) applied voltage of sinusoidal wave in frequency range 20 kHz-50 mHz at room temperature. The EIS measurements were conducted after 0.5 h immersion in experimental solution that ensured a system in equilibrium. The real (Z_r) and imaginary (Z_i) components of the impedance spectra in the complex plane were recorded using a Volta Lab PGZ 301 EIS voltametry system with an accompanying PC and software.

The polarization measurements were recorded at a scan rate of 20 mV s^{-1} using a Volta Lab PGZ 301 EIS voltametry system with an accompanying PC and software.

RESULTS AND DISCUSSION

Analytical, physical, electronic and characteristic IR spectral data of the Schiff bases and their complexes are given in Table-1. The ligands containing -CH=N- and -OH groups on adjacent carbons can exhibit -CH=NH- ↔ -CH=N- tautomerism[11]. The ligands show signals at 8.68-8.13 ppm which are attributed to the imine protons (-N=CH-). Signals at 9.19-9.30 ppm are assigned to the OH protons, respectively for (APh-OCH$_3$) and (APh-Cl).

These data strongly suggest that even in solution the imine forms remain as dominant species[11,12] (Fig. 2a).

^{1}H and ^{13}C NMR of Schiff bases and their Ni(II) complexes (due to diamagnetic) are given in Table-2. Due to the Co(II) and Cu(II) complexes are paramagnetic, their ^{1}H NMR spectra could not be obtained.

TABLE-1

ELEMENTAL ANALYSIS, PHYSICAL DATA, KEY IR BANDS (cm⁻¹) AND
ELECTRONIC SPECTRAL DATA FOR SCHIFF BASES AND THEIR METAL COMPLEXES

| Compd. Colour, μ BM | m.f. (m.p. °C) | Elemental analysis: Found (calcd.) % | | | | | ν(OH) | ν(CH=N) | ν(M-O) | ν(M-N) | λ nm, ($\varepsilon \times 10^{-4}$) |
		C	H	N	Cl	M					
(APh-Cl) Yellow, -	$C_{13}H_{10}NOCl$ (148-149)	67.32 (67.39)	4.14 (4.32)	6.32 (6.05)	14.89 (15.33)	–	2842	1626	–	–	275 (1001) 356 (724)
(APh-OCH₃) Yellow, -	$C_{14}H_{13}NO_2$ (151-153)	74.18 (74.01)	5.51 (5.73)	6.49 (6.17)	–	–	2851	1619	–	–	277 (943) 352 (627)
[Cu₂(APh-Cl)₂Cl₂] Black, 1.47	$C_{26}H_{18}N_2O_2Cl_4Cu_2$ (> 230)	58.79 (58.65)	3.32 (3.38)	5.71 (5.26)	26.22 (26.69)	23.51 (23.87)	–	1617	374	421	275 (873) 356 (524), 698 (2.31)
[Cu₂(APh-OCH₃)₂Cl₂] Black, 1.41	$C_{28}H_{24}N_2O_4Cl_2Cu_2$ (> 230)	51.21 (51.69)	3.88 (3.69)	4.13 (4.31)	10.54 (10.92)	19.32 (19.54)	–	1607	361	435	277 (776) 351 (441), 701 (1.92)
[Co(APh-Cl)₂].2H₂O Deep blue, 4.11	$C_{26}H_{22}N_2O_4Cl_2Co$ (> 201)	56.43 (56.13)	4.05 (3.96)	4.89 (5.04)	12.51 (12.77)	10.31 (10.60)	3218	1612	379	441	277 (104) 356 (724), 432 (7.85)
[Co(APh-OCH₃)₂].2H₂O Deep blue, 4.16	$C_{28}H_{28}N_2O_6Co$ (> 192)	57.17 (65.25)	5.32 (5.44)	5.39 (5.44)	–	10.51 (11.44)	3227	1600	370	451	277 (943) 352 (627), 428 (3.82)
[Ni(APh-Cl)₂].2H₂O Green, Diamagnetic,	$C_{26}H_{22}N_2O_4Cl_2Ni$ (> 230)	56.13 (56.15)	3.91 (3.96)	5.21 (5.04)	12.57 (12.78)	10.43 (10.56)	3251	1614	380	427	274 (749), 354 (4.21), 498 (1.41)
[Ni(APh-OCH₃)₂].H₂O Green, Diamagnetic,	$C_{28}H_{26}N_2O_5Ni$ (> 230)	63.41 (63.55)	4.09 (4.92)	5.22 (5.30)	–	11.37 (11.40)	3241	1603	368	432	274 (564), 354 (9.26), 502 (1.36)

imine form   amine form

(a)   (b)
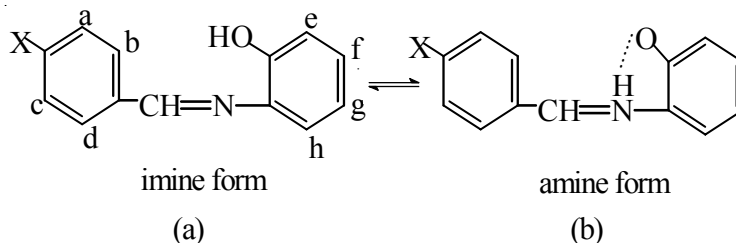
Fig. 2

TABLE-2
^{1}H NMR SPECTRAL DATA OF Ni(II) COMPLEXES

Compound	-CH=N	OH	OCH$_3$	Aromatic protons	
				a-d	e-h
(APh-Cl)	8.68 (s, 1H)	9.19 (b, 1H)	–	6.86-7.17 (m, 4H)	8.02-7.53 (m, 4H)
(APh-OCH$_3$)	8.13 (s, 1H)	9.30 (b, 1H)	3.71 (s, 3H)	6.85-7.01 (m, 4H)	7.52-7.28 (m, 4H)
[Ni(APh-Cl)$_2$].2H$_2$O	8.81 (s, 1H)	–	–	6.80-7.06 (m, 4H)	8.02-7.54 (m, 4H)
[Ni(APh-OCH$_3$)$_2$].H$_2$O	8.39 (s, 1H)	–	3.71 (s, 3H)	6.85-7.03 (m, 4H)	7.53-7.27 (m, 4H)

s = singlet; b = broad; m = multiple.

The signal disappeared in the Ni(II) complexes suggesting that the phenolic oxygen involved in coordination [Fig. 2(a)][13]. The azomethine proton signal observed at 8.68 and 8.13 ppm in the free ligand is shifted to different field in the complex indicating coordination of azomethine nitrogens. The multiplets at 6.85-8.02 ppm are due to aromatic protons[14]. The ν(OH)$_{(phenolic)}$ band at 2851-2842 cm^{-1} of the ligands is absent in the complexes suggesting coordination of phenolic oxygens for Cu(II) complexes. Other complexes show a broad diffuse strong absorption in the 3251-3218 cm^{-1} range attributable to ν(OH) for lattice water except Cu(II) complexes[15]. The ν(C=N) azomethine band observed at 1626-1619 cm^{-1} in the ligands has shifted to lower frequency by 10-20 cm^{-1} in the complex indicating coordination through the azomethine nitrogens. The coordination through nitrogen and oxygen is further supported by the appearance of new non-ligand bands in the regions 432-421 cm^{-1} ν(M-N) and 380-361 cm^{-1} ν(M-O)[16].

Magnetic and electronic spectral studies: The electonic absorption spectral data of the free ligands and their complexes in DMF are given in Table-1. The electronic spectra of the Co(II) complex shows an absorption band at 431-428 nm, which is compatible with this complex having a tetrahedral structure (Fig. 3a)[17]. The magnetic moment values of 4.11 and 4.16 BM observed for [Co(APh-Cl)$_2$Cl$_2$]·2H$_2$O and [Co(APh-OCH$_3$)$_2$Cl$_2$]·2H$_2$O, respectively, reveal the tetrahedral nature around Co(II) ion. The complexes of Ni(II) are diamagnetic suggesting a

square-planer geometry. The electronic spectra of the Ni(II) complexes shows an absorption band at *ca.* 510 nm, corresponding for square-planar geometry nickel compounds (Fig. 3b)[18]. Cu(II) complexes are five coordinated these with ligands. There are two different structures for five coordinated Cu(II) complexes, first the square pyramid, second the trigonal bipyramid. The electronic spectra of the Cu(II) complex shows a broad symmetric band at 700 nm. The band positions is consistent with this reported for the square-based pyramidal Cu(II) configuration (Fig. 3c)[19,20]. The low values of the room temperature magnetic moments of Cu(II) complexes may be due to an intermolecular interaction complexes of Cu(II) with ligands[19].
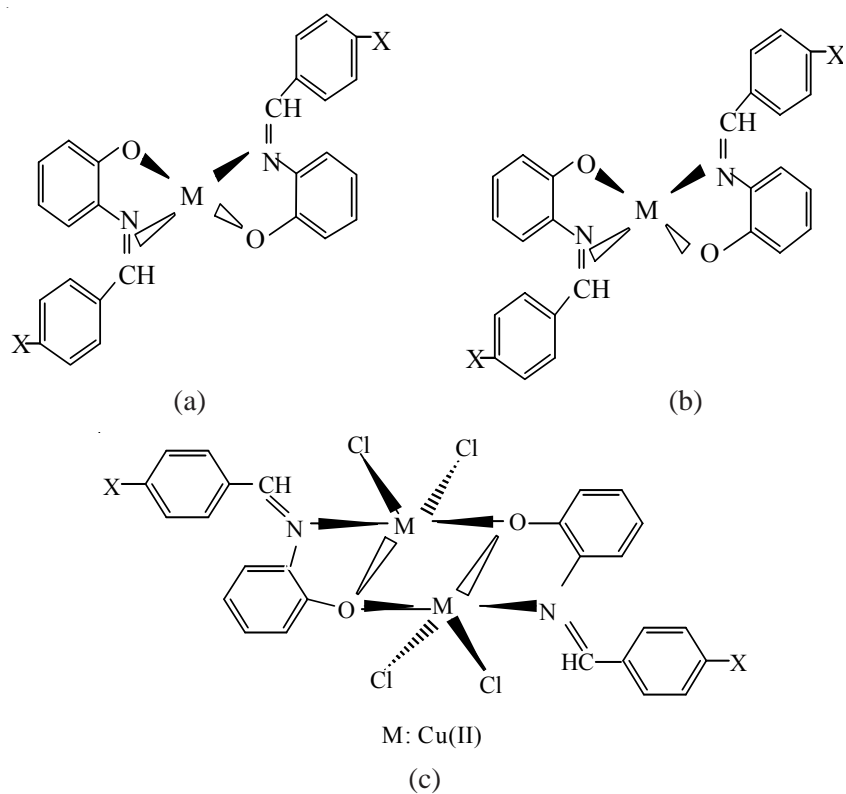

(a)   (b)

M: Cu(II)

(c)

Fig. 3.

Mass spectra of complexes: Mass spectra of the Cu(II) and Co(II) complexes show that Cu(II) complexes have a metal ligand stochiometry of 1:1 (M:L) (Fig. 3). The mass spectra give [M$^+$] 659, [M$^+$-1] 649, [M$^+$-1] 555, [M$^+$-4] 541 for [Cu$_2$(APh-Cl)$_2$Cl$_2$], [Cu$_2$(APh-OCH$_3$)$_2$Cl$_2$], [Co(APh-Cl)$_2$], [Co(APh-OCH$_3$)$_2$], respectively. So it is reasonable to conclude from the assignment of the fragments of the Co(II) and Cu(II) complexes that these compounds exist in a dimeric form for Cu(II) complexes, but not dimeric form for Co(II) complexes.

Potentiometric studies: Protonation constants and stability constants of the ligands and their metal complexes are given in Table-3. The Schiff bases have two protonation constants as expected. The first and second protonation constants refer to protonation of hydroxyl and imine nitrogen atom, respectively. First and second protonation constants of (APh-OCH$_3$) are higher than that the protonation constants of (APh-Cl). It may be attributed to higher inductive electron-withdrawing effect of methoxy group than chlorine atom. Deprotonation easy from -OH group due to decreases electron densities in the ring of the -OCH$_3$ group. Stability constants of the metal complexes of both ligands with the same metal ion also showed the same order protonation constants. This is an expected result, the chelation ability of the ligands increase due to increases of basic character of the donor atoms in the electron donating groups. The order of the stability constants for the same ligand with different metal ions, are found to be Co(II) < Ni(II) < Cu(II), conformity with Irving-Williams order for bivalent ions.

Corrosion behaviour of Schiff bases and their Co(II), Ni(II) and Cu(II) complexes: Impedance measurements on aluminium electrode in solution with and without 10 ppm Schiff bases and the metal complexes with an immersion time of 0.5 h were performed at open circuit potential. Nyquist plots of mild steel in uninhibited and inhibited acid solutions containing Schiff bases and the metal complexes is given in Fig. 4. The polarization resistance (Rp) and inhibition efficiency (η %) values of the Schiff bases and the metal complexes in 0.1 M HCl solution were given in Table-3.
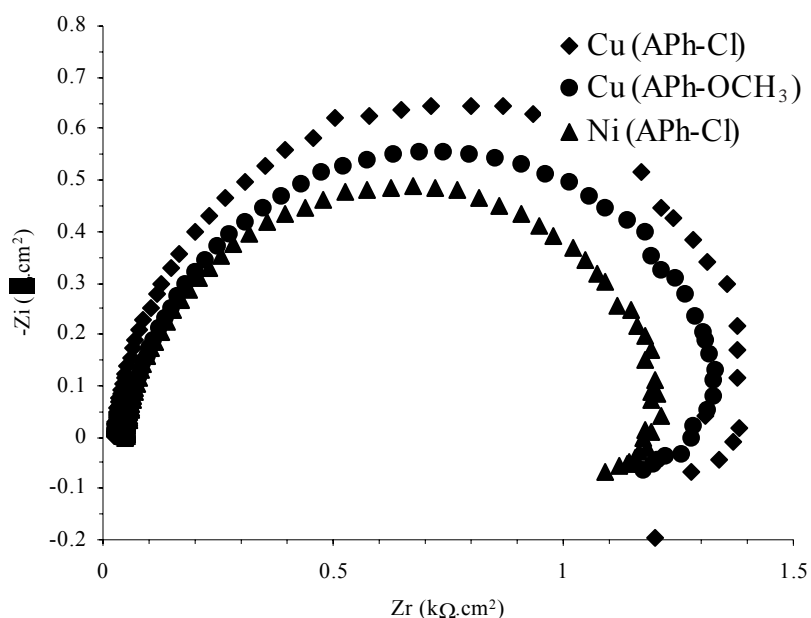

Fig. 4.

TABLE-3
PROTONATION CONSTANTS, STABILITY CONSTANTS AND INHIBITOR
EFFICIENCY OF THE SCHIFF BASES AND THE METAL COMPLEXES

Compound	$\log K_1^H$	$\log K_2^H$	i_{corr}	E_{corr} (mV)	η %	Rp (ohm cm^2)	$\eta (R_p)$ %
Bare			9.74	-737.2		491.5	
(APh-OCH$_3$)	9.87±0.03	6.42±0.03	9.25	-776.0	5	574.2	14
(APh-Cl)	8.69±0.02	3.86±0.02	7.25	-750.1	26	786.6	38
[Cu(APh-OCH$_3$)]	6.73±0.02	5.24±0.01	4.79	-744.1	56	1333.0	63
[Cu(APh-Cl)]	4.21±0.04	3.37±0.04	3.44	-697.6	65	1382.0	64
[Ni(APh-OCH$_3$)]	5.17±0.02	3.91±0.01	3.97	-736.3	39	889.7	45
[Ni(APh-Cl)]	4.05±0.02	3.07±0.01	4.61	-755.7	53	1189.0	59
[Co(APh-OCH$_3$)]	5.83±0.02	4.24±0.01	7.57	-749.7	22	674.4	27
[Co(APh-Cl)]	4.07±0.02	3.11±0.01	7.53	-764.7	23	686.8	28

Potentiodynamic polarization and AC impedance studies were carried out on the inhibition of aluminium in 0.1 M HCl solution with 2-aminophenol-Schiff basses and their metal complexes. 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.

From the impedance measurements, inhibition efficiencies were calculated using the following expression:

$$\eta(\%) = \frac{R_p - R_p^o}{R_p}$$

where R_p and R_p^o denote polarization resistance of electrode with and without inhibitor, respectively, evaluated from Nyquistic diagrams using circular recreation analysis.

It is noticed from Fig. 4 that all the plots display a single capacitive loop, the impedance diagrams show semi-circles indicating a barrier layer formed on the surface and a charge transfer process mainly controlling the corrosion of aluminium.

The diameter of the semi-circles decreases the order [Cu(APh-Cl)] > [Cu(APh-OCH$_3$)] > [Ni(APh-Cl)] >[Ni(APh-OCH$_3$)] >(APh-Cl) > [Co(APh-Cl)]) > [Co(APh-OCH$_3$)] > (APh-OCH$_3$) depend on the influence of the structure.

In order to better define the action of different additives on the corrosion process a series of anodic and cathodic polarization curves were recorded after an immersion of 0.5 h. Table-3 shows the curves recorded in 5 % HCl solution with and without inhibitor additive. Table-3 shows the values of corrosion current densities, corrosion potential and inhibitor efficiency (η %) as a function of each addives. η is defined as

$$\eta\% = \frac{i_{corr} - i_{corr(inh)}}{i_{corr}}$$

where i_{corr} and $i_{corr\ (inh)}$ are corrosion currents without and with inhibitor present, respectively[21]. The E_{corr} and i_{corr} shown in Table-3 demonstrated that compounds under study reduce the corrosion current and render the corrosion potential more negative except (APh-Cl). The Schiff base (APh-OCH$_3$) render the corrosion potential more positive. It should be noted that inhibiting efficiency of copper complex of Schiff bases is the highest; reaching a value of 65.0 % likely is measurement.

Conclusion

(i) Three basic coordination structures of metal complexes have been determined by spectral analyses. Cu(II), Ni(II) and Co(II) complexes have square-based pyramidal, square-planer and tetrahedral geometric structure, respectively. These geometric structures originate from three different tendencies of the complexes behaviour as corrosion inhibitor in acidic solution. The copper complexes of the Schiff bases shows 64 %, Ni and Co complexes shows 59 and 28 protection to aluminium in 0.1 M HCl with two different techniques. (ii) 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. (iii) The difference in the inhibitive efficiencies of the (APh-Cl) and (APh-OCH$_3$) 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. (iv) The conjugation ligend 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.

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