



## Synthesis, characterization and corrosion inhibition of cobalt (II) azo schiff base chelate

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### ABSTRACT

The azo Schiff base (A.S.B) under study was synthesized by mixing Schiff base and 2-aminobenzoic acid, whereas, the used Schiff base was obtained from the refluxing of salicylaldehyde and 2-aminothiophenol. The azo Schiff base reacted with Co(II) ion giving a chelate. The synthesized azo Schiff base and its Co(II) chelate were subjected to several physicochemical techniques; such as, CHNS elemental analyses, molar conductivity, IR, electronic, <sup>1</sup>HNMR and mass spectra. The used techniques showed the formation of 2:1[M:L]chelate and confirm the geometrical structures of the azo Schiff base and its Co(II) chelate. A square planar geometry was established for the chelate. The inhibition characteristics of azo dye on steel corrosion in hydrochloric acid media is investigated at 30<sup>0</sup>C. The results showed a high protection efficiency (greater than 85%) for acid corrosion of steel at its low concentration (3×10<sup>-3</sup>M).

**Keywords:** Synthesis, Characterization, Azo Schiff base, Co(II) Chelate, Corrosion Inhibition, physicochemical techniques.

### INTRODUCTION

Schiff bases derived from salicylaldehyde and primary amines and their complexes played an important part in the development of inorganic chemistry as widely studied coordination compounds and are increasingly important in applications such as biochemical, analytical and antimicrobial reagents [1, 2]. Also they have been used as antibacterial, antifungal, anticancer, antitubercular, hypertensive and hypothermic reagents [3]. Azo Schiff base complexes of VO(II), Mn(II), Co(II), Ni(II) and Cu(II) ions have been synthesized from N-5-(4-chlorophenyl)diazonyl-2-hydroxybenzyl-idene)-2-hydroxybenzohydrazide. The nature of bonding and the structural features of the complexes have been deduced from applying of several physicochemical techniques. The used techniques revealed a square planar geometry for Cu(II) complex, square pyramidal for oxovanadium complex and tetrahedral structure for the other complexes[4]. The azo Schiff base derived from N-4-methoxybenzylidene-3-hydroxyphenylamine(SB) and 2-aminophenol reacted with Ni(II) ion to form azo Schiff base chelate. The azo Schiff base and its Ni(II) chelate were characterized by CHN elemental analyses, molar conductivity, IR, UV-Vis, <sup>1</sup>HNMR and mass spectroscopies. The analytical and spectral results supported the formation of the azo Schiff base and the Ni(II) chelate in 2:1[M:L] ratio. And confirmed a square planar geometry for the chelate [5].

This study aims to synthesis, investigate the capability of the diazo Schiff base in coordination and study the corrosion inhibition of azo Schiff base and its Co(II) chelate.

## EXPERIMENTAL SECTION

### Chemicals and Methods

All chemicals used in this study are of high grade (BDH\Aldrich) including; salicylaldehyde, 2-aminothiophenol, 2-aminobenzoic acid, ethanol, dimethylformamide (DMF), sodium hydroxide, dimethylsulphoxide (DMSO),  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  and double distilled water. The synthesized azo Schiff base and its Co(II) chelate were subjected to CHNS elemental analyses using Perkin-Elmer 2400 elemental analyzer, infrared spectra were obtained by KBr disc technique by using IFS-25DPUSR\IR spectrometer (Bruker) in the range of  $4000\text{-}400\text{ cm}^{-1}$ , proton nuclear magnetic resonance spectrum of the azo Schiff base was recorded on Varian Gemini 200-200MHz spectrometer using TMS as internal standard and  $\text{D}^6$  DMSO as a solvent, The electronic spectra of the azo Schiff base and its Co(II) chelate were measured in DMSO solvent using a Perkin-Elmer-Lambda  $\beta$ -spectrophotometer. The mass spectra were carried out by using Shimadzu QP-2010 Plus. The molar conductivity of the chelate was measured in DMF solvent using digital conductivity meter CMD 650, at chemistry department, Sebha University, Sebha, Libya. All the mentioned analyses were done at Micro analytical center, Cairo University, Giza, Egypt.

### Synthesis of Schiff base (SB)

The Schiff base was synthesized by dissolving 0.01 mole; 1.22 g of salicylaldehyde and 0.01 mole; 1.25 g of 2-aminothiophenol in 50 ml ethanol. The mixture was refluxed for two hours, then the obtained product was concentrated in vacuum to remove ethanol. The product was filtrated, dried and recrystallized from suitable solvent (yield = 70.72 %).

### Synthesis of azo Schiff base (ASB)

The azo Schiff base (ASB) under investigation was synthesized by mixing 0.01 mole; 2.29 g of Schiff base with 0.01 mole; 1.37 g of 2-aminobenzoic acid in 50 mL of ethanol in the presence of 10% NaOH,  $\text{NaNO}_2$  solution and conc. HCl. The obtained azo Schiff base was acidified by dilute hydrochloric acid until pH= 2-4. The isolated compound was filtrated, washed several times with distilled water until the filtrate becomes free from chloride ion by testing it with silver nitrate solution, dried and recrystallized from suitable solvent then dried in desecrator over calcium chloride (yield = 64.94%).

### Synthesis of azo Schiff base Co(II) chelate

The reaction of azo Schiff base (ASB) ( 0.01 mole; 3.77 g) with 0.01 mole; 2.37g of  $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$  in 50 mL ethanol was refluxed for three hours, then filtered and washed several times with hot ethanol until the filtrate becomes colorless. The chelate was dried in desecrator over calcium chloride for a night.

### Corrosion

The corrosion rate of steel sample in 0.5M, HCl was determined by mass loss technique, the specimens used were cut in the form of rods of dimensions 40 mm length and 10 mm diameter. The commercial steel rods that collected from Musrata steel factory was of composition given as: C= 0.32, Si= 0.21, Mn= 0.75, P= 0.014, S= 0.004, Cr= 0.20, Ni= 0.001, Cu= 0.001, Al= 0.002, Fe to 100 (by weight). Before the measurements, the samples were mechanically polished with a series of emery papers with different grades (60,100,120,180,220,320,400 and 1200) starting with coarse one and proceeding to the finer grades. Both sample and solution were allowed to attain temperature equilibrium for a minimum of 20 min prior to starting the corrosion experiments. The reactions were under stagnant conditions at  $30^\circ\text{C}$  and rates followed for a maximum of 1 hour to avoid drastic changes in surface characteristics.

### Inhibitors

All the chemicals used are analytical grade. Freshly distilled deionized water was used in all preparations. Azo Schiff base namely (ASB) as corrosion inhibitor in 0.5M, HCl medium was prepared in dimethylformamide. All tested solutions containing 10 vol. percent of DMF to maintain complete soluble.

## RESULTS AND DISCUSSION

The azo Schiff base (ASB) and its Co (II) chelate have been investigated on the basis of elemental analysis, molar conductivity and spectroscopic techniques. The analytical, IR, electronic,  $^1\text{H}$ NMR and mass spectral data (Table 1) of the azo Schiff base product proposed that the reaction occurred in 1:1: ratio. The azo Schiff base and its Co(II) chelate are colored solids and stable in air. They are insoluble in water but soluble in coordinating solvents, such as DMF solvent. The melting points of the azo Schiff base and its Co(II) chelate are 132.20 and  $>250\text{ }^\circ\text{C}$ , respectively. The CHNS elemental analyses exhibit that the calculated values are in a good agreement with found data (Table I). The CHNS elemental analysis data together with the non-electrolytic nature, [6] in DMF solvent suggest 2:1 [M:L] ratio.

**Table-1: Elemental analyses, some physical properties, infrared and electronic spectral data of ASB and its Co(II) chelate**

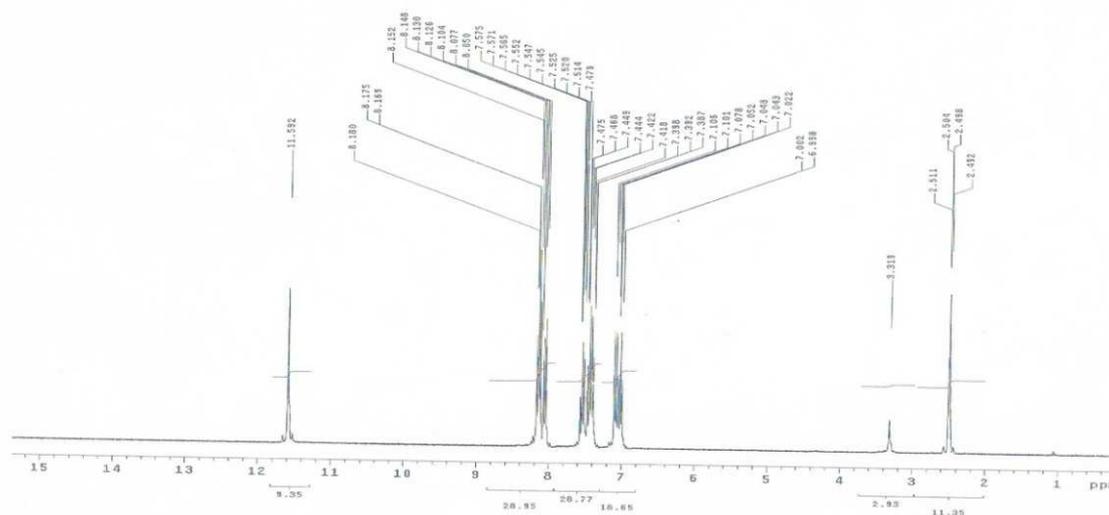
azo Schiff base/ Chalets	M. Wt	Color	M.P °C	Yield %	Found (Calcd.), %				UV-Vis nm (cm-1)
					C%	H%	N%	S%	
ASB (C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S); L	377.00	Bright , golden	132 .1	70.72	63.66 (63.68)	3.98 (3.00)	11.14 (11.73)	8.49 (8.25)	2874(34843), 329(30395)
[Co <sub>2</sub> (ASB)(OH) <sub>2</sub> (H <sub>2</sub> O)]H <sub>2</sub> O	561	light Olive	>250.00	54.00	44.04 (44.68)	3.12 (3.90)	7.71 (7.55)	5.87 (5.27)	290(34483), 332(30120)
azo Schiff base/ Chalets	IR (cm-1)								m/e+
	$\nu(\text{OH})$	$\nu(\text{HCN})$	$\nu(\text{COOH})$	$\nu(\text{N}=\text{N})$	$\nu(\text{C}-\text{OH})$	$\nu(\text{SH})$	$\nu(\text{M}-\text{O})$	$\nu(\text{M}-\text{N})$	
ASB (C <sub>19</sub> H <sub>15</sub> N <sub>3</sub> O <sub>3</sub> S); L	3416	1616	2762	1482	1311	3055	-	-	377, 330, 302, 285, 258, 52
[Co <sub>2</sub> (ASB)(OH) <sub>2</sub> (H <sub>2</sub> O)]H <sub>2</sub> O	3436	1598	-	1475	1273	3052	626	549	450, 421, 259, 227, 55

### Infrared spectra of azo Schiff base and its Co(II) chelate

The infrared spectral data of the azo Schiff base (ASB) and its Co(II) chelate were listed in table 1. The infrared spectrum of the synthesized azo Schiff base chelate exhibits a band at 3436 cm<sup>-1</sup> due to the existence of water molecule as hydrated and coordinated [7]. Meanwhile, the same spectrum shows a band at 1598 cm<sup>-1</sup> attributed to  $\nu$  (-HC=N) vibration, the changing of this band comparing to the free ligand (1616 cm<sup>-1</sup>) confirmed the involvement of this group in chelation through nitrogen atom [8]. The spectrum of the chelate exhibits a change in the position of the thio group (SH) indicating the involvement of this group in complexation through sulfur atom [9]. Also the azo Schiff base spectrum displays the azo (-N=N-) group at 1482 cm<sup>-1</sup>, this group is changing to lower frequency suggests its participation in bonding with the metal ions [10]. New bands at 626 and 549 cm<sup>-1</sup> which are not present in the azo Schiff base are attributed to  $\nu(\text{M}-\text{O})$  and  $\nu(\text{M}-\text{N})$  vibrations [11], and the their appearance of these vibrations support the participation of oxygen and nitrogen atoms of the azomethine, azo and OH groups of the azo Schiff base in chelation process.

### Proton nuclear magnetic resonance spectrum of azo Schiff base

The <sup>1</sup>HNMR spectrum of the azo Schiff base compound (Fig. 1) was measured using in d<sup>6</sup>-DMSO solvent. The azo Schiff base spectral results show signals at 8.19 and 11.58 ppm which are assigned to the presence of protons of azomethine and hydroxyl groups, respectively. Also, the same spectrum displays signal between 7.00-7.56 ppm attributed to phenyl rings. The signals at 2.51 and 3.51 ppm due to the existence of methyl and DMSO solvent groups in the compound. Meanwhile, the signal which appeared at 3.31 ppm in the spectrum of the free compound is attributed to the presence of thio (SH) group [12].

**Fig.(1): <sup>1</sup>HNMR spectrum of ASB**

### Mass spectra of the azo Schiff base and its Co(II) chelate

The mass spectral fragmentations of the azo Schiff base (ASB) and its Co(II) chelate are shown in schemes 1 and 2, table 1 and figures (2, 3). The base peak of azo Schiff base at m/e+ = 377. is attributed to the original molecular weight. Meanwhile, the peak at m/e+ = 330 is analogous to the loss of COOH and two hydrogen atoms from the azo Schiff base. The loss of two nitrogen atoms give a peak at m/e+ = 302. The peak at m/e+ = 285 due to loss of hydroxyl group. The same spectrum shows a peak at m/e+ = 258 corresponding to loss of azomethine (HCN) group. A peak at m/e+ = 52 is analogous to the appearance of C<sub>4</sub>H<sub>7</sub> ion. For Co(II) chelate, the spectrum exhibits a peak at m/e+ = 450 due to loss of water molecule, COOH and two oxygen atoms. The peak at m/e+ = 421 corresponding to

the loss of azomethine group and two hydrogen atoms. The peak at  $m/e = 259$  due to the loss of azo group, two cobalt and oxygen atoms. The loss of the thio group (SH) gives a peak of  $m/e = 227$ . The same spectrum shows a peak at  $m/e = 55$  analogous to the appearance of  $C_4H_4$  ion.

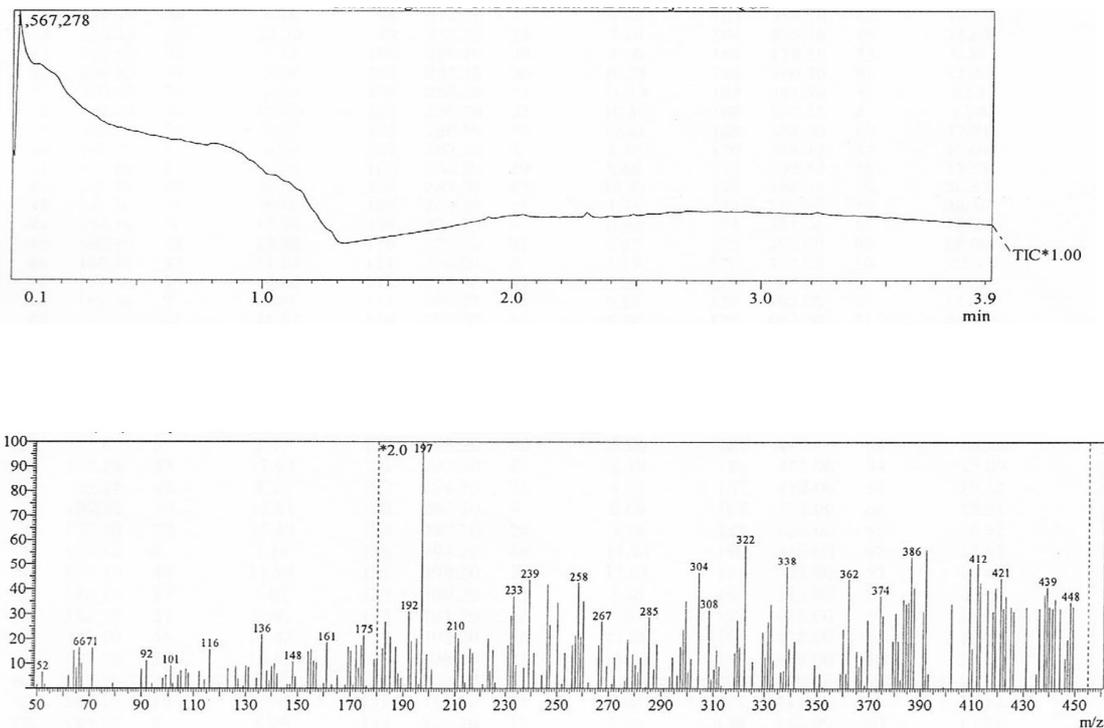
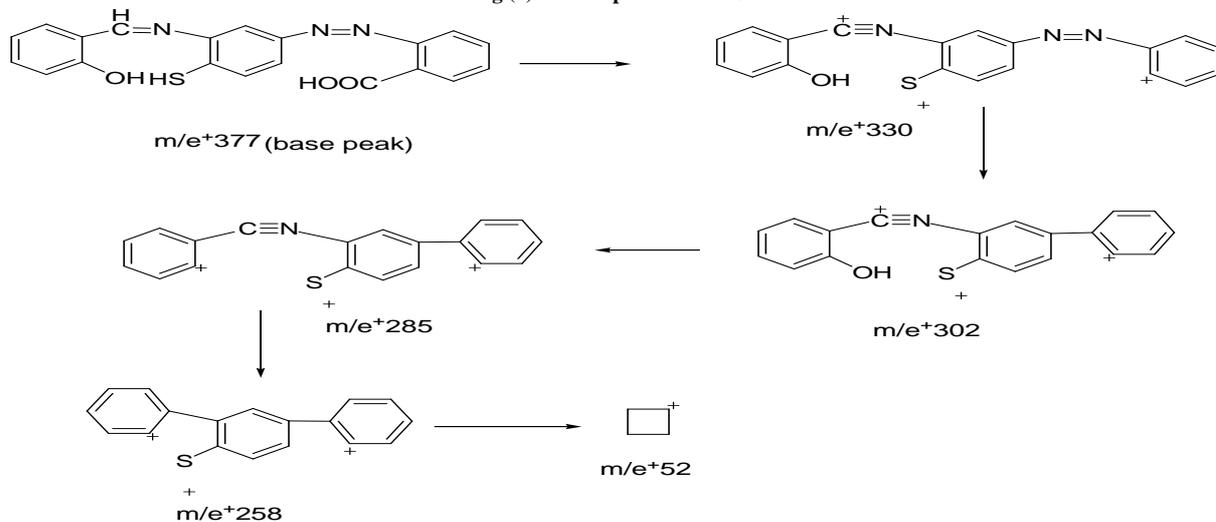
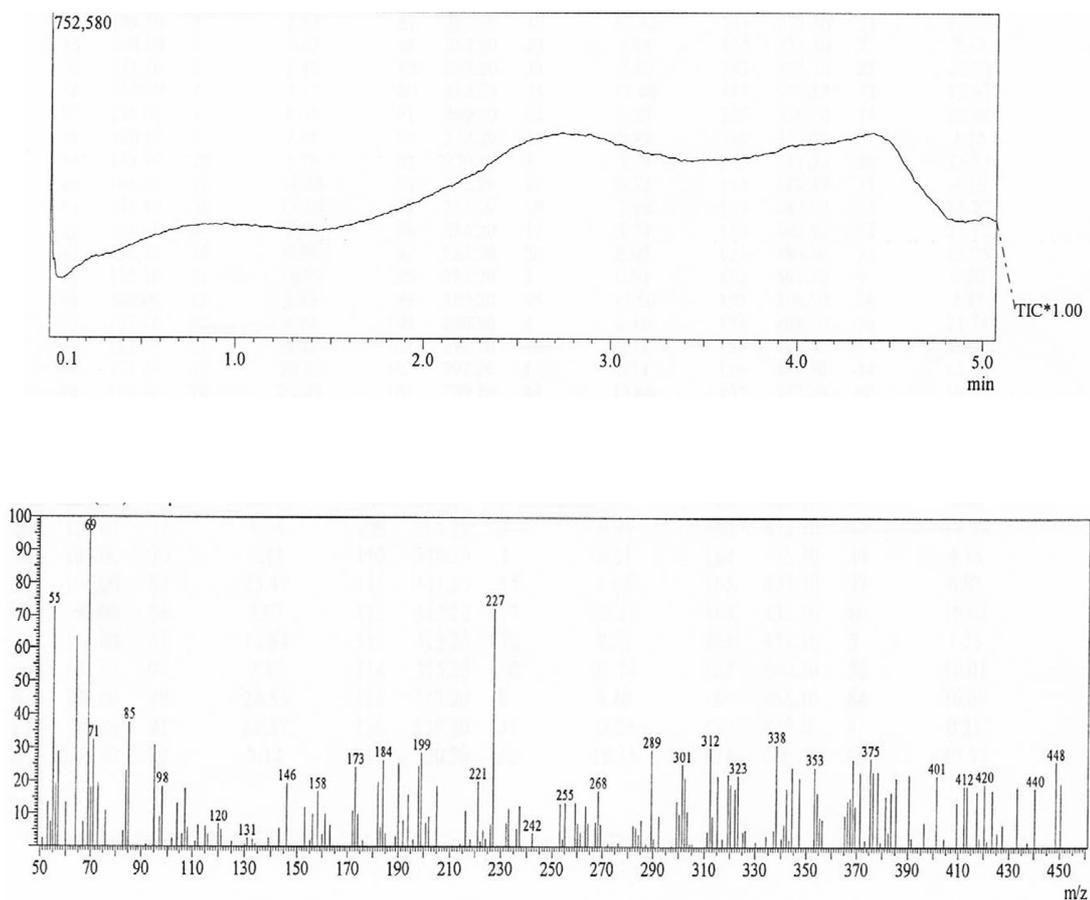
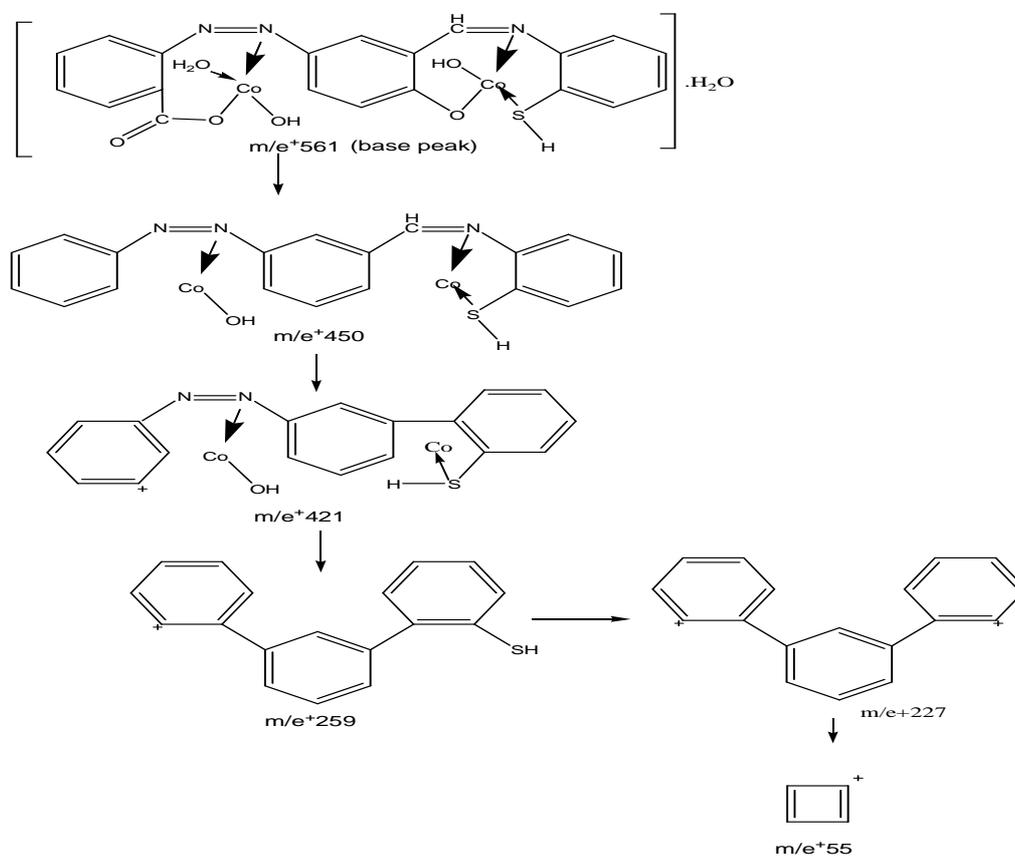


Fig.(2): Mass spectrum of ASB



Scheme (1): Mass spectral fragmentation of ASB

Figure (3): Mass spectrum of  $[\text{Co}_2(\text{ASB})(\text{OH})_2\text{H}_2\text{O}]\text{H}_2\text{O}$ Scheme (2): Mass spectrum of  $[\text{Co}_2(\text{ASB})(\text{OH})_2\text{H}_2\text{O}]\text{H}_2\text{O}$

### Electronic spectra of azo Schiff base and its Co(II) chelate

The electronic spectral results of the azo Schiff base show two bands at 287 nm ( $34843\text{ cm}^{-1}$ ) and 329 nm ( $30395\text{ cm}^{-1}$ ) due to  $\pi\rightarrow\pi^*$  (Phenyl rings) and  $n\rightarrow\pi^*$  (H-C=N and azo group) transitions [13]. The electronic spectral studies of Co(II) chelate with the azo Schiff base was carried out in DMSO solvent. The square planar chelate that contains a metal ion of  $d^7$  electronic configuration is paramagnetic. The spectrum of Co(II) chelate shows two bands at 290 nm ( $34483\text{ cm}^{-1}$ ) and 332 nm ( $30120\text{ cm}^{-1}$ ) ascribed to the two component excitation  ${}^1A_{1g}\rightarrow{}^1B_{3u}$ ,  $B_{2u}$  transitions [14].

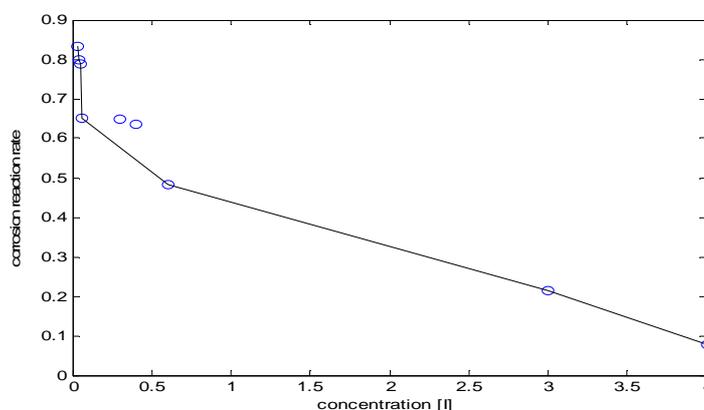
### Corrosion Inhibitions

Rates of dissolution were determined chemically by WL at  $30^\circ\text{C}$ . Table 2 gives the corrosion rate and inhibitor efficiency for mild steel in 0.5M HCl, 10% DMF in absence and presence of different concentration of azo Schiff base (ASB) at  $30^\circ\text{C}$ . This shows that the corrosion rate decreases and inhibitor efficiencies increase with increasing concentration of each inhibitor at given temperature.

**Table-2: Corrosion parameters obtained from WL data for mild steel in 0.5 M, HCl, 10% DMF in absence and presence of different concentrations of azo Schiff base (ASB) at  $30^\circ\text{C}$**

Inhibitor concentration $\times 10^{-3}\text{M/litter}$	$\log[I]$	$C.R.\times 10^{-5}\text{ mg/cm}^2\text{ min}$	Inh%
4	-2.39794	0.0785	98.55
3	-2.52287845	0.2133	96.07
0.6	-3.2218487	0.4823	91.12
0.5	-3.30102999	0.5669	89.61
0.4	-3.39794000	0.6364	88.29
0.3	-3.522878745	.64760	88.08
0.06	-4.22184875	0.6506	88.03
0.05	-4.301029996	0.7880	85.50
0.04	-4.397940009	0.7983	85.31
0.03	-4.522878745	0.8336	84.66

Figure (4) shows the variation of the corrosion rate as a function of the concentration of azo Schiff base (ASB) at  $30^\circ\text{C}$ . As shown in this figure on increasing the concentration of azo Schiff base inhibitor, the corrosion rate decreases.



**Fig (4) :Variation of the corrosion rate with the concentration of Azo Schiff base at  $30^\circ\text{C}$**

Figure (5) represents the variation of percentage inhibitor as a function of the logarithmic concentration of azo Schiff base at  $30^\circ\text{C}$ . As shown in this figure that the efficiency of inhibition of acid corrosion of steel by azo Schiff base is increased as concentration of inhibitor increases at  $30^\circ\text{C}$ .

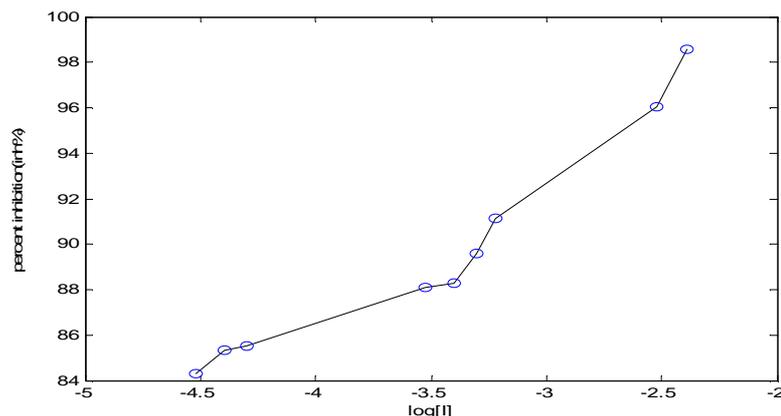


Fig (5): Variation of percentage inhibitor with the logarithmic concentration of azo Schiff base

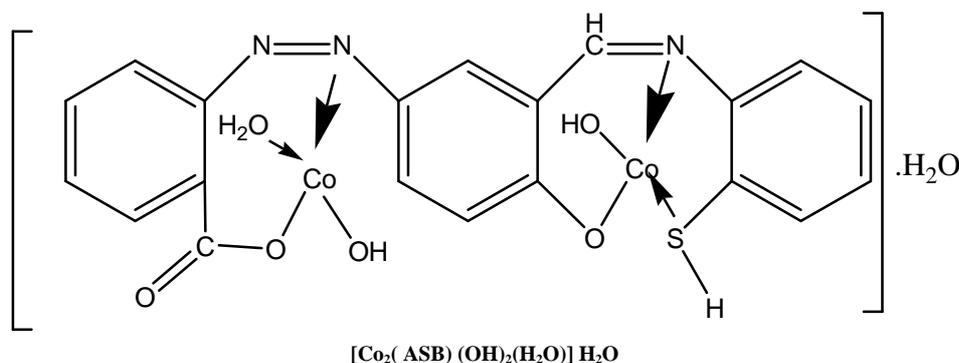
In figure (5), the results have characteristics of S-shaped adsorption isotherm indicative of adsorption mechanisms for the inhibition process.

### DISCUSSION

It is evident that the presence of different withdrawing groups have clear influence on inhibitor efficiency created by adsorption centers (HC=N-, N=N-, -SH, -OH, -COOH). The inhibition effect could be attributed to physisorption process between clean charged steel surface in acidic medium followed by chemisorptions forming coordinate-covalent bond due to its free electron pair atoms. The results show that at 30 °C and low concentration range ( $4 \times 10^{-3}$  -  $4 \times 10^{-5}$  M) gives (85-98%) protection efficiency. The gradual increase in these protection efficiency percentages can be discussed on the basis that presence of double bonds and hetero-electron pair atoms resulting of interaction between this molecule and the metal surface.

### CONCLUSION

From the obtained results, we can suggest the following structure for Co<sub>2</sub> chelate.



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