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Corrosion Inhibition Studies of Benzilic Acid-Tyrosine Ligand and their Metal Complexes

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Abstract: A novel amino acid ligand derived from Benzilic acid and Tyrosine and its Cr (II), Fe (III), Co (II) and Ni (II) transition metal complexes were synthesized. The structure elucidation of the ligand and its complexes were derived on the basis of various spectroscopic methods such as Infrared and electronic spectra along with the aid of CHN, magnetic and conductometric measurements[1, 2, 3]. The corrosion inhibition efficiency of newly synthesized amino acid-mixed ligand and their metal complexes were studied in 0.5M HCl solution. The results show that the inhibitors exhibits an inhibition efficiency of 40-67% at 200ppm.The ligand shows the maximum efficiency whereas on complexation the efficiency tend to decrease. When the concentration of the inhibitor increases, then the efficiency of the inhibitor will increase[4]. The adsorption studies reveal that iron complex with the mild steel is chemisorption and the thermodynamic parameters such as adsorption, equilibrium constant (K) and free energy of adsorption (ΔG_{ads}) were calculated. The curve of the adsorption fits well with Langmuir adsorption isotherm.

Keywords: Benzilic acid, tyrosine, Mild steel, Hydrochloric acid, weight loss, Adsorption

I. INTRODUCTION

Corrosion is the conversion of metals to its native form on reaction with their favorable conditions such as moisture, air, acidic and alkaline media. One of the effective methods to reduce corrosion is the use of corrosion inhibitor. Amino acids are the ecofriendly, non-toxic, biodegradable and cheap alternative against the hazardous compound which can act as a better corrosion inhibitor molecule. Mild steel is an inexpensive, easily available, durable and cheapest form of steel which is widely used for both domestic and industrial applications. Study of corrosion using mild steel is effortless as it easily undergoes rusting when exposed to corrosive environments containing humidity, acids etc. The addition of minute quantities of corrosion inhibitors can make a remarkable change in the rate of corrosion reaction thereby protect the metals from corrosion. The inhibition action of corrosion inhibitors is the result of surface adsorption of inhibitors and the protection layer formation on the metal surface[5,6]. The inhibition action depend on the structure and concentration of inhibitors, microstructure of metal surface, temperature of exposure, pH of the reaction medium and the extent of immersion time[7,8,9].

II. MATERIALS AND METHODS

A. Materials

All the chemicals such as Benzilic acid, tyrosine and metal salts were used without purification. The solvents were purified using standard procedure. The melting points of the ligand and the complexes were recorded with the melting point apparatus. The Gouy balance is used to determine the magnetic susceptibility. The characterization of the prepared compounds was conducted with the help of elemental analysis and various spectral measurements.

B. Synthesis of Benzilic acid - tyrosine ligand (HBT)

Benzilic acid (0.1 M) in aqueous ethanol was mixed with ethanolic solution of tyrosine (0.1 M) potassium salt and refluxed for 3 hours on water bath. The resulting solution concentrated for few minutes and the ligand crystallizes out and washed with ethanol and dried over anhydrous $CaCl_2$.The melting point of the ligand was found to be 298^0 C.

C. Synthesis of the metal complexes

The metal complexes of Benzilic acid –tyrosine (HBT) solution were prepared by adding the metal acetate/chloride solution dropwise to the hot ethanolic solution of Benzilic acid –tyrosine (HBT) and refluxed for 1 hour. A pinch of sodium acetate trihydrate was added and was refluxed for 1 hour, and cooled to room temperature. The precipitate of the prepared complexes were collected and washed several times with aqueous ethanolic solution. These complexes were dried by storing it in the dessicator.

D. *Method*

1) *Weight Loss Method:* In the weight loss measurement method, 0.5 M HCl solutions are prepared by diluting the 37% HCl using the double distilled water. Different concentrations (50ppm, 100 ppm, 150 ppm, 200 ppm) of the inhibitor solution were prepared by dissolving the required amount of inhibitor ligand in 80 ml of 0.5 M HCl solution. Blank solution used for the analysis is 80 ml of 0.5 M HCl solution without any inhibitor. During the experiment, beakers of 100 ml capacity were marked, which are holding 80 ml of the inhibitor solution and in one beaker blank solution is taken. Mild steel coupons of 1×1×0.1 cm dimension were used for the study of corrosion inhibition and these mild steel coupons were abraded with emery paper, washed with ethanol, acetone and distilled water, then dried and weighed. With the help of these dimensions, the measurement of the area of the mild steel coupons has been carried out. The mild steel coupons were hanged in the inhibitor solutions for 24 hrs at room temperature and weight of the coupons was measured after cleaning thoroughly with distilled water and acetone. Weight loss of the coupons (ΔW) was determined by measuring the difference between coupons before immersion and after immersion, i.e,

$$\Delta W = m_1 - m_2 \qquad \ldots\ldots\ldots\ldots\ldots\ldots\ (1)$$

Where m_1 is the mass of the specimens before immersion and m_2 be the mass of the specimen after corrosion.
The corrosion rate was calculated from the following equation

$$\text{Corrosion rate, CR} = (87600 \times Wt)/dt$$

Where W is the weight loss in mg, d is the density of the specimen and t is the time of exposure of the sample in hours.
The inhibition efficiency of the inhibitor was equated with the help of the following formula

$$\text{Inhibition efficiency, \% IE} = [(\Delta W_1 - \Delta W_2)/\Delta W_1] \times 100$$

Where, ΔW_1= weight loss without inhibitor
ΔW_2 = weight loss with inhibitor

2) *Adsorption Studies:* The inhibitory action of the organic inhibitors is proposed to be due to the adsorption of inhibitor organic molecules on the metal surface by the replacement of water molecules which is already adsorbed on the metal surface which act as a compact barrier film that blocks the active sites of corrosion.

$$\text{inh}_{\text{soln}} + xH_2O_{\text{metal}} \longrightarrow \text{inh}_{\text{metal}} + xH_2O_{\text{soln}}$$

The evaluation of process of adsorption has been carried out by fitting the surface coverage, θ as a function of concentration at constant temperature. The various adsorption isotherms like Langmuir, Freundlich, Temkin etc was plotted with the given data and the best fitted isotherm was selected. In the current work the best fit isotherm was chosen to be Langmuir, which can be represented by the following equation

$$C_{\text{inh}}/\theta = 1/K_{\text{ads}} + C_{\text{inh}}$$

and is given by a plot of C_{inh}/θ vs C_{inh} where surface coverage θ was determined from the charge transfer resistance using the relation

$$\theta = \frac{R_{ct} - R^0_{ct}}{R_{ct}}$$

The equilibrium constant (K_{ads}) was obtained from the reciprocal of the slope and it is used to determine the strength of the adsorption. The free energy of adsorption G^0_{ads} is correlated to the equilibrium constant (K_{ads}) using the equation

$$G^0_{ads} = -RT\ln(55.5\ K_{ads})$$

Where R is the universal gas constant in KJ mol^{-1}, 55.5 is taken as concentration of water in mol/L and T is the temperature. The G^0_{ads} values gave an idea about the type of adsorption like physisorption, chemisorption or mixed. The high value of adsorption constant indicates the stronger adsorption of the inhibitor, typically values up to -20 KJ /mol related to the electrostatic interactions between the charged molecules and the metal (physisorption), whereas around -40 KJ/mol or more negative associated with the chemisorption as a result of sharing or transfer of electron pair or π electrons from the organic inhibitor molecules to the mild steel coupon surface to form a coordinate bond.

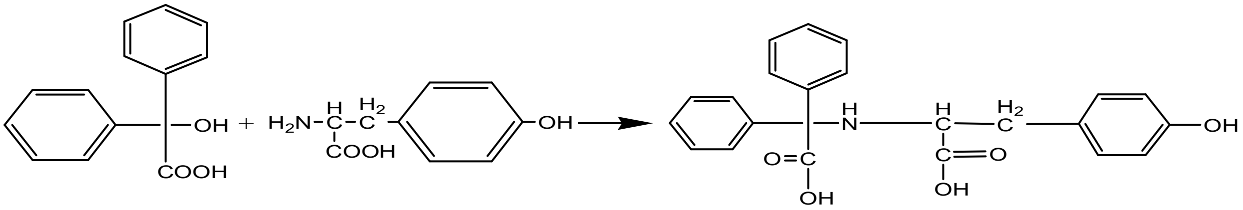
III. RESULTS AND DISCUSSION

A. Characterization Of The Synthesized Compounds

Compound	Molecular Weight	Melting point	Colour	yield	Ω^{-1}	μ_{eff}	M%
$C_{23}H_{19}NO_5$(HBT)	391.43	290^0	Pale yellow	80	-	-	-
Cr(BT)$(H_2O)_4$	515.43	$>300^0$	Dark green	65	8.55	1.52	10.08 (10.27)
Fe(BT)$(H_2O)_2Cl_2$	554.27	$>300^0$	Light brown	70	9.73	3.18	10.07 (10.12)
Co(BT)$(H_2O)_4$	522.36	$>300^0$	Pink brown	60	4.56	4.32	11.28 (11.90)
$Ni(BT)_2(H_2O)$	877.69	$>300^0$	Bluish green	60	4.79	3.38	6.68 (6.40)

TABLE 1.Analytical data of ligand (HBT) and its complexes

1) *Benzilic acid-tyrosine Ligand:* The FT-IR spectrum of the ligand was recorded in the range 4000-400 cm^{-1}. In which the band at 3207 cm^{-1} may due to N-H stretching vibration. The broad band observed at 3437 cm^{-1} is due to the O-H stretching vibration[10]. The bands at 1609 and 1416 cm^{-1} are assigned to υ (COO_{asymm}) and υ (COO_{symm}) respectively. The υ (C=O) band is at 1732 cm^{-1} and the υ (C-O) band is at 1244 cm^{-1}. The electronic spectrum of the HBT ligand was recorded in the range 200-900 nm. The compound gives peaks at 233,279 and 330 nm in which former peak indicates the $\pi\rightarrow\pi^*$ transition and the latter may be due to $n\rightarrow\pi^*$ transition.



Scheme. 1. Preparation of HBT ligand

2) *Chromium complex of Benzilic acid-tyrosine Ligand:* In the IR spectra of Chromium complex a band observed at 3205cm^{-1} can be assigned to the N-H vibration, suggesting that NH bond do not involve in the complexation. The disappearance of band at 3437 cm^{-1} predicts the involvement of OH group of carboxylic acid in the coordination to the metal ion. The bands at 1491 and 1344 cm^{-1} are attributed to υ (COO_{asymm}) and υ (COO_{symm}) respectively. The difference between υ (COO_{asymm}) and υ (COO_{symm}) is ≈200 cm^{-1} which suggests the monodentate behaviour of the carboxylate anion. The band at 841 cm^{-1} assigned to the coordinated water. Band at 698 cm^{-1} is assigned to the υ (M-O) stretching of the complex. The solid state uv-visible spectrum gives peaks at 233,279 and 330 nm in which former peak indicates the $\pi\rightarrow\pi^*$ transition and the latter may be due to $n\rightarrow\pi^*$ transition. They exhibits three spin-allowed transitions i.e. ^4A_2g (F) → ^4T_2g (F) (v_1), ^4A_2g (F) → ^4T_1g (F) (v_2), ^4A_2g (F) → ^4T_1g (P) (v_3) at 340 nm, 351 nm and 594 nm respectively suggesting the octahedral stereochemistry of the chromium complexes.
3) *Iron complex of Benzilic acid-tyrosine Ligand:* The IR of Iron complex shows a band at 3205 cm^{-1} is assigned to the N-H vibration. The bands at 1512 and 1330 cm^{-1} are attributed to υ (COO_{asymm}) and υ (COO_{symm}) respectively. The difference between υ (COO_{asymm}) and υ (COO_{symm}) is ≈200 cm^{-1} which suggests the monodentate behaviour of the carboxylate anion. The band of OH group of carboxylic acid at 3437cm^{-1} is absent in the complex proposed the complexation of the carboxylic group to the metal ion. The band at 840 cm^{-1} assigned to the coordinated water. Peak at 649 cm^{-1} is due to the υ (M-O) stretching of the complex. The solid state uv-visible spectrum gives peaks at 233,279 and 330 nm in which former peak indicates the $\pi\rightarrow\pi^*$ transition and the latter may be due to $n\rightarrow\pi^*$ transition. In the current work absorption band of Fe (III) complex are in the range 891 nm assigned to$^5T_2g\rightarrow{}^5Eg$ transition. A strong charge transfer band is observed at 389 nm. From spectral data, an octahedral geometry is proposed for the Fe (III) chelate.

4) *Cobalt complex of Benzilic acid-tyrosine Ligand:* The IR of chromium complex shows a peak at 2919cm^{-1} is assigned to the N-H vibration. The bands at 1466 and 1382 cm^{-1} are attributed to υ (COO$_{asymm}$) and υ (COO$_{symm}$) respectively. The difference between υ (COO$_{asymm}$) and υ (COO$_{symm}$) is ≈200 cm^{-1} which suggests the monodentate behaviour of the carboxylate anion. The band of OH group of carboxylic acid at 3437cm^{-1} is absent in the complex suggests the complexation of the group with the metal ion. The band at 824 cm^{-1} assigned to the coordinated water. Peak at 495 cm^{-1} is due to the υ (M-O) stretching of the complex. The solid state uv-visible spectrum gives peaks at 233,279 and 330 nm in which former peak indicates the $\pi \rightarrow \pi^*$ transition and the latter may be due to $n \rightarrow \pi^*$ transition. Two bands present in electronic spectra of Co (II) at ≈881 and 260 nm. It is assignable to octahedral geometry.
5) *Nickel Complex of Benzilic acid-tyrosine Ligand:* The IR of chromium complex shows a peak at 2971 cm^{-1} is assigned to the N-H vibration. The bands at 1466 and 1382 cm^{-1} are attributed to υ (COO$_{asymm}$) and υ (COO$_{symm}$) respectively. The difference between υ (COO$_{asymm}$) and υ (COO$_{symm}$) is ≈200 cm^{-1} which suggests the monodentate behaviour of the carboxylate anion. The band of OH group of carboxylic acid at 3437cm^{-1} is absent in the complex suggests the complexation of the group with the metal ion. Peak at 515 cm^{-1} is due to the υ (M-O) stretching of the complex. The solid state uv-visible spectrum gives peaks at 233,279 and 330 nm in which former peak indicates the $\pi \rightarrow \pi^*$ transition and the latter may be due to $n \rightarrow \pi^*$ transition. Nickel complex exhibits three bands in the region 895 nm, 670 nm and 371 nm. Using energy level diagram these band are assigned to the transition $^{3}A_{2}g$ (F) → $^{3}T_{2}g$ (F) (υ_1), $^{3}A_{2}g$ (F) → $^{3}T_{1}g$ (F) (υ_2) and $^{3}A_{2}g$ (F) → $^{3}T_{1}g$ (P) (υ_3) respectively, for an octahedral stereochemistry.

B. *Corrosion Inhibition Study*

The current work discussed about the corrosion inhibition efficiency of the amino acid ligand and their metal complexes which depends on the nature of the metal ion present in the complexes as well as the number of lone pair of electrons. Generally ligands exhibit high potential due to more number of unpaired electrons which is getting bonded in the case of metal complexes during their formation.

Inhibition	Inhibitor Concentration(ppm)	Weight loss	IE(%)	CR(mmy^{-1})
Ligand	50	0.354	22.491	41.6065
	100	0.32	30.795	37.1487
	150	0.1309	47.239	15.1961
	200	0.0908	63.401	10.5409
Cr complex	50	0.388	45.428	45.042
	100	0.337	52.601	39.122
	150	0.32	54.571	38.077
	200	0.159	77.637	18.458
Fe complex	50	0.778	43.31	47.480
	100	0.414	46.78	37.148
	150	0.409	47.42	15.196
	200	0.344	55.78	10.540
Co complex	50	0.758	4.353	87.99
	100	0.682	10.02	79.173
	150	0.574	24.27	66.635
	200	0.452	40.36	52.472
Ni complex	50	0.699	5.485	81.146
	100	0.672	6.446	78.012
	150	0.651	8.438	75.574
	200	0.514	27.707	59.670

TABLE.2.Corrosion rate (CR) and Percentage Inhibition Efficiency (IE) in the absence and presence of inhibitor for the mild steel in 0.5M HCl for 24 hrs

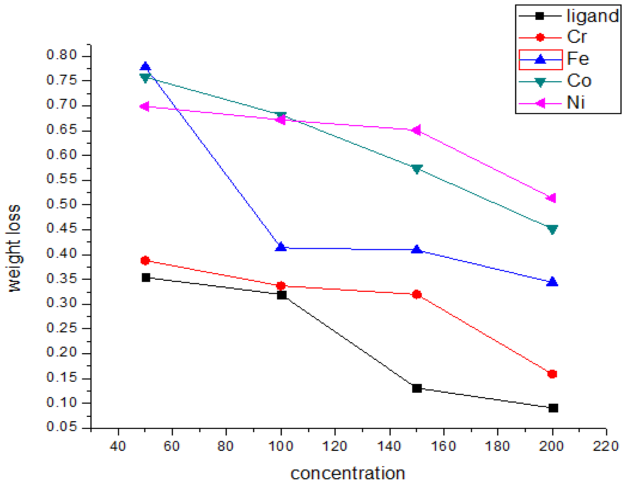


Fig.1.Variation of weight loss against concentration of HBT ligand and its metal complexes at 24 hrs

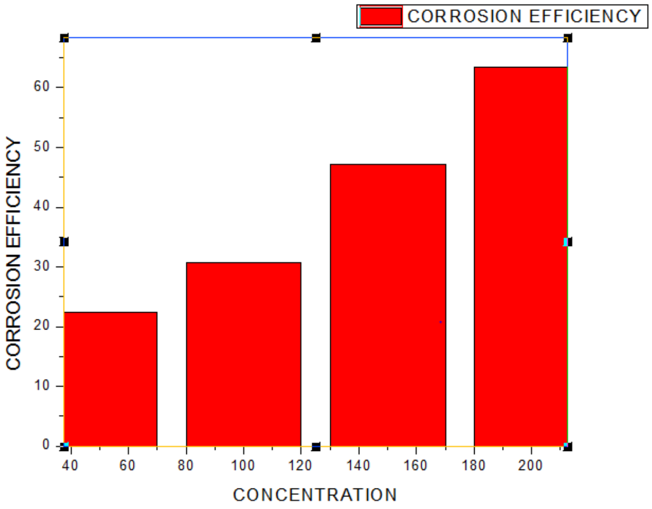


Fig.2.Variation of Inhibition efficiency against concentration of HBT ligand at 24 hrs

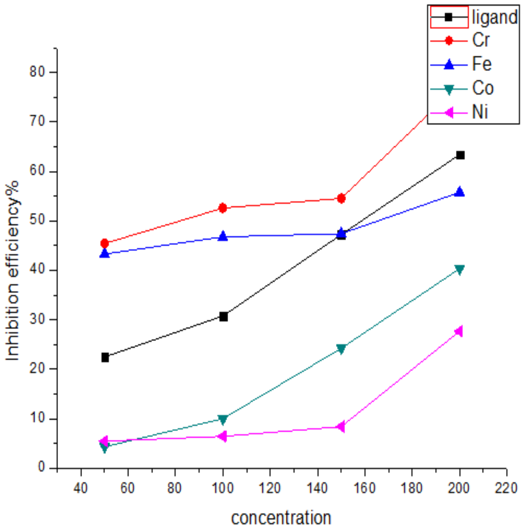


Fig.3.Variation of Inhibition efficiency against concentration of HBT ligand and its metal complexes at 24 hrs

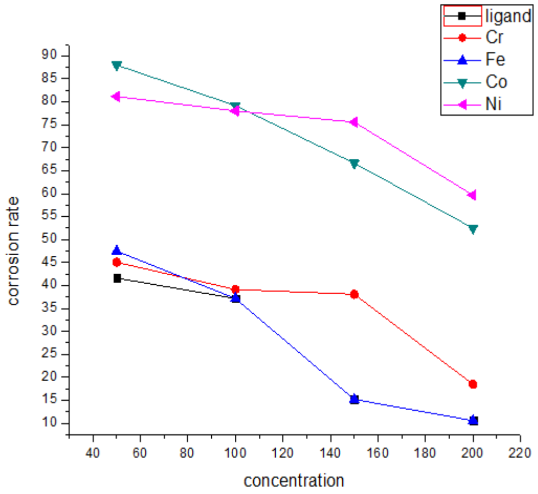


Fig. 4.Variation of corrosion rate against concentration of HBT ligand and its metal complexes at 24 hrs

C. Adsorption Studies

Concentration	ligand	Cr	Fe	Co	Ni
50	0.2249	0.4542	0.4331	0.0435	0.05485
100	0.3079	0.5260	0.4678	0.1002	0.06444
150	0.4723	0.5457	0.4742	0.2427	0.08438
200	0.6340	0.7763	0.5578	0.4036	0.277

TABLE.3.The value of θ for the DT Ligand & its complexes calculated from weight loss measurements

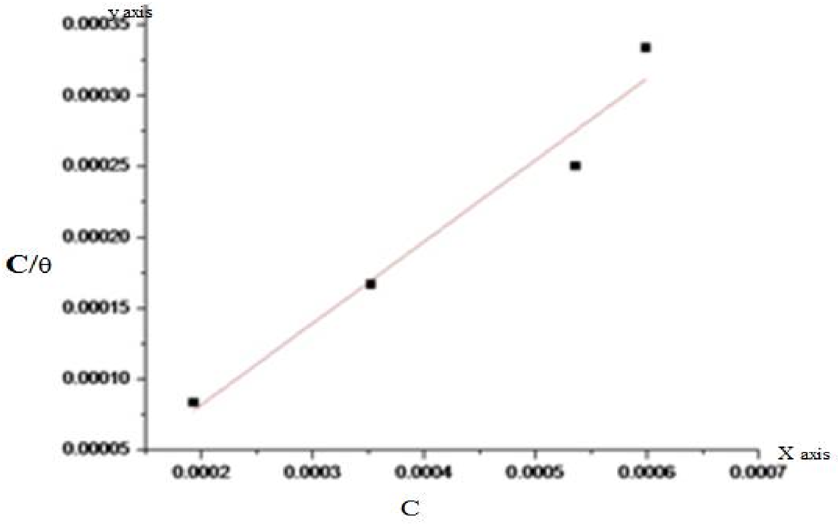


Fig.5. Adsorption isotherm of Fe complex

Sl no	Parameters	Values
1	Intercept	3.3166×10^{-5}
2	K_{ads}	3.0152
3	ΔG^0_{ads}	-35.7
4	R^2	0.9505

Table.4. Adsorption and Activation Parameters obtained from Langmuir Adsorption plots of Fe complex.

IV. CONCLUSION

Benzilic acid-tyrosine ligand (HBT) and its Cr (III), Mn (II), Fe (III) and Ni (II) metal complexes were synthesized and characterized with the help of IR and electronic spectra. The HBT ligand which coordinates with metal ion changes its color from pale yellow indicates the coordination of the metal ion to the binding sites of the ligand. The electronic spectra and magnetic measurements suggest the octahedral nature of the complexes. The lower value of molar conductance indicates the non-electrolyte nature of the complexes. The newly synthesized Benzilic acid derivatives were not reported so far and the current study involves the inhibition mechanism of the compounds on the mild steel in an acidic medium. The ligand possesses an activity of 63% where all other ligands except Cr (III) metal complexes shows slightly lower inhibition efficiency. The Cr (III) complex have an increased efficiency of 77%.Typically the inhibitory action decreases on coordination due to non-availability of the lone pair of electrons which involved in the coordination. The compounds show the order of inhibition as follows: HBT> Cr (II) > Fe (III) >Co (II) >Ni (II). The Ligand and complexes exhibits maximum inhibition action at a concentration of 200 ppm. As the concentration of the inhibitor increases the inhibition efficiency also increased. The corrosion rate of these compounds decrease as the concentration increases.

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REFERENCES

[1] R. Sudha, Charles. C. Kanakam and G. Nithya, International Journal of Chem Tech Research, 2015,5;383-387
[2] G. Indiradevi, N. P. Pranamya and M. Ali Hassan, World Journal of Pharmaceutical and Life Sciences, 2019, 5; 71-76
[3] G. Indiradevi, International Journal of Environment, Ecology, Family and Urban Studies, 2019, 9; 71-78
[4] Djamel Daoud , Tahar Douadi , Hanane Hamani , Salah Chafaa , Mousa Al-Noaimi, Corrosion inhibition of mild Steel by two new S-heterocyclic compounds in 1 M HCl: Experimental and computational study, Corrosion Science (2015)
[5] K. Ramya, Revathi Mohan, K.K. Anupama, Abraham Joseph, Mater. Chem. Phys. 149–150 (2015) 632–647.
[6] M. Yadav, S. Kumar, R.R. Sinha, I. Bahadur, E.E. Ebenso, J. Mol. Liq. 211 (2015) 135–145.
[7] Y. Tang, F. Zhang, S. Hu, Z. Cao, Z. Wu, W. Jing, Corros. Sci. 74 (2013) 271–282.
[8] R. Mohan, A. Joseph, Egyptian Journal of Petroleum 27 (2018) 11–20
[9] P. Rugmini Ammal, M. Prajila, Abraham Joseph, Journal of Environmental Chemical Engineering 6 (2018) 1072–1085
[10] K. Nakamoto, P.J. McCarthy,'Spectroscopy and Structure of Metal Chelate Compounds', John Wiley and sons, Inc.,1968; 289.