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A Comparison of the Corrosion Inhibition Efficiency of the Schiff Bases for Mild Steel in Acidic Medium

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ABSTRACT: The corrosion behavior of mild steel in 1M HCl solution in the presence of Isatin based Schiff bases of thiosemicarbazide, aniline, sulphanilic acid as inhibitors has been studied, and the rate of corrosion has been calculated. The characterization of these Schiff bases was done using elemental analysis, IR, H-NMR. Corrosion studies were carried out at various concentrations, time of immersion and at different temperatures. The inhibition efficiency of each of these compounds and the effect of temperature were evaluated using classical weight loss method. As the temperature increases, the corrosion rate also increases which means that there is a decrease in the inhibition efficiency. It was found that the inhibition efficiency increases with the increase in the concentration of each inhibitor. Thermodynamic and absorption parameters were calculated and absorption isotherms were plotted from the experimental data. Surface investigation was done through SEM analysis and concluded that isatin-sulphanilic acid proves to be a better inhibitor than isatin-aniline and isatin-thiosemicarbazide.

Keywords: Adsorption isotherm; corrosion, inhibition; elemental analysis; weight loss method

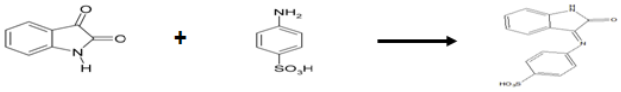
INTRODUCTION

Organic compounds containing heteroatoms with high electron density such as phosphorus, nitrogen, sulphur, oxygen, with double or triple bonds in their structures are effective corrosion inhibitors due to their high tendency for adsorption. The compounds having both nitrogen and sulphur in their molecular structure have excellent corrosion inhibition ability compared to those containing only nitrogen or sulphur; moreover, sulphur-containing compounds have generally stronger corrosion inhibition ability compared to nitrogen containing compounds. The adsorption mechanism of organic inhibitors at metal/solution interface is, the adsorption of an organic inhibitor on a metal surface usually involves replacement of one or more water molecules initially adsorbed at the metal surface. Subsequently, the inhibitor may then combine with the newly generated metal ions M^{+2} on the surface, as a result of metal oxidation or dissolution process, forming metal inhibitor complex._Schiff bases are the organic compounds that can be considered as the sub class of imines, being either secondary ketimines or secondary aldimines depending on their structure. They are usually formed by the condensation of a primary amine with an active carbonyl compound. Isatin (1H-indole-2, 3-dione), an endogenous compound identified in many organisms. The isatin ring is a prominent structural motif found in several pharmaceutically active compounds. Schiff bases of isatin were investigated for their pharmaceutical properties and they are good corrosion inhibitors.

MATERIAL NAD METHODS

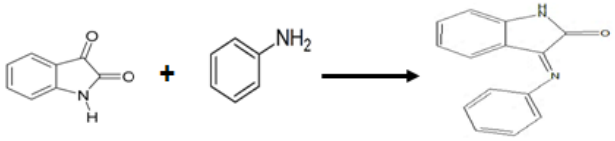
Preparation of Schiff Bases

Isatin – Sulphanilic acid (Inhibitor-1): In a RB flask with a water condenser, Isatin (0.005 moles) and sulphanilic acid (0.005 moles) was dissolved separately using methanol. The reaction mixture was refluxed in a water bath for about 4 hours. After cooling, the orange crystals formed were isolated from methanol by evaporation. It was cooled, dried and finely powdered.



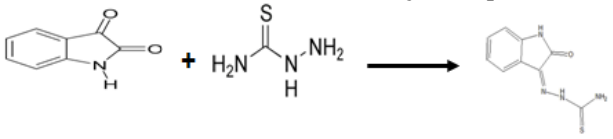
Characterization of the ligand: It is an orange coloured crystal, soluble in methanol, ethanol, DMSO. The analytical data is in agreement with the empirical formula, $C_{14}H_{10}N_2O_4S$.The ligand was found to melt at 189^0C. Further characterized using IR and H-NMR studies.

Isatin– Aniline (Inhibitor-2): In a R.B flask with a water condenser, isatin (0.005 moles) and aniline (0.005 moles) was dissolved using methanol. The reaction mixture was refluxed in a water bath for about 4 hours. After cooling, reddish brown crystals formed were isolated from methanol by evaporation. It was cooled, dried and finely powdered.



Characterization of the ligand: It is a reddish brown coloured crystal, soluble in methanol, ethanol, DMSO. The analytical data is in agreement with the empirical formula, $C_{14}H_{10}N_2O$. The ligand was found to melt at 178^0C. Further characterized using IR and H-NMR studies

Isatin – Thiosemicarbazide (Inhibitor-3): In a R.B flask with a water condenser, isatin (0.005 moles) and thiosemicarbazide (0.005 moles) was dissolved using methanol. The reaction mixture was refluxed in a water bath for about 4-5 hours. After cooling, red crystals was isolated from methanol by evaporation. It was cooled, dried and finely powdered.



Characterization of the Ligand: It is a red coloured crystal, soluble in methanol, ethanol, DMSO. The analytical data is in agreement with the empirical formula, $C_9H_8N_4OS$. The ligand was found to melt at 212^0C. Further characterized using IR and H-NMR studies

Preparation of Acid Solution (1m HCl): 91 ml of HCl dissolved in 1000 ml of distilled water.

Weight Loss Method: Mild steel coupons were weighed and immersed in 200 ml solution of 1M hydrochloric acid containing 0.05, 0.1, 0.15 and 0.2 g (concentrations 50, 100, 150, 200ppm respectively) of Schiff bases separately in a beaker. The beaker was placed in a thermostat at 311 K. After 3 hours, the specimens were removed from the thermostat and cleaned with distilled water, dried & weighed. The experiment was repeated at 321 K &331 K.

RESULTS AND DISCUSSION

Weight Loss Method: Corrosion rate of mild steel in 1M HCl with inhibitor-1 at 311K, 321K and 331K is given in Table 1.

Effect of Temperature: The corrosion rate of mild steel in 1M HCl is found to be increasing with increase in temperature from 311-331 K. It has been evident from the straight-line behaviour obtained by plotting a graph between corrosion rate vs. temperatures. From the tables, it is observed that the inhibition efficiency decreases with increase in temperature. The decrease in inhibition efficiency with temperature may be attributed to desorption of Schiff bases from the metal surface at higher temperature. At higher temperature, more desorption of inhibitor takes place and greater surface area of mild steel is exposed to the acid environment, resulting in an increase in corrosion rate. The decrease in inhibition efficiency with rise in temperature is actually suggestive of physical adsorption mechanism.

Effect of Inhibitor Concentration: It is observed that inhibition efficiency increases with inhibitor concentrations. From the table 1, it can be seen that corrosion rate of mild steel decreases with increasing percentage of Isatin-Sulphanilic acid Schiff base up to 200ppm/200ml. It is also observed that the inhibition efficiency increases with respect to the inhibitor concentration up to 200ppm/200ml. The inhibitor efficiency is also equal to surface coverage (θ) and the maximum inhibition efficiency obtained is 84.25% at 321K. From the table 2, it can be seen that corrosion rate of mild steel decreases with increasing percentage of Isatin- Aniline Schiff base up to 200ppm/200ml. It is observed that the inhibition efficiency is found to increase with respect to the inhibitor concentration up to 200ppm/200ml. The inhibitor efficiency is also equal to surface coverage (θ) and the maximum inhibition efficiency obtained is 81.21% at 321K. From the table 3, it can be seen that corrosion rate of mild steel decreases with increasing percentage of Isatin-Thiosemicarbazide Schiff base up to 200ppm/200ml. It is also observed that the inhibition efficiency increases with respect to the inhibitor concentration up to 200ppm/200ml. The inhibitor efficiency is also equal to surface coverage (θ) and the maximum inhibition efficiency obtained is 77.83% at 331K. On comparing the three Schiff base inhibitors, finally Isatin-Sulphanilic acid is found to be a good inhibitor in the inhibition of mild steel corrosion in 1M Hydrochloric acid at 321K, since the maximum efficiency obtained is 84.25%.

Effect of Time of Immersion: Corrosion rate of mild steel in 1M HCl is found to be increasing with increase in time from 2 to 6 hours. The effect of time on the inhibitive action of the Schiff bases on the corrosion of mild steel was determined at the various time range of 2-6 hours. From the tables, it is observed that the increase in hours enhanced the corrosion rate by the corrosion process.

Thermodynamic Parameters: The thermodynamic functions for dissolution of mild steel without and with the addition of optimum concentration of inhibitors at various temperatures were calculated from the logarithm of corrosion rate of metal in HCl by using the Arrhenius equation:

$$\log CR = Ea/2.303RT + \log A$$

CR - corrosion rate, Ea - activation energy, and A - pre exponential factor. The Arrhenius plots of log CR versus 1/T for the blank and different concentrations of inhibitors gives a straight line. In the presence of

Table 1: Corrosion rate of mild steel in 1M HCl with inhibitor-1 at 311K, 321K and 331K.

Concentration of Inhibitor-1 (ppm/200ml)	Initial weight (g)	2 hrs (g)	Weight Loss (g)	4 hrs (g)	Weight Loss (g)	6 hrs (g)	Weight loss (g)	Corrosion rate (mg cm-2 hr-1)	Inhibitor efficiency (%)	Surface coverage (g)
Temperature 311 K										
0	3.6904	3.6767	0.0137	3.6631	0.0273	3.652	0.0384	1.67563636		
50	3.7501	3.7492	0.0009	3.7311	0.019	3.7173	0.0328	1.43127273	14.5833333	0.14583333
100	3.0797	3.0665	0.0132	3.0599	0.0198	3.0555	0.0242	1.056	36.9791667	0.36979167
150	2.9759	2.9685	0.0074	2.9603	0.0156	2.9589	0.017	0.74181818	55.7291667	0.55729167
200	2.5339	2.5318	0.0021	2.5301	0.0038	2.5216	0.0123	0.53672727	67.96875	0.6796875
Temperature 321 K										
0	3.652	3.5581	0.0939	3.4299	0.2221	3.3624	0.2896	12.6370909		
50	3.7173	3.6798	0.0375	3.5432	0.1741	3.4731	0.2442	10.656	15.6767956	0.15676796
100	3.0555	3.0097	0.0458	2.9946	0.0609	2.9071	0.1484	6.47563636	48.7569061	0.48756906
150	2.9589	2.9143	0.0446	2.8675	0.0914	2.8496	0.1093	4.76945455	62.2582873	0.62258287
200	2.5216	2.4806	0.041	2.444	0.0776	2.476	0.0456	1.98981818	84.2541436	0.84254144
Temperature 331 K										
0	3.3624	3.304	0.0584	3.1746	0.1878	3.0101	0.3523	15.3730909		
50	3.4731	3.337	0.1361	3.1892	0.2839	3.1435	0.3296	14.3825455	6.44337213	0.06443372
100	2.9071	2.843	0.0641	2.7981	0.109	2.6542	0.2529	11.0356364	28.2145898	0.2821459
150	2.8496	2.7609	0.0887	2.6388	0.2108	2.5999	0.2497	10.896	29.1229066	0.29122907
200	2.466	2.3814	0.0846	2.3028	0.1632	2.2965	0.1695	7.39636364	51.8875958	0.51887596

Table 2: Corrosion rate of mild steel in 1M HCl with inhibitor-2 at 311K, 321K and 331K

Concentration of Inhibitor-2(ppm/200ml)	Initial weight (g)	2 hrs (g)	Weight Loss (g)	4 hrs (g)	Weight Loss (g)	6 hrs (g)	Weight loss (g)	Corrosion rate (mg cm-2 hr-1)	Inhibitor efficiency (%)	Surface coverage (g)
Temperature 311 K										
0	3.6904	3.6767	0.0137	3.6631	0.0273	3.652	0.0384	1.67563636		
50	3.6611	3.6502	0.0109	3.6399	0.0212	3.6252	0.0359	1.56654545	6.51041667	0.06510417
100	3.6425	3.6309	0.0116	3.6232	0.0193	3.6136	0.0289	1.26109091	24.7395833	0.24739583
150	3.7636	3.7566	0.007	3.7516	0.012	3.7456	0.018	0.78545455	53.125	0.53125
200	3.6738	3.6705	0.0033	3.6674	0.0064	3.6623	0.0115	0.50181818	70.0520833	0.70052083
Temperature 321 K										
0	3.652	3.5581	0.0939	3.4299	0.2221	3.3624	0.2896	12.6370909		
50	3.6252	3.555	0.0702	3.5077	0.1175	3.4304	0.1948	8.50036364	32.7348066	0.32734807
100	3.6136	3.5285	0.0851	3.5148	0.0988	3.5023	0.1113	4.85672727	61.5676796	0.6156768
150	3.7456	3.6933	0.0523	3.6845	0.0611	3.676	0.0696	3.03709091	75.9668508	0.75966851
200	3.6623	3.6421	0.0202	3.6103	0.052	3.6079	0.0544	2.37381818	81.2154696	0.8121547
Temperature 331 K										
0	3.3624	3.304	0.0584	3.1746	0.1878	3.0101	0.3523	15.3730909		
50	3.4304	3.3528	0.0776	3.2432	0.1872	3.1227	0.3077	13.4269091	12.6596651	0.12659665
100	3.5023	3.4389	0.0634	3.3291	0.1732	3.2627	0.2396	10.4552727	31.9897814	0.31989781
150	3.676	3.6423	0.0337	3.5174	0.1586	3.4762	0.1998	8.71854545	43.2869713	0.43286971
200	3.6079	3.5325	0.0754	3.4602	0.1477	3.4256	0.1823	7.95490909	48.2543287	0.48254329

Table 3: Corrosion rate of mild steel in 1M HCl with inhibitor-3 at 311K, 321K and 331K

Concentration of Inhibitor-3(ppm/200ml)	Initial weight (g)	2 hrs (g)	Weight Loss (g)	4 hrs (g)	Weight Loss (g)	6 hrs (g)	Weight loss (g)	Corrosion rate (mg cm-2 hr-1)	Inhibitor efficiency (%)	Surface coverage (g)
Temperature 311 K										
0	3.6904	3.6767	0.0137	3.6631	0.0273	3.652	0.0384	1.67563636		
50	3.7141	3.6912	0.0229	3.6842	0.0299	3.6764	0.0377	1.64509091	1.82291667	0.01822917
100	3.6827	3.6786	0.0041	3.6614	0.0213	3.6507	0.032	1.39636364	16.6666667	0.16666667
150	3.6525	3.6436	0.0089	3.6353	0.0172	3.6229	0.0296	1.29163636	22.9166667	0.22916667
200	3.7878	3.7814	0.0064	3.7798	0.008	3.7645	0.0233	1.01672727	39.3229167	0.39322917
Temperature 321 K										
0	3.652	3.5581	0.0939	3.4299	0.2221	3.3624	0.2896	12.6370909		
50	3.6764	3.6068	0.0696	3.5449	0.1315	3.4904	0.186	8.11636364	35.7734807	0.35773481
100	3.6507	3.5853	0.0654	3.521	0.1297	3.4778	0.1729	7.54472727	40.2969613	0.40296961
150	3.6229	3.586	0.0369	3.5468	0.0761	3.5033	0.1196	5.21890909	58.7016575	0.58701657
200	3.7645	3.7399	0.0246	3.7129	0.0516	3.6892	0.0753	3.28581818	73.9986188	0.73998619
Temperature 331 K										
0	3.3624	3.304	0.0584	3.1746	0.1878	3.0101	0.3523	15.3730909		
50	3.4904	3.3708	0.1196	3.2818	0.2086	3.1971	0.2933	12.7985455	16.7470905	0.16747091
100	3.4778	3.3999	0.0779	3.2955	0.1823	3.2366	0.2412	10.5250909	31.535623	0.31535623
150	3.5033	3.4575	0.0458	3.3936	0.1097	3.2897	0.2136	9.32072727	39.3698552	0.39369855
200	3.6892	3.6621	0.0271	3.6414	0.0478	3.6111	0.0781	3.408	77.8313937	0.77831394

Table 4: Activation parameters for the dissolution of mild steel in the presence of inhibitors

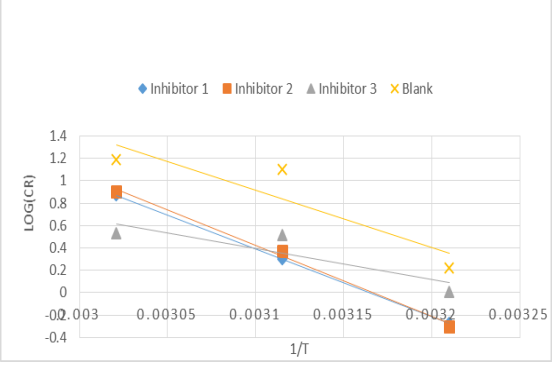
Composition	Free energy of adsorption(ΔG°) (kJ/mol)	Activation energy (Ea) (kJ/mol)	Enthalpy(ΔH°) (kJ/mol)	Entropy of activation(ΔS°) (J/K mol)
Blank	-3.634	26.66	-8.885	8.1213
Inhibitor 1	-8.647	31.50	-9.491	-6.5008
Inhibitor 2	-10.36	33.20	-11.267	-11.117
Inhibitor 3	-10.94	30.24	-9.765	-12.265

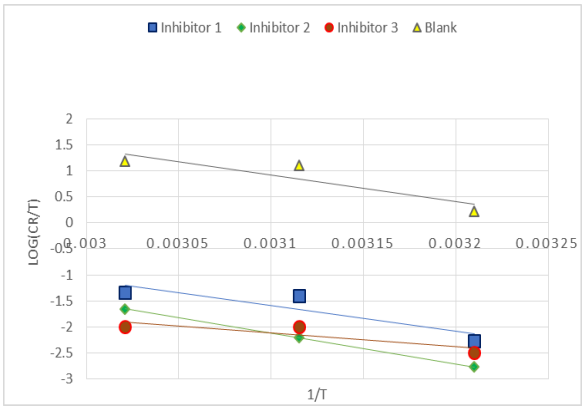
inhibitors, the activation energies increased, compared to the acid solution revealing the retardation of the corrosion reaction. The marked changes in Ea suggest that the inhibitor may either participate in the electrode or may change the potential difference of the metal-solution interface by adsorption.

The increase in apparent activation energy in the presence of the Schiff bases denotes physical adsorption mechanism. Physical adsorption happens due to the electrostatic force between negatively charged metal surface and positive charged of organic species. The higher activation energy implies a slow dissolution of the mild steel. A form of Arrhenius equation is:

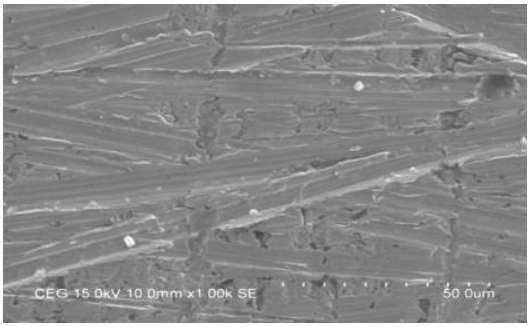
$$\mathbf{CR/T = (R/Nh)\ exp(\Delta S°/R)\ exp(-\Delta H°/RT)}$$

h - Plank's constant, N - Avogadro's number, ΔH° - enthalpy of activation, **ΔS°** - entropy of activation. A plot of log CR/T versus 1/T gave a straight line with a slope of -ΔH°/2.303R and an intercept of log(R/Nh) + (ΔS°/2.303R), from which the values of ΔH° and ΔS° were calculated. The Gibb's free energy ΔG^0 can be obtained by the equation: $\mathbf{\Delta G^0 = \Delta H^0 - T\Delta S^0}$. The negative signs of enthalpies reflect the exothermic nature of dissolution process. This indicates that IE% decreases when the temperature increases. The negative values of ΔS° is explained as molecules that might freely move in the bulk solution, but with the progress in the adsorption, inhibitor molecules were orderly adsorbed onto the metal surface, and as a result, there was a decrease in entropy. Small negative values of ΔS° for inhibited system showed a number of water molecules on mild steel surface, being displaced by the inhibitor molecules.

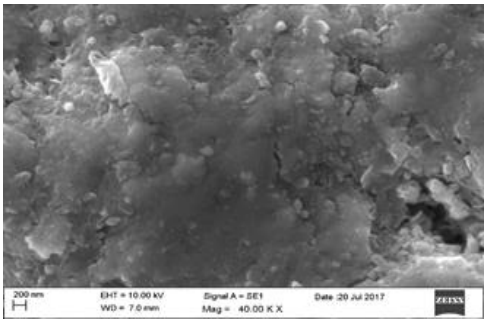




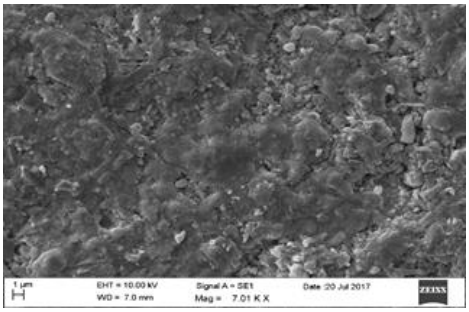
Surface Investigation (SEM Analysis): The formation of an adsorbed protective film of the inhibitor molecule on the mild steel surface is confirmed by SEM studies. The surface morphology of the uninhibited mild steed is characterized by a rough surface due to rapid corrosion attack; it can be concluded that mild steel surface was greatly damaged in absence of inhibitors. SEM obtained for inhibited mild steel specimen indicates that the metal surface is fully covered with inhibitor molecules giving it high degree of protection. The inhibitor molecules reduces the corrosion by decreasing the active surface area of the substrate and inactivate only the available part of surface imposed into corrosive medium, which is termed as simple blocking of the surface area. This finding further suggests the formation of protective film of inhibitors on the mild steel surface.



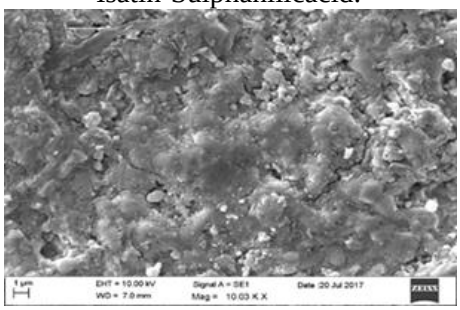
SEM image of mild in 1M HCl



SEM image of mild steel in 1M HCl in presence of Isatin-aniline



SEM image of mild steel in 1M HCl in presence of Isatin-Sulphanilicacid.



SEM image of mild steel in 1M HCl in presence of Isatin-thiosemicarbazide

CONCLUSIONS

Schiff base ligands of isatin-sulphanilic acid, isatin-aniline, isatin-thiosemicarbazide was studied for their role as corrosion inhibitors. The CR was reported at maximum in blank solution when there is no inhibitor to retard the deterioration process. The higher the concentration of inhibitor, the higher the percentage of Inhibitor efficiency and lower the rate of corrosion. For isatin-sulphanilic acid, the maximum Inhibitor efficiency was found to be 84.25% at 321K for a concentration of 200 ppm/200 ml with increase in Inhibitor concentration. But with increase in temperature the Inhibitor efficiency was found to decrease. However, for isatin-aniline the maximum Inhibitor efficiency was found to be 81.21% at 321K temperature for an inhibitor concentration of 200 ppm/200 ml. Moreover, for isatin -thiosemicarbazide the maximum Inhibitor efficiency was found to be 77.83% at 331K for 200 ppm/200 ml with increase in Inhibitor concentration. Therefore, it is clear that the increase in concentration of inhibitor increases the efficiency of the inhibition process.

Adsorption mechanism of molecules on mild steel surface can be explained from thermodynamic analysis of activation energy, free energy, enthalpy and entropy. For isatin-sulphanilic acid, the activation energy of the corrosion inhibition process increased from 26.66 kJ /mol to 31.50 kJ /mol with increasing inhibitor concentration. Similarly, for isatin-aniline and isatin-thiosemicarbazide, the activation energy of the corrosion inhibition process increased with the inhibitor concentration. The value of activation ener-

gy can be used to identify the type of adsorption process involved whether, chemical adsorption or physical adsorption. The data shows that the E_a values in the presence of different concentrations of the Schiff bases in three cases, are higher than that in the free acid. The increase in apparent activation energy in the presence of the Schiff bases denotes physical adsorption mechanism.

The negative values of enthalpies also indicates that the process is physical adsorption as well as exothermic. All entropy parameters for adsorption of inhibitors molecule on mild steel are negative for the three Schiff bases indicating that the entropy of inhibitor molecules in solution phase is higher than in solid phase indicating a spontaneous process. It also suggest the strong interaction of the inhibitor molecules on to the mild steel surface. For the inhibitors, ΔG^0 values are greater than the threshold values of -40 kJ /mol, which again emphasis physical adsorption. From this study it can be concluded that, isatin-sulphanilic acid proves to be a better Inhibitor than the other two.

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