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RESEARCH ARTICLE

Antoxidative Effect of 1-((5-Nitrofuran-2-yl)methylene)-semicarbazide and its Inner Transition Metal Complexes: A Thermodynamic Approach

V. R. RAJEWAR[1], M. K. DHARMALE[*2], K.L.KENDRE[2] and S. R .PINGALKAR[1]

[1,4]Department of Chemistry, N. E. S.Science College, Nanded (M.S), India
[2,3]Department of Chemistry, Yeshwant Mahavidyalaya, Nanded (M.S), India
dharmalevaishu@rediffmail.com

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Abstract: The present work deals with the corrosion behavior of mild steel in acidic medium. The inhibitive effect of 1-((5-nitrofuran-2-yl)methylene)semicarbazide lanthanide complexes on the corrosion of mild steel in 0.2 M HNO_3 has been studied by weight loss and thermodynamic methods. The thermodynamic parameters for mild steel in acidic medium with and without inhibitor were calculated. The effect of concentration temperature on the corrosion rate, activation energy and free energy of adsorption were also calculated.

Keywords: Corrosion, Inhibition, NFS Complexes, Chemical adsorption

Introduction

Corrosion is the destructive attack on metal by surrounding environment. The spontaneous destruction of the metal due to heterogeneous chemical reaction is the chemical corrosion, which leads to huge economical loss of the metal[1,2].

A corrosion inhibitor is a chemical substance which when added in small concentration to an environment minimizes or prevents corrosion. Corrosion inhibitors are used to protect metals from corrosion, including temporary protection during storage or transport as well as localized protection, required to prevent corrosion that may result from accumulation of small amount of an aggressive phase. An efficient inhibitor is compatible with the environment, economical for application and produces the desired effect when present in small concentration[3].

Hetero atoms such as N, O, S and some cases Se and P present in compounds are capable of forming coordinate covalent bond with metals owing to their free electron pairs. Compounds with pi bonds also generally exhibit good inhibitive properties, due to interaction of pi orbital with the metal surface[4].The chelating agents NFS 1-((5-nitrofuran-2-yl)methylene) semicarbazide have both O, N atoms and can be used as potential corrosion inhibitors.

The development of inhibitors of steels in acid solutions has been the subject of great interest especially, from the point of view of their efficiency and applications. The most important feature in carbon steel is its corrosion resistance to the atmosphere and too many aqueous media due to rapidly formed thin and highly protective barrier oxide film which can bond strongly to the surface of metal and protects the metal from the corrosive environment[5].

In the present work, inhibition efficiency of selected mixed ligand complexes in 0.2 N nitric acid medium was evaluated and an attempt was made to correlate weight loss with different thermodynamic parameters. In view of the thermodynamic parameters it was proposed to investigate efficient corrosion inhibitor for mild steel in nitric acid environment.

Experimental

Mild steel wire from local manufacturer with 4" length and 0.095 cm in diameter were used for corrosion study. The specimen wire was first of all cleaned with dil. hydrochloric acid and then by sand paper followed by distilled water wash. After, it was dried by keeping in oven at 120 ^{0}C for 1 h.

In the first beaker 50 mL 0.2 N nitric acid was taken and labeled as **1** for control system. Beaker no. **2** along with 50 mL 0.2 N nitric acid, 50 mg NFS was added. In labeled beakers 3,4,5,6 and 7 50 mL of 0.2 N nitric acid along with 50 mg of La, Pr, Nd, Sm, Tb ligand complexes were added respectively. The previously weighed steel wire was dipped for 48 h.

At the end wire pieces were taken out from the beaker, washed with distilled water and dried. The weight of each wire was recorded by using electronic balance in grams up to three digits and is presented in Table1.

Table 1. % Inhibition efficiency of metal complexes

Beaker No.	Compound	Initial Wt. g	Final Wt., g	Loss in Wt., g	% loss in Wt.	% I.E.
1	Control	0.580	0.300	0.280	48.27	-
2	HNO_3+ L	0.540	0.300	0.240	44.44	14.28
3	HNO_3+ La Complex	0.560	0.360	0.200	35.71	28.57
4	HNO_3+ Pr Complex	0.510	0.320	0.190	37.25	32.14
5	HNO_3+ Nd Complex	0.580	0.410	0.170	29.31	39.28
6	HNO_3+ Sm Complex	0.520	0.360	0.160	30.76	42.85
7	HNO_3+ Tb Complex	0.530	0.360	0.170	32.07	39.28

Results and Discussion

Weight loss measurement

Weight of metal wire pieces before and after dipping in corrosion solution, loss in wt, % loss in weight was calculated by usual method. The % inhibition efficiencies were calculated by using following formula:

$$\%\ \text{Inhibitor Efficiency (P)} = \left(\frac{We - Wi}{Wu}\right) x100$$

From data it can be seen that, the Nd Sm and Tb complexes have maximum inhibition efficiencies than La and Pr complexes. The ligand shows the least inhibitor efficiency (Figure 1).

Free energy of adsorption

The values of free energies of adsorption (ΔG_a) were calculated (Table 2) using the following equation[6].

$$\log C = \log\left(\frac{\theta}{1-\theta}\right) - \log B$$

Where, log B = -1.74 x (ΔG_a/2.303 RT), C= Inhibitor concentration and $\theta = \left(\frac{Wu - Wi}{Wu}\right) x100$ is the fraction of metal surface covered by the inhibitor[7].

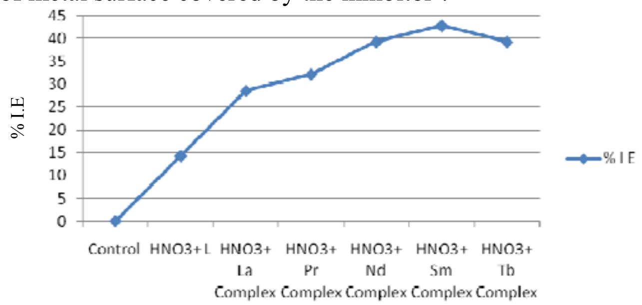

Figure 1. Comparison of % I.E. with different metal complexes

Table 2. Free energy values for ligand and complexes

Beaker. No.	Concentration	θ	$\log\left(\frac{\theta}{1-\theta}\right)$	log B	ΔG_a
1	-	-	-	-	-
2	0.005046	0.1666	-0.6991	1.5978	-5274.7735
3	0.001299	0.4000	-0.1767	2.7102	-8947.294
4	0.001296	0.4736	-0.0459	2.7870	-9200.6308
5	0.001290	0.6470	0.2631	3.1525	-10407.1019
6	0.001281	0.7500	0.4770	3.3694	-11123.1690
7	0.001266	0.6470	0.2631	3.1606	-10433.8718

Calculation of ΔG_a values

The free energy of adsorption for Sm complex is maximum compared to free energy of adsorption of La , Pr, Nd ,Tb complexes and ligands.

Corrosion rate and energy of activation

The corrosion rate in g cm^{-2} h^{-1} was calculated (Table 3) from the following formula[8]

$$\rho = \left(\frac{\Delta W}{At}\right)$$

Where ΔW is the weight loss, A is the total area of the wire and t is the immersion time. The relationship between the corrosion rate (ρ) and Temperature (T) in acid medium is given by the Arrhenius equation:

$$\log\rho = \log A \frac{Ea}{2.303RT} \quad \text{OR} \quad Ea = 2.303RT\log\frac{A}{\rho}$$

Where E_a is the apparent activation energy, R is the molar gas constant and T is the absolute Temperature. The results of corrosion rate and energy of activation also show similar trends as that for % I.E.

Enthalpy of adsorption and entropy of adsorption

The enthalpy of adsorption (ΔH^o_{ads}) and entropy of adsorption (ΔS^0_{ads}) were calculated (Table 4) using the following equation: $\Delta H^o_{ads} = E_a - RT$

$$\Delta S^0_{ads} = \frac{\Delta H_{ads} - \Delta G_{ads}}{T}$$

Table 3. Values of corrosion rate and energy of activation

Beaker No.	ρ	E_a, $kJmol^{-1}$
1	-	-
2	0.004190	14098.4235
3	0.003492	14553.3596
4	0.003317	14681.4540
5	0.002968	14958.896
6	0.002793	15110.5415
7	0.002968	14958.8961

Table 4. ΔH^0_{ads} and ΔS^0_{ads}

Beaker No.	ΔH^0_{ads}, $kJmol^{-1}$	ΔS^0_{ads} $Jmol^{-1}$ K^{-1}
1	-	-
2	11604.2235	56.2633
3	12059.1596	70.0215
4	12187.254	71.2929
5	12464.696	76.2393
6	12616.3415	79.1317
7	12464.696	76.3285

Nd, Sm and Tb complexes show maximum enthalpy of adsorption as compared to La, Pr complexes and free ligand. While Sm complex shows highest entropy of adsorption than La, Pr, Nd and Tb complexes. The free ligand has the least entropy of adsorption.

Conclusion

From this study it reviles that the % I.E., free energy of adsorption, corrosion rate, enthalpy of adsorption and entropy of adsorption has more values for the metal complexes than that of free ligand. The Sm complex has maximum efficiency while Lanthum complex has the least efficiency of inhibition. Thus Sm complexes of these ligand can be efficiently employed as potential corrosion inhibitor.

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