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Inhibition Effect of 2-Dimethyl Amino Ethanol on the Corrosion Behaviour of Austenitic Stainless Steel (Type 304) in 0.1M H₂SO₄

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Abstract: The corrosion inhibition of type 304 grade stainless steel in 0.1 M H₂SO₄ solution by 2-dimethyl amino ethanol (DMAE) has been studied by weight loss method. The effect of temperature on the corrosion behavior of stainless steel was studied at 303 K and 333 K. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature. The adsorption of 2-dimethyl amino ethanol on austenitic stainless steel in sulphuric acid within the chosen temperature obeyed the Langmuir isotherm with very high negative value of the free energy of adsorption. Thermodynamic calculations reveal physicochemical interactions and spontaneous adsorption mechanism.

Keywords: Austenitic stainless steel, DMAE, Free energy, enthalpy, entropy

1. INTRODUCTION

Austenitic stainless steel (ASS) is a material applied in many fields due to the wide range of useful properties such as corrosion resistance, formability etc. It is characterized by a high level of Cr (about 18 wt %) and 8 wt % of Ni. The presence of chromium on the level of 13 wt % in SS causes the salutatory variation of electrochemical potential and this a broad lower limit for higher corrosion resistance^[1]. Generally, chromium contained in ASS reacts with oxygen and as a result a thin passive layer of Cr₂O₃ for protection from corrosion is formed on the surface. It is well known that the corrosion of metallic structures has a significant impact on economy, including infrastructure, transportation, utilities, production, manufacturing, and government^[2]. The annual world production of the steel is approximately 400 million, and of this about 2% is stainless. Demand for stainless steel increases by 3-5% per annum with major applications in extractive industries, petrochemicals, chemical processing plants, automotive and aerospace structural alloy, construction materials, petroleum industry, marine environments, sugar industries, food industry and breweries, energy production, pulp and paper and textile industry^[3].

In the past few decades, stainless steel 304, identified for their brilliant corrosion resistance have attracted much attention owing to a native surface passive layer. However when they are subjected to some corrosive fluids in the presence of halide ions, they tend to be corroded locally^[4,5]. It is necessary to use acid solutions to remove undesirable scale and corrosion products from metals. These acids attack the metal and initiate corrosion. This corrosion can cause serious damage to the metal and degrade its properties, thereby limiting its application^[6]. The use of inhibitors is one of the most convenient means for protection of steel corrosion in acidic solution as they can prevent metal from dissolution and consequently reduce the operation cost^[7]. The corrosion inhibitors are introduced in the different components of the coating system such as pretreatment, primer and top coat^[8]. Adsorbed inhibitor structures are highly substrate-dependent. Surface properties such as charge density, chemical composition, hydrophilicity/hydrophobicity differ for each substrate, both for model surfaces and between different alloys of steel^[9]. The most effective and economical measure of corrosion

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control is through the use of inhibitors with particular attention on organic compounds. Organic compounds have shown good application as corrosion inhibitors for steel in acidic environments^[10-18,11]. It is necessary for the development of new approach to introduce environmentally friendly corrosion inhibitors, which can provide prolonged and even smart release of inhibiting species on demand becomes an important issue for many industries where an adequate corrosion protection is needed^[19]. 2-dimethyl amino ethanol (DMAE) is a primary alcohol with a 4-carbon structure and the molecular formula is $C_4H_{11}NO$, belonging to the higher and branched chain alcohols without any record of harm to humans and the environment. This investigation aims to assess the inhibitive effect of 2-dimethyl amino ethanol as non toxic inhibitor on the type 304 stainless steel in dilute HCl.

2. Material and Methods

Commercially available type 304 stainless steel was used for all experiments of average nominal composition; 18.21 % Cr, 8.42 % Ni, 68.12 % Fe, 0.08% C, 2% Mn, 0.75 % Si, 0.04-5% P and 0.03% S respectively. The material is cylindrical with a diameter of 18 mm. 2-dimethyl amino ethanol (DMAE), a yellowish translucent liquid is the inhibitor used. The molecular formula is $C_4H_{11}NO$, while the molar mass is 89.14 g/mol. DMAE was prepared in volumetric concentrations of 2.5 %, 5 %, 7.5% and 10 % per 100 ml of the acid solution respectively. 0.1 M H_2SO_4 solutions of analytical grade were used as the corrosion test media. Stainless steel specimen of the size (18 mm) was used for measurement of weight loss study. The strips were mechanically polished using 1/0, 2/0, 3/0 and 4/0 emery paper and finally degreased with the organic solvent like trichloroethylene and dried before use.

Weight loss measurements were carried out by weighing the specimens in triplicate before and after immersion in 100 ml of 0.1 M H_2SO_4 for 24, 48, 120 h at optimum temperature. Each of the test specimens was taken out every 24 h, washed with distilled water, dried and re-weighed. The corrosion rate (R), inhibition efficiency (% IE) and surface coverage (θ) were calculated from the following equations;

$$R(\text{mpy}) = 534 \times W \dots\dots\dots (1)$$

$$\% \text{ IE} = \frac{A \times D \times T}{W_b - W_i} \dots\dots\dots (2)$$

$$\theta = \frac{W_b}{W_i} = \% \text{ IE} / 100 \dots\dots\dots (3)$$

Where W is the weight loss in milligrams, D is the density in g/cm^3 , A is the surface area in cm^2 , T is the immersion time, W_b and W_i are the corrosion rates of 304 stainless steel without and with inhibitor, respectively. The same procedure was carried out at 303 K and 333 K using thermostat to study the inhibition efficiency of inhibitor. This study gives details about the rate of adsorption and activation energy.

3. Results & Discussions

3.1 Weight Loss Measurements

The weight loss of austenitic stainless steel in 0.1 M H_2SO_4 solution without (Blank) and with different concentrations of inhibitor for 24, 48 and 120 h at optimum temperature are provided in Table 1. The values of weight loss (W), Corrosion rate (R) and the % Inhibition efficiency (IE) and surface coverage (θ) are presented in Table 1. It obviously shows that the corrosion rate decreases with increase inhibitor concentration at optimum temperature, the % IE increases with the presence of higher concentration of inhibitor. As inhibitor concentration increases, the barrier film formed on the steel surface becomes more compact, effectively separating the specimen from aggressive anionic species within the test solution while at the same time, stifling the redox reactions associated with the corrosion process. The diffusion of Fe^{2+} and Cl^-/SO_4^{2-} is thus effectively inhibited^[20]. The barrier film is strongly adsorbed through physisorption mechanism by weak van der waal's force. Effective inhibition occurred from 7.5- 10.0 % inhibitor concentration, most probably through the adsorption of the functional hydroxyl group of the inhibitor on the steel surface by the interaction of π - electrons or lone pair of electron of hetero atom with the metal^[19].

3.2 Effect of Temperature

The effect of temperature on the corrosion rate of 304 stainless steel in 0.1M H_2SO_4 solution in absence and presence of different concentrations (2.5 %, 5.0% 7.5 % and 10.0 %) of inhibitor was studied at 303 and 333 K. The inhibition efficiency is reduced to 70.16% for 120 h at 333 K as compared to 81.22% for 120 h at 303 K. As the temperature of the inhibitor's free solution increases above 303 K, the corrosion rate of austenitic steel increases and the rate in 0.1 M H_2SO_4 solution with low concentration of inhibitor were even higher than that in the blank solution. Similarly, the rate of corrosion increases and inhibition efficiency decreases with increase in temperature above 303 K for non ionic surfactant TRITON-X-405 on ferritic stainless steel in 0.1 M H_2SO_4 solution^[11]. The activation energy can be calculated from the slope, by plotting the natural logarithm of the corrosion rate against 1/T. The negative slope of E_a indicates the adsorption of organic compounds on the metal surface. It is clear that the activation energies of the

corrosion process for protecting steel using the tested inhibitor are higher than that of the unprotected stainless steel in 0.1 M H₂SO₄ solution. The greater increase for the activation energy in the presence of the inhibitor indicates physisorption or weak chemical bonding between the inhibitor molecules and the metal surface. Mazhar et al. explained that the increase in the activation energy with respect to uninhibited solution was due to diffusion of metal ions through the protective film on the metal surface.

3.3 Thermodynamic Parameters

The free energy of adsorption ΔG is an important thermodynamic parameter, because it provides useful information about the type of adsorption process. The ΔG values calculated were found to be -8.53 KJ and -7.11 KJ at 303 and 333 K respectively, which ensure the spontaneity of the adsorption process. The ΔH and ΔS values calculated were found to be 22.92 KJ and -47.48 KJ respectively. The negative value of ΔH and ΔS indicates that the adsorption of the non toxic inhibitor on the steel surface in 0.1 M H₂SO₄ solution is an exothermic process and accompanied by decrease in entropy. Similarly, the adsorption of TRITON-X-405 on the steel surface throughout the process showed that the inhibitor molecules were orderly adsorbed onto the surface, $\Delta S < 0$ and the diffusion of metal ions through the protective film on the metal surface is rate controlling when concentration of inhibitor was greater than critical micelle concentration ^[1].

3.4 Adsorption Isotherm

The corrosion inhibition process is based on an adsorption of the inhibitor's molecules on the metal surface. Therefore, it is of great importance to find an appropriate adsorption isotherm that fits the experimental results. It is well-known that adsorption isotherms provide useful insights into the mechanism of corrosion inhibition. In order to get a better understanding for the adsorption isotherm, the Langmuir adsorption isotherm equation was employed ^[22].

$$C/\theta = 1/K_{ads} + C \quad \text{-----(4)}$$

Where θ is the surface coverage, which can be calculated from the weight loss measurement results, C is the molar concentration of the inhibitor and K_{ads} is the standard adsorption equilibrium constant. This isotherm clearly revealed that the adsorption of DMAE on austenitic steel 304 type obeyed the Langmuir adsorption isotherm and the inhibitor molecules are adsorbed on metal surface forming a film, which prevents the austenitic stainless steel 304 from corrosion induced by the medium. It can be seen that K_{ads} values decreased with increase in temperature, suggesting that the elevated temperature facilitates the desorption of the DMAE from austenitic stainless steel surface, and hence the adsorption of the inhibitor decreased with increased in temperature ^[22].

4. Conclusions

Experimental analysis of the corrosion inhibition properties of 2-dimethyl amino ethanol showed that the compound to be an efficient inhibitor in the acidic environment at 303 K and 333 K respectively, giving a maximum inhibition efficiency from weight loss analysis. The maximum inhibition efficiency of DMAE on stainless steel was found to be 70 % and 63.6 % at 303 and 333 K respectively. Inhibition efficiency values increased with increase in inhibitor concentration and decrease with temperature. Thermodynamic variables of adsorption deduced revealed a physisorption with the steel surface and spontaneous adsorption of DMAE.

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Table 1 Corrosion parameters obtained from weight loss measurements for stainless steel 304 in 0.1M H₂SO₄ solution without and with different concentrations of inhibitors for different time intervals at 303 and 333 K

Time (h)	Concentration (mM)	303 K				333 K			
		Weight loss (mg)	Corrosion rate (mY)	% IE	Θ	Weight loss (mg)	Corrosion rate (mY)	% IE	θ
24	Blank	7.186	110.62	-	-	9.346	143.87	-	-
	2.5	5.912	91.01	17.73	0.1773	7.234	111.36	22.60	0.2260
	5	3.793	58.34	35.84	0.3584	5.486	84.85	41.30	0.4130
	7.5	2.056	31.65	47.79	0.4779	4.007	61.68	44.61	0.4461
	10	1.386	16.72	47.18	0.4718	2.104	32.39	61.65	0.6165
48	Blank	11.237	86.49	-	-	13.189	101.51	-	-
	2.5	7.316	56.31	21.38	0.2138	11.567	89.03	12.30	0.1230
	5	5.014	38.59	55.38	0.5538	8.986	69.16	37.81	0.3781
	7.5	2.913	22.44	60.18	0.6018	5.032	38.73	56.50	0.5650
	10	1.905	14.66	62.01	0.6201	2.989	23.01	66.74	0.6674
120	Blank	15.187	77.93	-	-	17.487	89.73	-	-
	2.5	11.463	58.82	24.52	0.2452	14.984	76.89	14.31	0.1431
	5	8.106	41.59	46.63	0.4663	11.087	56.89	36.60	0.3660
	7.5	3.751	19.25	67.28	0.6728	8.432	43.27	43.73	0.4373
	10	2.195	12.37	70.26	0.7026	4.009	20.57	63.84	0.6384

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