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2-Dimethyl amino ethanol as a non toxic corrosion inhibitor for austenitic stainless steel 304 in 1 M HCl solution

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ABSTRAC: *The inhibiting action of 2-dimethyl amino ethanol (DMAE) on stainless steel type 304 grade in 1.0 M HCl solution within the temperature of 303 K and 333 K was studied using weight loss method. The inhibition efficiency was found to increase with the inhibitor concentration and decrease with temperature.. Thermodynamic calculations reveal physiochemical interactions and spontaneous adsorption mechanism.*

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

1. INTRODUCTION

It is well known that the corrosion of metallic structures has a significant impact on economy, including infrastructure, transportation, utilities, production, manufacturing, and government [1]. Austenitic steels are non magnetic stainless steels that contain high levels of chromium and nickel, low levels of carbon. They have good formability and weldability, as well as excellent toughness, particularly at low or cryogenic temperatures [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]. The poor wear properties and low surface hardness make extreme limits in many cases. The surface modification is needed to decrease the coefficient of friction of substrate and increase the mechanical and tribiological properties [4, 5]. It is necessary to use acid solutions to remove undesirable scale and corrosion products from metals. This corrosion can cause serious damage to the metal and degrade its properties, thereby limiting its applications [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].

Organic compounds have shown good application as corrosion inhibitors for steel in acidic environments [8-17,1]. So 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 and adequate corrosion protection is needed [18]. 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

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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. MATERIALS & METHODS

Commercially available type 304 stainlesss 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, 0.045% P and 0.03% S respectively. 2-dimethyl amino ethanol (DMAE), a yellowish translucent liquid is the inhibitor used. The structural formula is shown in Fig.1. The molecular formula is $C_4H_{11}NO$, while the molar mass is 89.14 g/mol.

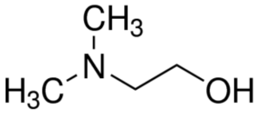

Fig.1 **Structure of 2-dimethyl amino ethanol**

DMAE was prepared in volumetric concentrations of 2.5 %, 5 %, 7.5% and 10 % per 100 ml of the acid solution respectively. Solutions of 1 M HCl of analytical grade was used as the corrosion test media.

Stainless steel specimen of the required size 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 1 M HCl for 24, 48 and 72h at optimum temperature. Each of the test specimen 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;

$$R(mpy) = \frac{534 \times W}{A x D x T} \qquad (1)$$

$$\% IE = \frac{W_b - W_i}{W_b} \qquad (2)$$

$$\Theta = \% IE / 100 \qquad (3)$$

Where W is the weight loss in milligrams, D is the density in g/cm^2, 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 298 K and 353 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 (W), Corrosion rate(R) and the % Inhibition efficiency (IE) and surface coverage (θ) of austentic stainless steel in 1 M HCl solution without(Blank) and with different concentrations of inhibitor for 24, 48 and 72 h at optimum temperature are provided 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 [19]. 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 [17].

3.2 Effect of temperature

The inhibition efficiency is reduced to 63.84% for 72 h at 333 K as compared to 70.26% for 72 h at 298 K. As the temperature of the inhibitor's free solution increases above 298 K, the corrosion rate of austentic steel increases and the rate in 1 M HCl 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 1 M H_2SO_4solution [1].

3.3 Activation energy

Corrosion rate increases exponentially with temperature because the hydrogen evolution decreases; therefore the dependence of a corrosion rate (R) on temperature can be expressed by the Arrhenius equation,

$$\ln R = E_a/RT + A \qquad (4)$$

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Where E_a represents the apparent activation energy, R is the general gas constant, T is the absolute temperature, A is the Arrhenius pre-exponential constant depending on the metal type and the electrolyte [20]. The activation energy can be calculated from the slope, by plotting the natural logarithm of the corrosion rate against 1/T. The values of apparent activation energies obtained for various concentrations of DMAE at 298 and 333 K are 11.26 , 13.98, 14.21, 14.98KJ, respectively. 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. [21]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.

3.5 Thermodynamic parameters

Free energy of adsorption (ΔG) can be calculated using the equation,

$$\Delta G = RT \ln(C_{solvent} K) \quad (5)$$

$$\text{ie } K = \theta / C(1-\theta) \quad (6)$$

Where R is the universal gas constant, $C_{solvent}$ is the molar concentration of the solvent, which in the case of water is 55.5 mol/L, C is the concentration of the inhibitor and θ, the degree of surface coverage of the metal surface. The ΔG values calculated from equation (5) were found to be -4.98 KJ and -3.55 KJ at 298 and 333 K respectively, which ensures the spontaneity of the adsorption process. The standard adsorption heat (ΔH) and standard adsorption entropy (ΔS) were calculated according to van't Hoff equations. The plot of ln K versus 1/T gives a straight line with a slope of (-ΔH/R) and intercept. The ΔH and ΔS values calculated were found to be -47.34 KJ and -19.32 KJ respectively. The negative value of ΔH and ΔS indicates that the adsorption of the non toxic inhibitor on the steel surface in 1.0 M HCl 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, ΔS <0 and the diffusion of metal ions through the protective film on the metal surface is rate controlling [1].

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 298 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 298 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 1M HCl solution without and with different concentrations of inhibitors for different time intervals at 298 K and 333 K

Time (h)	Concentration (mM)	298 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
72	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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