The Influence of Diethylenetriaminepenta(Methylene Phosphonic Acid) and Sodium Potassium Tartrate on The Corrosion Inhibition of Stainless Steel in Acidic Media

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Abstract : **The effect of a new class of corrosion inhibitors, namely diethylenetriaminepenta(methylene phosphonic acid) and sodium potassium tartrate (abbreviated DTPMP and SPT, respectively) on the corrosion of stainless steel in 0.5 M H_2SO_4 solutions has been studied by weight loss measurements, Potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) methods. Polarization curves indicate that the compounds are mixed type inhibitors. The inhibition efficiency was found to increase with increase in inhibitor concentration but decreased with rise in temperature, which is suggestive of physical adsorption mechanism. Thermodynamic parameters were obtained from different experimental temperatures, which suggested that at different temperatures (303–333 K) the adsorption of inhibitors on metal surface obeyed Langmuir adsorption isotherm model.**

Keywords: DTPMP; Corrosion inhibitor; stainless steel; Acidic media; Adsorption isotherm

I. INTRODUCTION

Corrosion inhibitors are widely used in industry to prevent or to reduce the corrosion rates of metallic materials in reducing acid media. Type 304stainless steel (304 SS) has also found wide applications in a variety of industries. Since acidic media could attack it during the cleaning and pickling process, the presence of corrosion inhibitors in the cleaning and pickling solutions is very important to keep the surface of steel intact. For this reason, many researches were conducted to study its corrosion properties and to find out suitable chemical compounds to be used as corrosion inhibitors for it in acidic solutions [1-2]. The aim of this work was to investigate the adsorption and inhibition effect of DTPMP and SPT on 304stainless steel in 0.5 M H_2SO_4 solution. Moreover the effect of temperature on the dissolution of 304stainless steel was also investigated.

II. EXPERIMENTAL

A. *Preparation of Working electrode:*

Grade 304 Stainless steel strips were cut into 4 cm x 1 cm x 0.2 cm having the following compositions (C – 0.021 %, Si – 0.888 %, Mn – 1.42 %, P – 0.0177 %, S – 0.0268 %, Cr – 18.20 %, Mo – 0.0373 %, Ni – 9.43 %, Cu – 0.507 %, V – 0.1 %, and Fe – 69.36 %) were used for weight-loss studies, while coupons of size 1 cm^2 were used for electrochemical studies and SEM analysis. The stainless steel strips were cut and polished to mirror finish by table grinding wheels and degreased with Trichloroethylene.

B. *Preparation of 0.5 M H_2SO_4 solution*

0.5 M H_2SO_4 solutions were prepared by diluting 27.8 ml of 18 M AR-Grade H_2SO_4 to 1000 ml using double distilled water.

C. *Electrichemical Impedance Spectra*

The electrochemical measurements presented in this study were performed using the Electrochemical Workstation (Model No. CHI760, CH Instruments, USA). Prior to the electrochemical measurements, the metal specimens were prepared according to the above described procedure.

D. *Preparation of diethylenetriaminepenta(methylene phosphonic acid)*

1g of diethylenetriaminepenta(methylene phosphonic acid) (DTPMP) was dissolved in double distilled water and made up to 100 ml in a standard measuring flask. 1 ml of this solution was diluted to 100 ml to get 100 ppm of DTPMP.

E. Preparatrion of Sodium Potassium Tartrate

1 g of sodium potassium tartrate was dissolved in double distilled water and made up to 100 ml in a standard measuring flask. 1 ml of this solution was diluted to 100 ml to get 100 ppm of sodium potassium tartrate.

F. Electrochemical methods

Electrochemical measurements were performed using a CHI electrochemical analyzer model 760D instrument with CHI 760D operating software. A three-electrode electrochemical setup was used. A working stainless steel electrode embedded in Teflon holder was dipped in test solution. A saturated calomel electrode (SCE) and a platinum electrode were used and the reference and counter-electrode respectively. The double-layer capacitance (C_{dl}) and charge-transfer resistance (R_{ct}) were calculated from Nyquist plots.

III. RESULTS AND DISCUSSION

A. Weight – Loss method

The corrosion of stainless steel in 0.5 M H_2SO_4 in the absence and presence of DTPMP and SPT mixtures was investigated at temperature range of 303–333K using weight loss method. The calculated values of corrosion rate (mpy), inhibition efficiency (%) and surface coverage ( ) for stainless steel corrosion in 0.5 M H_2SO_4 (blank) and in the presence of inhibitor DTPMP and SPT in combination with different concentrations at 303–333K from the weight loss method are shown in Table 1. The corrosion rate, inhibition efficiency and surface coverage were evaluated using the following equations:

$$\text{Corrosion rate (mpy)} = \frac{534 \times \text{Weight Loss in mg}}{DAT} \quad \text{---------------- (1)}$$

$$\text{Inhibition Efficiency (\%)} = \frac{W_0 - W_1}{W_0} \times 100 \quad \text{-------------------- (2)}$$

W_0 and W_i are the weight loss in the absence and presence of inhibitor, respectively, and

$$\text{Surface coverage ( )} = \frac{W_0 - W_1}{W_0} \quad \text{----------------------- (3)}$$

TABLE 1: WEIGHT LOSS VALUES OF CORROSION RATES AND INHIBITION EFFICIENCIES OF STAINLESS STEEL IN PRESENCE AND ABSENCE OF INHIBITORS AT DIFFERENT TEMPERATURES.

H2SO4 (M)	Conc. Of DTPMP (ppm)	Conc. Of SPT (ppm)	303 K			313 K			323 K			333 K		
			CR		IE	CR		IE	CR		IE	CR		IE
0.5	0	0	41.56	--	--	42.95	--	--	44.89	--	--	47.66	--	--
	200	50	25.21	0.3933	39.33	30.48	0.2903	29.03	35.74	0.2037	20.37	38.51	0.1627	16.27
	20	100	18.01	0.5667	56.67	22.17	0.4839	48.39	27.71	0.3827	38.27	32.14	0.3012	30.12
	200	150	9.98	0.7600	76.00	14.69	0.6581	65.81	20.50	0.5432	54.32	24.94	0.4578	45.78
	200	200	4.99	0.8800	88.00	8.04	0.8129	81.29	13.58	0.6975	69.75	18.84	0.5904	59.04

It can be observed from the table that the inhibition efficiency increases with increasing concentrations of inhibitors. The corrosion rate values increased and the inhibition efficiency decreased with increase in temperature. This is due to the fact that at higher temperatures, the metal dissolution process is enhanced and the adsorbed inhibitor molecules are partially desorbed from the surface of the metal [3-4].

B. Potentiodynamic Polarization

Figure 1 show polarization curves for stainless steel in 0.5M H_2SO_4 with and without various concentrations of DTPMP and SPT respectively. The values of all electrochemical parameters such as corrosion current density (I_{corr}), corrosion potential (E_{corr}) and IE obtained in the uninhibited and inhibited acidic solutions are listed in table 2. In the case of polarization curves, IE is calculated by the following equation.

$$\text{IE (\%)} = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \text{ -------------- (4)}$$
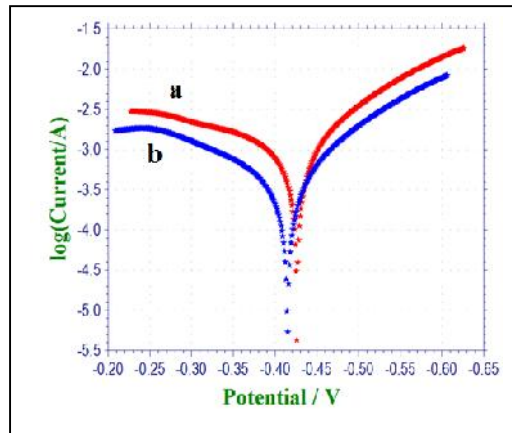

Figure 1: Potentiodynamic polarization curves for stainless steel in 0.5 M H_2SO_4 solution in (a) without (b) with the concentrations of the inhibitor.

TABLE 2: ELECTROCHEMICAL PARAMETERS OF STAINLESS STEEL IN 0.5M H_2SO_4 SOLUTIONS OBTAINED BY POLARIZATION METHOD.

System	b_a mV	b_c mV	E_{corr} mV V SCE	I_{corr} A/cm^2	IE %
Blank	2.66	7.22	-0.426	15.55 x 10^{-4}	-----
200 ppm DTPMP +200 ppm SPT	4.47	7.474	-0.415	5.59 x 10^{-4}	64.05

From the values of (I_{corr}) the inhibition of both anodic and cathodic reactions is more pronounced with the increasing inhibitor concentration. However, there is no absolute shift in corrosion potential to more anodic or more cathodic potential in comparison with corrosion potential observed in blank solution. These results suggest that DTPMP and SPT can be classified as mixed type corrosion inhibitor [5-6].

C. Electrochemical Impedance Spectroscopy

The corrosion behavior of mild steel in 0.5M H_2SO_4 was also investigated by electrochemical impedance spectroscopy (EIS). The Nyquist representations of impedance behavior of stainless steel in 0.5 M H_2SO_4 with and without addition of various concentrations of inhibitors are given in figure 2. The double layer capacitance (C_{dl}) is calculated from the following equation [7].

$$C_{dl} = \frac{1}{2 \pi R_{ct} F_{max}} \text{ ------------ (5)}$$
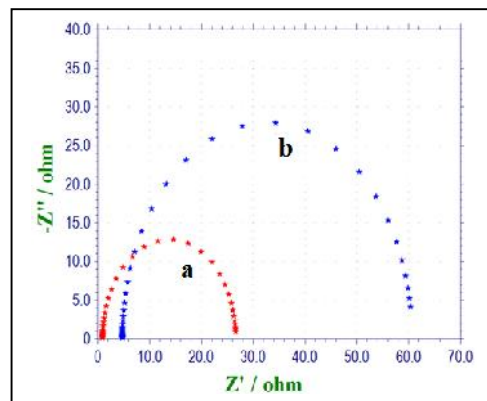

Figure 2: Nyquist plots for stainless steel in 0.5 M H_2SO_4 solution in (a) without and (b) with concentrations of the inhibitor.

It is seen that addition of inhibitor increases the values of R_{ct} values from 22.52 cm^2 to 55.98 cm^2 and reduces the C_{dl} values from 6.24 x 10^{-4} µF cm^2 to 1.03 x 10^{-4} µF cm^2. The decrease in C_{dl} is attributed to increase in thickness of electronic double layer. The increase in R_{ct} value is attributed to the formation of protective film on the metal surface [8].
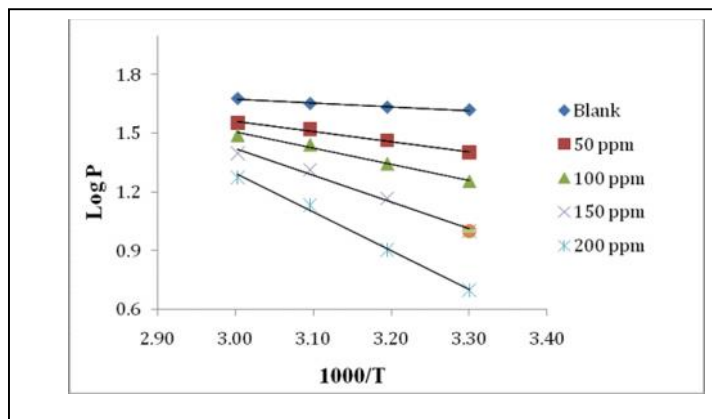
D. Thermodynamic Parameters

Figure 3: Arrhenius plots for corrosion of Stainless steel in 0.5M H$_2$SO$_4$ in absence and presence of different concentration of inhibitor

The activation energy (Ea) values are important to analyze the kinetic of the corrosion process. From the values obtained by weight loss measurements carried out at four different temperatures 303, 313, 323 & 333K. Energy of activation (E_a) was calculated from the slopes of plots log P versus 1/T in figure 3 and also calculated from Arrhenius equation are approximately almost similar [9]. The data shows that the activation energy (E_a) of the values is higher than the free acid solution. The changes in E_a values could be attributed to the fact that the energy barrier of the corrosion process increased after addition of inhibitor to the acid solution, which led to the inhibition of corrosion.

Table 3: THERMODYNAMIC PARAMETERS OF E$_a$ & - G$_{ads}$, FOR STAINLESS STEEL IN 0.5 M H$_2$SO$_4$IN PRESENCE AND ABSENCE OF INHIBITORS.

Medium	Conc. of DTPMP (ppm)	Conc. of SG (ppm)	E$_a$ (From equation) KJ/mol	Ea (From Arrhenius plot) KJ/mol	- G$_{ads}$ KJ/mol			
					303K	313K	323K	333K
0.5	0	0	5.36	5.79	--	--	--	--
	200	50	6.46	6.93	13.39	13.03	12.62	12.08
	200	100	10.12	10.6	13.41	12.98	12.29	11.61
	200	150	17.53	17.95	14.61	13.80	12.95	12.03
	200	200	29.28	29.91	16.00	15.17	13.95	12.69

E. Adsorption Isotherm

The Langmuir adsorption isotherm model has been used extensively in the literature for various metal, inhibitor and acid solution systems. The free energy of adsorption (G$_{ads}$) at different temperatures is calculated from the following equation.

$$\Delta G = - RT \ln(55.5\ K)$$ ----------------(6)

The negative value G$_{ads}$ is given in table 3. The negative value of G$_{ads}$ indicates the spontaneous adsorption of DTPMP – SG inhibitor on the stainless steel surface and also there is strong interaction between inhibitor molecule and metal surface. Generally values of G$_{ads}$ up to -20 kJ/mol are consistent with physisorption while those around -40 kJ/mol or higher are associated with chemisorption [10].

$$\frac{C}{\theta} = \frac{1}{K} + C$$ ---------------------------- (7)

Where C is the inhibitor concentration, K is the adsorption equilibrium constant and is degree of surface coverage. The plot of C/ versus C (Figure 4) gives a straight line confirming that the adsorption of this inhibitor on metal surface obeys the Langmuir adsorption isotherm [11].
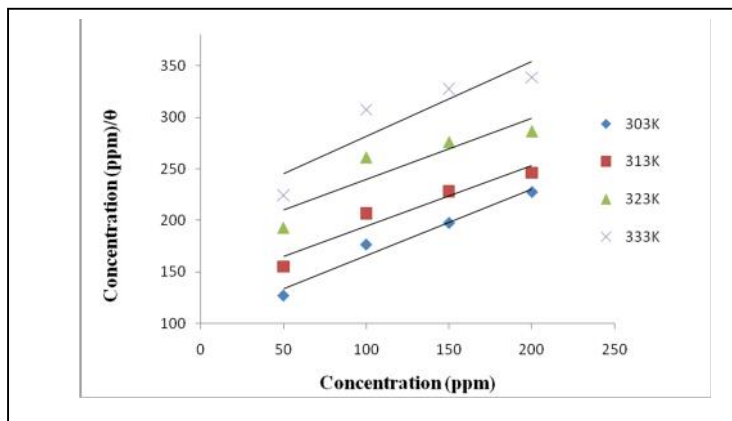

Figure 4: Langmuir adsorption isotherm of DTPMP – SPT on the stainless steel in 0.5 M H_2SO_4 (303 – 333 K)

IV.   CONCLUSIONS

The investigated compounds reduce the corrosion of stainless steel in 0.5 M H_2SO_4 solutions. The inhibitor showed maximum IE 88 % at 200 ppm of DTPMP and 200 ppm of SPT. The increase in temperature caused a decrease in the IE, suggesting physisorption. Potentiodynamic polarization curves indicate that DTPMP and SPT behaved as mixed type of inhibitor. Impedance study confirms that the adsorption of inhibitor molecules on to stainless steel. The value of G_{ads} ranges from -16 to -12 kJ/mol indicates that the adsorption is spontaneous, physisorption and follows Langmuir adsorption isotherm.

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