ADSORPTION AND THERMODYNAMIC STUDY OF CORROSION INHIBITION EFFECT OF AMINOTRIMETHYLENE PHOSPHONIC ACID (ATMP) – Al^{3+} SYSTEM ON CARBON STEEL IN GROUND WATER

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ABSTRACT

The synergistic inhibitor effect of 150ppm of TriMethylene Phosphonic acid (ATMP) with 50 ppm of Al^{3+} ion has 98% inhibition efficiency on controlling corrosion of steel immersed in ground water. Effect of temperature on Corrosion rate was studied and shows that the inhibition efficiency decreases with increase in temperature. Also, the inhibition efficiency of the inhibitor increases with increasing concentration of the inhibitor which offered the inhibition efficiency of 98%. The adsorption of the inhibitor on the surface of mild steel in the corrosive environment followed the Langmuir and Frumkin adsorption isotherm. Inhibition occurred through adsorption of the ATMP+ Al^{3+} ion molecules on the metal surface. The apparent activation energies, enthalpies and entropies of the dissolution process and the free energies and enthalpies for the adsorption process were determined and discussed. The fundamental thermodynamic functions were used to evaluate important inhibitive properties of ATMP+ Al^{3+} .

Key words: Synergistic inhibitors, TriMethylene Phosphonic acid (ATMP), Carbon steel, Activation energy, Gibb's Free Energy, Van't Hoff equation, Activation Parameters, Adsorption isotherms

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1. INTRODUCTION

Carbon steel is the most commonly used engineering material¹. Carbon steel is exposed to the attack of acid solutions during industrial processes such as acid cleaning, pickling and descaling. This results to easy corrosion of the mild steel, thereby necessitating the use of inhibitor²⁻⁵. There are numerous methods for controlling the corrosion of metals but the use of inhibitors is still one of the best methods of protecting metals against corrosion⁶⁻⁸. Many organic compounds are used as corrosion inhibitors for mild steel in acidic environments. Such compounds usually contain nitrogen, oxygen or sulphur in a conjugated system and function via adsorption of the molecules on the metal surface, creating a barrier to the corrosion attack^{3, 5, 8, 9}. The use of organic substances to inhibit corrosion of metals in acidic environments is well established¹⁰⁻¹⁶. Most of the effective and efficient organic inhibitors were those compounds that had p bonds and contained hetero-atoms such as oxygen, nitrogen, sulphur, and phosphorus which allowed adsorption on the metal surface¹⁷⁻²⁰.

Several researches have been done on the use of ex-tract of plant as inhibitor for metals against corrosion in different aggressive media^{21,22}.

Adsorption isotherms were obtained at 303-323 K for various concentrations of the inhibitor. In this work, we report the kinetic, activation and adsorption parameters. In addition, the adsorption isotherm for the different temperature range (303-323K) was also obtained to show the adsorption model of the inhibitor. Many organic compounds have been tested for corrosion inhibition.

The functionality of these compounds has been attributed to their electronegative functional groups and presence of π electrons in triple or conjugated double bonds. They also contain nitrogen, sulphur or oxygen atoms in their structures. Their mode of operation is by physical or chemical interactions between their molecules and the metal surfaces²³.

2. EXPERIMENTAL

In order to study the temperature effects on the performance of the ATMP+Al³⁺ ion against carbon steel in ground water solution without and with different concentrations of the inhibitor at 303-323 K using weight loss method The carbon steel specimens were chosen from the same sheet of the following composition shown in Table 1.

Table 1. Composition of Carbon Steel

Elements	S	P	Mn	C	Fe
Composition%	0.025	0.06	0.4	0.15	99.365

Prior to the experiment, all the samples were polished with different grades of emery papers, washed with doubly distilled water and degreased with acetone and dried. Ground water was collected from Ramanathapuram (near sea shore area), TamilNadu, India. Corrosion behaviour of carbon steel in this water was evaluated.

Inhibition efficiencies (I.E), corrosion rates and surface coverage (θ) were calculated by using following formula:

$$\text{I.E.} = 100 [1 - (W_2 / W_1)] \% \quad (1)$$

where W_1 = Corrosion rate in the absence of inhibitor and W_2 = Corrosion rate in the presence of inhibitor.

$$\text{Corrosion rate} = \frac{\text{Loss in weight (mg)}}{\text{Surface area of the specimen (dm}^2\text{)} \times \text{Period of immersion (days)}} \quad (2)$$

The corrosion rate is expressed in mdd units [$\text{mdd} = \text{mgm}/(\text{dm}^2) (\text{day})$].

$$\theta = \frac{\text{IE}}{100} \quad (3)$$

3. RESULT AND DISCUSSION

3.1. Effect of temperature on the inhibition efficiency and corrosion rate

Data derived from the weight loss study such as weight loss, inhibitor efficiency and surface coverage are listed in Table 2. Effect of temperature on Corrosion rate and inhibition efficiency of carbon steel without and with addition of different concentrations of ATMP and Al^{3+} ion is shown in Fig.1 and Fig.2.

Table 2. Effect of Temperature on corrosion rate and inhibition efficiency

Temperature (K)	Various concentration of ATMP+50ppm of Al^{3+}	Corrosion rate (CR) m.md	% I.E	Surface Coverage (θ)
303	Blank	19.52	----	--
	50	4.88	75	0.75
	100	3.51	82	0.82
	150	0.39	98	0.98
	200	2.92	85	0.85
313	Blank	15.06	----	----
	50	6.21	72	0.72
	100	3.31	78	0.78
	150	0.90	94	0.94
	200	2.10	86	0.86
323	Blank	17.54	----	---
	50	6.84	61	0.61
	100	5.26	70	0.70
	150	1.57	91	0.91
	200	2.80	84	0.84

Figure 1. Effect of concentrations of mixed inhibitors on corrosion rate of carbon steel corrosion in ground water

Figure 2. Effect of concentrations of mixed inhibitors on inhibition efficiency of carbon steel corrosion in ground water

A close up look at the Fig.1 reveals that the corrosion rate decreases as the concentration of inhibitor increases, while the corrosion rate increases with the increase in the temperature (Table 2.). This means that the inhibitor efficiency decreases with increase in the temperature but inhibitor efficiency increases with increase in the inhibitor concentrations for all the temperature ranges studied as shown in Fig.2. Such behaviour of 150ppm ATMP+50ppm Al³⁺ is due to the increase in surface coverage by increasing the inhibitor concentration⁴²⁻⁴⁴. When the temperature increases, surface coverage reduction causes desorption of 150ppm ATMP+50ppm Al³⁺ from the carbon steel surface and the carbon steel surface is exposed to the ground water. This may be due to decrease in the strength of the adsorption process at higher temperature, suggesting the physical adsorption of the inhibitor sample on the carbon steel surface^{45, 46}.

3.2. Adsorption Isotherms

3.2.1. Langmuir Isotherm

Langmuir adsorption isotherm is expressed according to Equation (4)²⁸

$$\log \left(\frac{C}{\theta} \right) = \log C - \log K \quad (4)$$

Where C is the concentration of the inhibitor, K is the adsorption equilibrium constant and θ is degree of surface coverage of the inhibitor.

Plotting $\log C / \theta$ Vs $\log C$ gave a linear relationship as shown in Fig.3. The parameters of Langmuir isotherm are presented in Table 3. The R^2 values of 0.989, 0.992 and 0.986 indicate that moderate adherence to Langmuir adsorption isotherm⁴⁷.

The application of Langmuir isotherm to the adsorption of 150ppm ATMP+50ppm Al³⁺ on surface of mild steel indicated that there is no interaction between the adsorbate and adsorbent⁴⁸.

Figure 3 Langmuir adsorption isotherm of mixed inhibitors (Different Con. of ATMP+ 50ppm Al³⁺) on carbon steel in ground water at various temperatures

Table.3. Adsorption parameters of various adsorption isotherms of mixed inhibitors (Different Con. of ATMP+50ppm Al³⁺) on carbon steel in ground water at various temperatures

Isotherm	Tempt. K	R ²	log K _{ads}	K _{ads} (mol ⁻¹)	α	a	1 / y	ΔG ⁰ _{ads} (kJ.mol ⁻¹)
Langmuir	303	0.9968	-0.3488	0.447	---	---	---	-8.093
	313	0.9927	-0.4216	0.378	---	---	---	-7.925
	323	0.9904	-0.6816	0.208	---	---	---	-6.569
Frumkin	303	0.9939	-1.4487	0.036	3.691	---	---	-1.717
	313	0.9900	-0.8728	0.134	2.903	---	---	-5.220
	323	0.9933	-0.3199	0.479	2.191	---	---	-8.806
Temkin	303	0.7029	1.2362	17.226	----	-4.444	---	-17.288
	313	0.8320	0.6597	4.567	---	-3.773	---	-14.405
	323	0.8944	-0.3931	0.404	---	-2.484	---	-8.353
EL-Awady et.al.	303	0.5255	-1.3364	0.0460	----	----	0.916	-2.364
	313	0.7231	-1.2111	0.0615	---	---	0.986	-3.193
	323	0.8274	-1.7761	0.0167	---	---	0.870	198.50

3.2.2. Temkin Isotherm

For Temkin adsorption isotherm, the degree of surface coverage (θ) is related to inhibitor concentration (C) according to Equation (6)^{29,30}

$$\theta = \frac{-2.303 \log K}{2a} - \frac{2.303 \log C}{2a} \quad (6)$$

Where K is the adsorption equilibrium constant and a , is the attractive parameter.

Plots of θ against $\log C$, as presented in Fig.4, gave linear relationship, which shows that adsorption data fitted Temkin adsorption isotherm. Adsorption parameters obtained from Temkin adsorption isotherms are recorded in Table 3. The values of attractive parameter (a) are negative in all cases, indicating that repulsion exists in the adsorption layer^{49, 50}.

Figure 4. Temkin adsorption isotherm of mixed inhibitors (Different Con. of ATMP+50ppm Al³⁺) on carbon steel in ground water at various temperatures

3.2.3. Frumkin Isotherm

Frumkin adsorption isotherm is given by Equation (7)^{28,31}.

$$\log \left[C \times \left(\frac{\theta}{1-\theta} \right) \right] = 2.303 \log K + 2\alpha\theta \quad (7)$$

where K is the adsorption-desorption constant and α is the lateral interaction term describing the interaction in adsorbed layer.

Plots of $\log \left[C \times \left(\frac{\theta}{1-\theta} \right) \right]$ Vs θ as presented in Fig.5 were linear which shows the applicability of Frumkin isotherm. The values for Frumkin adsorption parameters were recorded in Table. 3. This shows that values of the adsorption parameter α are positive suggesting the attractive behaviour of the inhibitor on the surface of carbon steel⁵¹.

Figure 5 Frumkin adsorption isotherm of mixed inhibitors (Different Con. of ATMP+50ppm Al³⁺) on carbon steel in ground water at various temperatures

3.2.4. El- Awady adsorption isotherm

For the higher temperature range the adsorption process did not follow the Langmuir adsorption isotherm. By testing other adsorption isotherms, the El- Awady adsorption isotherm for all the temperature range studied³²⁻³⁴. The characteristic of the isotherm is given by:

$$\log \left(\frac{\theta}{1-\theta} \right) = \log K + y \log C_{inh} \quad (8)$$

Thermodynamic/kinetic model of El-Awady et.al., adsorption isotherm provides important clues regarding the nature of the metal-inhibitor interaction shown in Fig.6. Inhibitor molecules adsorb on the metal surface if the interaction between molecule and metal surface is higher than that of the water molecule and the metal surface⁵².

Figure 6. EL - Awady et.al., adsorption isotherm of mixed inhibitors (Different Con.of ATMP+50ppm Al³⁺) on carbon steel in ground water at various temperatures

Value of $1/y$ less than unity implies the formation of multilayer of the inhibitor on the metal surface, while the value of $1/y$ greater than unity means that a given inhibitor occupy more than one active site⁵³⁻⁵⁵. Curve fitting of the data to the thermodynamic/kinetic model is shown in Figure 6. The plot gives straight lines which show that the experimental data fits the isotherm. The values of K_{ads} and $1/y$ calculated from the El-Awady et.al. Isotherm model is listed in Table 3.

It is evident from Table 3 that the value of $1/y$ is less than unity showing that there is multilayer adsorption of the inhibitor molecule. K_{ads} value is not at all varies with increase in the temperature indicating that adsorption of 150ppm ATMP+50ppm Al³⁺ on the carbon steel surface was unfavorable at higher temperature.

3.3. Thermodynamic Parameters

3.3.1. Activation parameters on the inhibition process

Temperature plays an important role in understanding the inhibitive mechanism of the corrosion process. To assess the temperature effect, experiments were performed at 303 - 323K in uninhibited and inhibited solutions containing different concentrations of 150ppm ATMP + 50ppm Al³⁺ and the corrosion rate was evaluated. The relationship between the corrosion rate (Cr) of carbon steel in water media and temperature (T) is expressed by the Arrhenius equation^{28, 35, 36}.

$$\text{LogCR} = \text{LogA} - \frac{E_a}{2.303 RT} \quad (9)$$

where, CR is the corrosion rate, A is the Arrhenius constant, E_a is the apparent activation energy, R is the molar gas constant and T is the absolute temperature.

A plot of log of corrosion rate (CR) obtained by weight loss measurement versus $1/T$ gave straight line with regression coefficient close to unity, as shown in Fig.7. The values of apparent activation energy (E_a) obtained from the slope ($-\frac{E_a}{2.303 RT}$) of the lines and the pre-exponential factor (λ) with the intercept ($\log \lambda$) are given in Table 3. It is evident from Table 3 that the apparent energy of activation increased on addition of mixed inhibitors (150ppm ATMP+50ppm Al³⁺) in comparison to the uninhibited solution. The increase in the apparent activation energy suggests physical adsorption⁵⁶⁻⁵⁸. Increase in the activation energy is attributed to appreciable decrease in the adsorption of inhibitor on carbon steel surface by increase in the temperature⁵⁹. This decrease in adsorption leads to increase in corrosion rate due to the greater exposed surface area of the carbon steel in ground water.

It is clear from equation (9) that corrosion rate is influenced by higher E_a value leads to the lower corrosion rate. It is evident that the effect of activation energy on carbon steel corrosion is larger than that of the pre-exponential factor. Decrease in the corrosion rate by increasing inhibitor concentration in this study suggests that E_a is the deciding factor. Moreover, increase in concentration of mixed inhibitors to an increase in the value of E_a , indicating strong adsorption of the inhibitor molecules at the metal surface.

Figure 7 Arrhenius plot for carbon steel corrosion in ground water in presence and absence of mixed inhibitors. (Different Con. of ATMP+ 50ppm Al³⁺).

Experimental corrosion rate values evaluated from the weight loss data for carbon steel in ground water in the absence and presence of mixed inhibitors was used to determine the enthalpy of activation (ΔH^*) and apparent entropy of activation (ΔS^*) for the formation of the activation complex in the transition state equation.

An alternative formula for the Arrhenius equation is the transition state equation (10).

$$R = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(-\frac{\Delta H^*}{RT}\right) \quad (10)$$

where, h is Planck's constant, N the Avogadro's number, the apparent entropy of activation ΔS^* and the enthalpy of activation ΔH^*

A plot of $\log (CR/T)$ versus $1/T$ is shown in Fig.8. Straight lines were obtained with slope $\left(\frac{-\Delta H^*}{2.303R}\right)$ and intercept $\left[\log \frac{R}{Nh} + \left(\frac{\Delta S^*}{2.303R}\right)\right]$ from which and were calculated and listed in Table 4.

Table 4. Activation parameters of 50ppm Al^{3+} with different concentration of ATMP in ground water at various temperatures

ATMP(ppm)	E_a (kJ.mol ⁻¹)	ΔH^* (kJ.mol ⁻¹)	ΔS^* (kJ.mol ⁻¹)	ΔG^*		
				303 K	313 K	323 K
Blank	10.45	7.80	-0.197	67.70	69.68	71.66
50	28.88	26.32	-0.148	71.31	72.79	74.27
100	32.70	30.35	-0.137	72.10	73.48	74.86
150	75.50	77.01	-0.018	77.57	77.59	77.60
200	72.85	45.95	-0.223	72.29	74.52	76.76

The positive value of enthalpy of activation (ΔH^*) in the absence and presence of various concentration of inhibitor reflects the endothermic nature of carbon steel dissolution process meaning that dissolution of steel is slow or difficult.^{60,61} It is well noticed that the values of E_a are larger than the analogous values of ΔH^* indicating that the corrosion process involved a gaseous reaction, simply the hydrogen evolution reaction, associated with a decrease in the total reaction volume^{62,63}.

Figure 8. Transition plot for carbon steel corrosion in ground water in presence and absence of mixed inhibitors (Different Con. of ATMP+ 50ppm Al^{3+})

Moreover, in lower concentration of mixed inhibitors the average difference value of the $E_a - \Delta H^*$ is 2.52 kJ/mol, which is more or less equal to the average value of RT (2.60 kJ/mol). Therefore, it is indicated that the corrosion process is a unimolecular reaction as it is characterised by the following equation 11⁶³

$$E_a - \Delta H^* = RT \quad (11)$$

It is evident from the Table .3 that the value of increased in the presence of the inhibitor than the uninhibited solution indicating higher protection efficiency. This may be attributed to the presence of energy barrier for the reaction; hence the process of adsorption of inhibitor leads to rise in enthalpy of the corrosion process.

On comparing the values of entropy of activation (ΔS^*) listed in Table .3, smaller negative values of entropy of activation (ΔS^*), show that the activated complex in the rate determining step represents an association rather than a dissociation, meaning that a decrease in disordering takes place on going from reactants to the activated complex. It is clear from data listed in Table 4, from top to bottom ΔS^* value increased in the presence of various concentration of the studied inhibitor compared to free solution. The adsorption of inhibitor molecules in aqueous phase to metal surface can be regarded as quasi-substitution process between the inhibitor molecules in the aqueous phase and water molecules on the metal surface⁶⁴. The adsorption of inhibitors on carbon steel surface would be in equilibrium with desorption of water molecules from the surface:

The adsorption process for the inhibitor is believed to be exothermic and accompanied with the decrease in entropy of the solute (inhibitor) and increase in entropy of the solvent (water). The thermodynamic values obtained for entropy of activation are the algebraic sum of the adsorption of inhibitor molecules (solute) and desorption of water (solvent) molecules⁶⁵. Hence, the increase in entropy is attributed to increase in solvent entropy⁶⁶. The positive ΔS^* meaning that an increase in disordering takes place in going from reactants to the activated complex on metal/solution interface⁶⁷ which is driving force for the adsorption.

The increase of ΔS^* (-0.197 to -0.018 kJ/mol) with increasing inhibitor concentration, reveals that an increase in disordering takes place ongoing from reactant to the activated complex. This behaviour can be explained as a result of the replacement process of water molecules during adsorption of 150ppm ATMP+50ppm Al³⁺ on C-steel surface.⁶⁸

The change in activation free energy ΔG^* of the corrosion process can be calculated from equation 13.

$$\Delta G^* = \Delta H^* - T\Delta S^* \quad (13)$$

The obtained ΔG^* values are listed in Table 4. The values of ΔG^* were positive and showed almost no change with increasing temperature, indicating that the activated complex was not stable and the probability of its formation decreased somewhat with rise in temperature. However, ΔG^* values for inhibited systems reveal that in the course of inhibitor addition, the activated corrosion complex becomes less stable as compared to its absence.

3.3.2. Adsorption parameters on the inhibition process

The value of K_{ads} is related to the free energy of adsorption, ΔG_{ads} by the equation 14.

$$\Delta G_{\text{ads}} = -2.303RT \log(55.5K_{\text{ads}}) \quad (14)$$

K_{ads} and ΔG_{ads} values were taken from Langmuir adsorption isotherm (correlation coefficient $R^2 = 0.9968, 0.9927$ and 0.9904 at $303, 313$ and 323K respectively). The negative values of ΔG_{ads} indicate the spontaneity of the adsorption process and the stability of the adsorbed species on the carbon steel surface^{69,70}. Usually the values around -20 kJ mol^{-1} or lower are consistent with physisorption, while those higher than -40 kJ mol^{-1} involve chemisorption⁷¹. When charged species are adsorbed on the metal surface, there is possibility of coulombic interaction between adsorbed cation and anion thereby causing increase in the Gibb's free energy even if no chemical bonds are formed.⁷²

The values of ΔG_{ads} for the studied inhibitors are listed in Table 2. These values indicate physical adsorption of studied inhibitors on carbon steel surface. The adsorption is enhanced by means of the presence of nitrogen atoms with lone pair of electrons and π electrons in the inhibitor molecule influence it to adsorb electrostatically on the carbon steel surface forming the insoluble and stable inhibitor film on metal surface that decreases the metal dissolution.

Assuming the thermodynamic model, corrosion inhibition of carbon steel in presence of studied inhibitors can be better explained using the enthalpy of adsorption ΔH_{ads} and entropy of adsorption ΔS_{ads} which can be calculated from the integrated van't Hoff equation 15, Gibbs-Helmholtz equation 16 and basic thermodynamic equation 17.

$$\log K_{ads} = \frac{-\Delta H_{ads}}{2.303RT} + \frac{\Delta S_{ads}}{2.303R} + \log \frac{1}{55.5} \quad (15)$$

$$\left[\frac{\partial(\frac{\Delta G_{ads}}{T})}{\partial T} \right] = \frac{-\Delta H_{ads}}{T^2} \quad (16)$$

$$\frac{\Delta G_{ads}}{T} = \frac{\Delta H_{ads}}{T} + k \quad (17)$$

The calculated values of the heat of adsorption and entropy of adsorption are evaluated from Fig.9, Fig.10 and Fig.11 were listed in Table 5.

Table 5 Heat of adsorption and entropy of adsorption derived from Langmuir adsorption isotherm

Different thermodynamic equations	$-\Delta H_{ad}(\text{kJ.mol}^{-1})$	$-\Delta S_{ad}(\text{J.mol}^{-1} \text{ K}^{-1})$
Vant Hoff equation	31.86	77.85
Basic thermodynamic equation	31.38	76.20
Gibbs-Helmholtz equation	31.85	----

Figure 9. van't Hoff plot between $\log K$ versus $1/T$

Figure 10. Basic thermodynamic plot between ΔG_{ads} versus T

Figure 11. Gibbs-Helmholtz Plot plot between $\Delta G_{\text{ads}} / T$ versus $1/T$

The values calculated from different equations are in good agreement with each other. The negative value of ΔH_{ads} indicates that the adsorption of studied inhibitors is an exothermic nature of carbon steel corrosion. It is meaning that the dissolution process of carbon steel.⁷³ which means that corrosion process is controlled by activated complex. If the value is less than 40 kJ mol⁻¹ the adsorption process is physisorption while the value is more than 100 kJ mol⁻¹ the adsorption of inhibitor follows chemisorption process^{74,75}. In the present case, ΔH_{ads} value is 31.86 kJ mol⁻¹, suggesting the physical adsorption (physisorption). The entropy of adsorption obtained from Fig.9 is negative, which suggests the adsorption is an exothermic phenomenon accompanied by the decreasing in entropy⁷⁶. The negative value of entropies ΔS_{ads} in the presence of indicators indicate that the inhibitor molecules are adsorbed onto the carbon steel surface. This can be obtained by the formation of activated complex and more fixation of the system during the process⁷³.

4. CONCLUSION

- 150ppm ATMP+50ppm Al³⁺ ion act as a good inhibitor for carbon steel in ground water.
- Inhibition efficiency values increased with increase in inhibitor concentration but decreased with increase in temperature
- Enthalpy of activation reflects the endothermic nature of the carbon steel dissolution process.
- Entropy of activation increased with increasing inhibitor concentration; hence increase in the disorderliness of the system.
- Based on the correlation coefficient the adsorption of 150ppm ATMP+50ppm Al³⁺ ion on the carbon steel in ground water follows the Langmuir and Frumkin isotherm model.
- Gibbs free energy of adsorption, heat of adsorption and entropy of adsorption indicated that the adsorption process is spontaneous and exothermic and the molecules adsorbed on the metal surface by the process of physical adsorption.

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