Sodium tripolyphosphate (STPP) as a novel corrosion inhibitor for mild steel in 1 M HCl

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The corrosion inhibition of mild steel in 1 M HCl solution by sodium triphosphate (STPP), $Na_5P_3O_{10}$, has been studied using potentiodynamic polarisation as an electrochemical technique, weight loss and UV–vis spectrophotometric measurement. The results of weight loss and Tafel polarization measurements showed that this compound has fairly good inhibiting properties for steel corrosion in acidic bath, with 87% inhibition efficiency at optimum concentration 10^{-3} M. The inhibition is of a mixed anodic–cathodic nature. The adsorption behaviour of the investigated compound is found to obey Langmuir adsorption isotherm. Negative value was calculated for the energy of adsorption indicating the spontaneity of the adsorption process. The formation of complex between metal cations and sodium triphosphate is also proposed as additional inhibition mechanism of mild steel corrosion.

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1. Introduction

Acids are widely used in many industries. Some of the important areas of application are industrial acid cleaning, acid pickling, acid descaling and oil well acidizing [1]. Due to the aggressiveness of acids, inhibitors are used to reduce the rate of dissolution of metals and has been investigated by several workers [2-4]. The unsaturated bonds or aromatic rings in the molecular structure of the inhibitor favour the adsorption on the metal surface [5].

Most of the efficient inhibitors used in industry are organic compounds which mainly contain oxygen, sulphur, nitrogen atoms and multiple bonds in the molecule through which they are adsorbed on metal surface [6,7].

Moreover, many phosphorus compounds have been proved to be effective inhibitors for the corrosion of metals and alloys in aqueous media, as found by Soylev et al [8].

Indeed, previous papers have shown that sodium tripolyphosphate (STPP) was an efficient inhibitor against steel corrosion in concrete reinforcement. Ltifi et al has studied the inhibition effect of mild steel by sodium tripolyphosphate (STPP) archaeologically, which emphasize the effect of STPP on steel corrosion [9,10].

To the best of our knowledge, no data are available in the literature regarding the behaviour of sodium tripolyphosphate (STPP) as corrosion inhibitors for metals. In the present work the inhibitive behaviour of sodium phosphate (STPP) with mechanism of corrosion inhibition of mild steel in 1 N HCl discussed on the basis of intensive corrosion studies is reported for the first time : Two techniques were employed to carry out the measurements: (a) electrochemical (potentiodynamic polarisation) and (b) non-electrochemical (weight loss and UV–vis spectroscopy).

2. Experimental

The mild steel strips having composition (wt%): C 0.19, Si 0.25, Mn 0.04, S 0.04, P 0.07, Al 0.01 and balance Fe were used for weight loss as well as electrochemical studies. Prior to each experiment, pre-treatment of the surface of specimens was carried out, by grinding with paper of 600–1200 grit, rinsing with bidistilled water, ultrasonic degreasing in ethanol and dried at room temperature before use. The tested sodium tripolyphosphate (STPP) was purchased from sigma-aldrich, as a purum p.a grade. The compound is in its purest state (98.0 %), its chemical structure is shown in fig. 1. The aggressive solution (1M HCl) was prepared by dilution of analytical grade 37% HCl with bidistilled water. The concentration range of the inhibitor employed was 10^{-5} to 10^{-3} M.

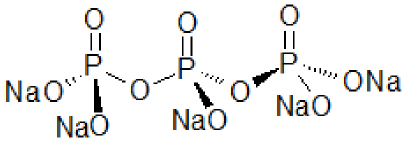

Fig. 1. Molecular structure of sodium tripolyphosphate (STPP)

2.1. Weight loss studies

The weight loss study is done on mild steel strips of 2.5 cm× 1.0 cm× 0.006cm sizes. The coupons, initial weight using an analytic balance was recorded before immersion in 250 ml open beakers containing 200 ml of corrodent (1 M HCl) without and with different concentrations of sodium tripolyphosphate (STPP). The specimens were taken out, washed, dried, and reweighed accurately. The average weight loss of the three parallel mild steel sheets could be obtained. The corrosion rates of mild steel have been determined for 24 h immersion period at 25 ± 0.1°C from mass loss, using Eq. (1) where Δm is the mass loss, S is the area, and t is the immersion period [11].

$$W = \frac{\Delta m}{St} \tag{1}$$

The inhibition efficiency *E(%)* was determined using Eq. (2) where W_0 and W_i is the weight loss value in the absence and in the presence of inhibitor [12].

$$IE(\%) = (\frac{W_0 - W_i}{W_0}) \times 100 \tag{2}$$

2.2 Potentiodynamic polarisation measurements

Electrochemical measurements were carried out in a conventional three electrode electrolysis cylindrical Pyrex glass cell. The working electrode (WE) had the form of a disc cut from the steel sheet. The area exposed to the corrosive solution was 1 cm^2, and the rest being covered by commercially available lacquer. A saturated calomel electrode (SCE) and a platinum electrode are used respectively as reference and auxiliary electrodes. The temperature is controlled at 298±1K. The working electrode was polished with different grades of emery papers, washed with water and degreased with acetone. Polarization curves were recorded with a potetiostat type Amel 549 using a linear sweep generator type Amel 567. The anodic and cathodic polarization curves were recorded by a sweep rate 30 mV.mn^{-1}.

Before recording the polarization curves, the open-circuit potential was stable within 30 mn. The cathodic branch was allayed determined first; the open-circuit potential was then re-established and anodic branch determined. The linear Tafel segment of anodic and cathodic curves were extrapolated to corrosion potential in order to obtain the corrosion current densities (I_{corr}). The corrosion inhibition efficiency E(%) was evaluated from the measured I_{corr} values using Eq. (3). All plotted and calculated parameters were means of three independent experiments.

$$E(\%) = (\frac{I_{Corr} \quad mI^{inh}_{Corr}}{I_{Corr}}) \times 100 \tag{3}$$

Where I_{Corr} and I^{inh}_{Corr} are the corrosion current densities in the absence and in the presence of various concentrations of the inhibitor [13].

2.3 Spectrophotometric measurements

Using UV-vis spectrophotometric method, some experiments, were carried out on the electrolyte solution of the unprotected samples. All the spectra measurements were carried out using a perkin-Elmer UV-vis Lambda 35 spectrophotometer.

3. Result and discussion

3.1. Effect of concentration on corrosion of mild steel and potetiodynamic polarization measurements

The values of inhibition efficiency, corrosion rate and weight loss obtained from gravimetric method at different concentrations of sodium tripolyphosphate (STPP) after 24 h of immersion in 1 M HCl solutions at 25 ± 0.2°C are summarized in Table 1, and the inhibition efficiency as a function of concentration is reported in Fig. 2. It was observed that (STPP) inhibits the corrosion of mild steel in HCl solution at all concentrations used in the study i.e 10^{-5} – 10^{-3}M. Maximum inhibition efficiency (86.04%) encountered at an optimum concentration of 10^{-3} M of (STPP) in 1M HCl at 298K. A further increase of inhibitor concentration does not significantly change the protective effect.

Table 1. Weight loss, corrosion rate and inhibition efficiency for various concentrations of sodium phosphate (STPP) for the corrosion of mild steel in 1M HCl from weight loss measurements.

Inhibitor	*Am*	*W*	*E*(%)
concentration (M)	(mg.cm^{-2})	($\times 10^{-2}$mg.cm^{-2}h^{-1})	
Blank	15.09	62.95	
10^{-5}	8.73	36.42	42.13
5×10^{-5}	4.27	17.81	71.70
10^{-4}	3.23	13.47	78.60
5×10^{-4}	2.24	09.35	85.15
10^{-3}	2.11	08.79	86.04

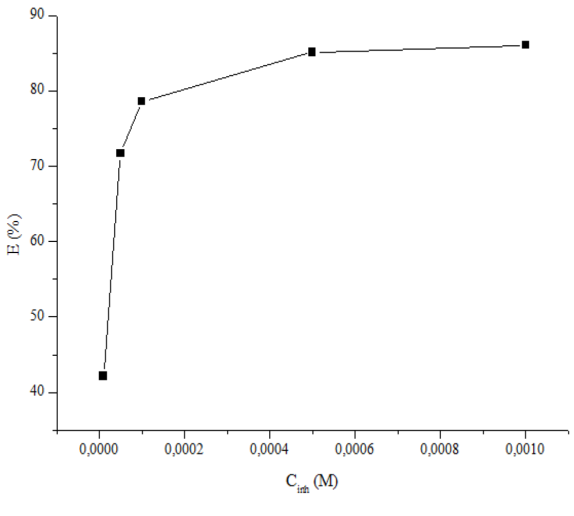

Fig. 2. Variation of inhibition efficiency with respect to the concentration, for mild steel in 1 M HCl at 25°C.

Tafel polarization curves for mild steel in molar HCl in the absence and presence of STPP at various concentrations at 298 K are presented in Fig.3. the important corrosion parameters derives from these curves such as, corrosion potential (Ecorr), corrosion current density (Icorr), cathodic Tafel constant (bc), anodic Tafel slope (ba) and inhibition efficiency E(%) were calculated and given in Table 2. From Table 2 it is clear that the addition of the STPP at various concentrations leads to a decrease of the corrosion current (I_{corr}) from 19.55 to 2.39 mA.cm^{-2}. This indicates that this compound is adsorbed on the metal surface and hence inhibition occurs.

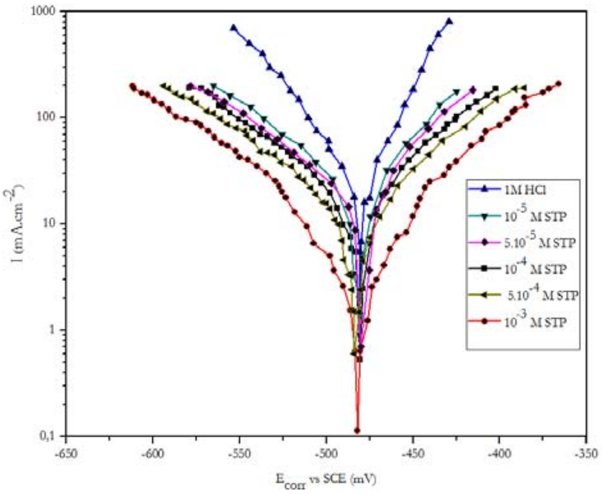

Fig. 3. Polarization curves of mild steel in 1 M HCl with different concentration of inhibitor.

The polarisation curves (Fig. 3) shows that this inhibitor has an effect on both, the cathodic and anodic slopes (bc and ba) and suppressed both cathodic and anodic processes. This indicates a modification of the mechanism of cathodic hydrogen evolution as well as anodic dissolution of iron, which suggest that sodium tripolyphosphate (STPP) powerfully inhibits the corrosion process of steel, and its ability as corrosion inhibitor is enhanced as its concentration is increased. The suppression of cathodic process can be caused by the covering of the surface with monolayer of the adsorbed inhibitor molecules. It can also be seen from Table 2, that anodic Tafel slope b_a increases in the presence of (STPP). This observation may be ascribed to changes in the charge transfer coefficient α_a for the anodic dissolution of Fe by virtue of the presence of an additional energy barrier due to the presence of adsorbed inhibitor. The addition of STPP does not alter the value of E_{corr} significantly indicating the mixed type of inhibiting behavior of (STPP). And that is, it influence both metal dissolution and hydrogen evolution. Such behavior has been developed by Palmer and Dhouibi. [10,14].

Table 2. Corrosion characteristics from tafel polarization curves obtained in 1M HCl solution at 298K of different concentration of inhibitor

Inhibitor concentration (M)	E_{corr} (mV SCE^{-1})	-b_c (mV dec^{-1})	b_a(mV dec^{-1})	I_{corr} (mA. cm^{-2})	E(%)
Blank	-477	51	35	19.55	
10^{-5}	-479	84	59	11.04	43.50
5.10^{-5}	-477	90	67	5.23	73.20
10^{-4}	-481	91	79	4.12	78.90
5. 10^{-4}	-483	89	78	2.80	85.59
10^{-3}	-482	78	62	2.39	87.77

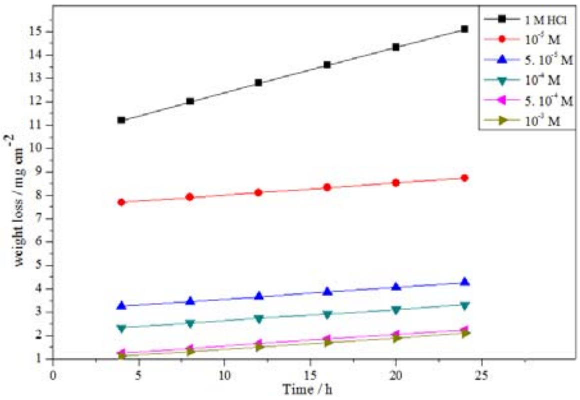

Fig. 4 Variation of the weight loss time of mild steel coupound in aerated solutions of 1M HCl in absence of different concentrations.

3.2. Effect of immersion time on corrosion of steel

Fig. 4 represents the relation between time and weight losses of mild steel coupons in 1 M HCl solution devoid of and containing different concentrations of (STPP). Inspection of this figure reveals that, the linear variation of weight loss with time in uninhibited and inhibited 1 M HCl solution indicates the absence of insoluble surface films during corrosion, i.e. the inhibitor are first absorbed on metal surface and thereafter impede corrosion either by merely blocking the reaction sites (anodic and cathodic) or by altering the mechanism of the anodic and cathodic processes. The relatively large decrease in the weight loss in presence of different concentrations from the additive indicates that the additive under study has an inhibition effect on the corrosion of mild steel in 1 M HCl solution.

3.3. UV–vis spectroscopy

The absorption of monochromatic light is a suitable method for the identification of complex ions, the absorption of light is proportional to the concentration of the absorbing species. For routine analysis a simple conventional technique based on UV–vis absorption is the more sensitive direct spectrophotometric detection. Change in position of the absorption maximum and or change in the value of absorbance indicate the formation of a complex between two species in solution [7].

In order to confirm the possibility of the formation of $(P_3O_{10})_2Fe_5$ complex, UV–Vis absorption spectra obtained from 1M HCl solution containing 10^{-3} M (STPP) before and after 10 days of mild steel immersion are shown in Fig. 5.

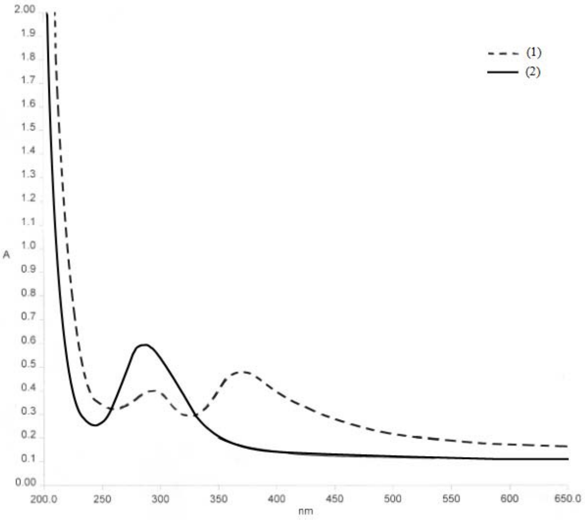

Fig. 5. UV-spectra of the solutions containing 1 M HCl 10^{-3} M STPP before mild steel immersion (1) and after 10 days immersion (2).

The absorption spectrum of the solution containing 10^{-3} M (STPP) before the steel immersion (curve 2: solid line) shows a band of shorter wavelength in the range 250-350 nm which corresponds to the n-π* electronic transition involving the lone paire of electrons on the STPP oxygene atom and/or phosphate group. After 10 days of steel immersion (curve 1: dashed line), it is clearly seen that the band in the region of 250–350 nm has been shifted to around 260–325 nm. In the mean time there is a decease in the absorbance of this band, this can be justified by the decrease of the concentration of STPP at the expense of the formation of the complex.

The apearance of a broad band at around 350-450 nm can be explained by the formation of the complex in which the oxygene and/or phosphate groups are strongly held up with Fe^{+2} cation.

These experimental findings give a strong evidence of the possibility of the formation of a complex between Fe^{+2} cation and (STPP) in 1 M HCl solution.

3.4. Adsorption isotherm

It is well recognized that the first step in inhibition of metallic corrosion is the adsorption of inhibitor molecules at the metal/solution interface this adsorption depends on several factors such as : the molecule's chemical composition, the temperature and the electro-chemical potential at the metal/solution interface. In fact, the solvent H_2O molecules could also be adsorbed at metal/solution interface. So the adsorption of inhibitor molecules from the aqueous solution can be regarded as a quasi-substitution process between the compounds in the aqueous phase [$Inh_{(sol)}$] and water molecules at the electrode surface [$H_2O_{(ads)}$] [15;17].

$$Inh_{(sol)} + x\,H_2O_{(abs)} \leftrightarrow Inh_{(ads)} + x\,H_2O_{(sol)} \qquad (4)$$

where x is the size ration, that is, the number of water molecules replaced by one inhibitor molecule.

Basic information on the interaction between the inhibitor and the mild steel surface can be provided by the adsorption isotherm. In order to obtain the isotherm, the linear relation between degree of surface coverage (θ) values and inhibitor concentration (C_{inh}) must be found. θ was calculated using Eq. 5

$$\theta = E(\%)/100. \qquad (5)$$

Where E(%) is the inhibition efficiency.

Attempts were made in order to fit the θ values to various isotherms including Langmuir, Temkin, Frumkin and Flory-Huggins. By far the best fit is obtained with the Langmuir isotherm. This model has also been used for other inhibitor systems [18,19]. According to this isotherm, θ is related to C_{inh} by:

$$C_{inh}/\,\theta = 1/K_{ads} + C_{inh} \qquad (6)$$

where Kads denotes the equilibrium constant for the adsorption process.

The plot of C_{inh}/θ versus C_{inh} and the expected linear relation-ship is obtained for compound (Fig.6). the strong correlation (R^2= 0.999) for STPP confirm the validity of this approach. The slope of straight line is 1.15 suggesting that the adsorbed inhibitor molecule form a monolayer on the mild steel surface.

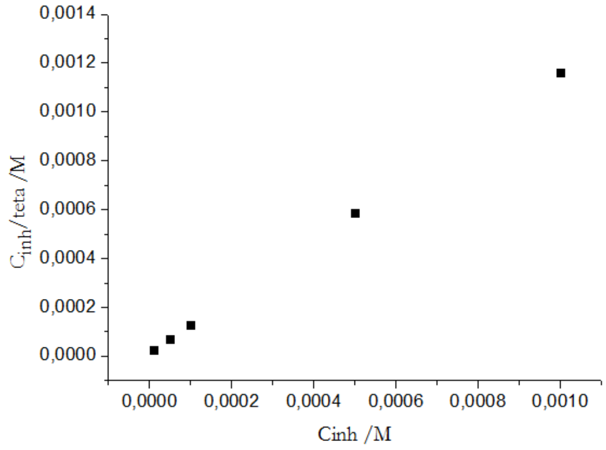

Fig. 6. Langmuir isotherm adsorption model of the steel surface of inhibitor in 1M HCl

The values of equilibrium constant K(M^{-1}) obtained from the Langmuir adsorption isotherm and the values of the Gibbs free energy of adsorption ΔG_{ads} are listed in table 3. ΔG_{ads} was calculated using Eq(7).

$$\Delta G^\circ_{abs} = -RT\ln(55.5K_{ads}) \qquad (7)$$

where R is the universal gas constant, T the thermodynamic temperature and the value of 55.5 is the concentration of water in the solution [20].

The value of K_{ads} for STPP ($\geq 100\ M^{-1}$) indicates the stability of the formed layer. The negative value of ΔG_{abs}, calculated from (eq. 7) is consistent with the spontaneity of the adsorption process and the stability of the adsorbed layer. Generally, the energy values of -20 $kJ.mol^{-1}$ or less negative are associated with an electrostatic interaction between charged molecules and charged metal surface, physisorption; those of -40 kJ mol^{-1} or more negative involve charge sharing or transfer covalent bond, chemisorptions [21]. In the present study, the ΔG_{abs} value (39.08 $kJ.mol^{-1}$) obtained for STPP on mild steel in 1 M HCl solution, which is lower than -20 $kJ.mol^{-1}$ (Table 3); this indicates that the adsorption is neither typical physisorption nor typical chemisorptions but it is complex mixed: involves both physisorption and chemisorption, however chemisorption is the predominant mode of adsorption.

Table 3. Slope, equilibrium constant, regression coefficient and free enthalpy of adsorption of sodium phosphate (STPP) on mild steel in 1 M HCl at 298 K

Slope	1.15
$K(M^{-1})$	81756.71442
Regression coefficient	0.9987
$-\Delta G$ ($kJmol^{-1}$)	39.98

3.5. UV-Vis spectroscopy and mechanism of corrosion and inhibition

The inhibition efficiency depends on many factors, which include the molecular size, heat of hydrogenation, mode of interaction with the metal surface, formation of metallic complexes and the charge density on the adsorption sites. We can note that a plausible mechanism of corrosion inhibition of mild steel in 1 M HCl by the compound under study may be deduced on the basis of adsorption. In acidic solutions, this inhibitor can exist as cationic species (Eq. (8)) which may be adsorbed on the cathodic sites of the mild steel and reduce the evolution of hydrogen:

$$\mathrm{STPP} + x\mathrm{H}^{+} \leftrightarrow [\mathrm{STPPH}_x]^{x+} \qquad (8)$$

The protonated STPP, can also be adsorbed on the metal surface by means of electrostatic interaction between Cl− (which act as a bridge between the metal surface and the electrolyte) and protonated STPP. Moreover, the adsorption of this compound on anodic sites can be explained by the presence of electrons of phosphorus, oxygen and π-electrons of phosphate group, which will then reduce the anodic dissolution of mild steel. On the other hand inspection of the chemical structure of STPP (Fig.1) revels that the STPP molecules exhibit a chelation center in its own structure have structure. Such structure facilitates the formation of a complex with the dissolved irons ions (Fig.7).

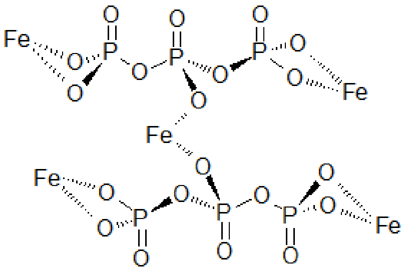

Fig.7 Structure formula of the complex compound.

The UV-Vis adsorption spectra of the mild steel specimen indicate the formation of a soluble complex with the cation (Fe+), allowing the formation of adhesive film. Such adhesive film covers the metal surface and thus isolates the metal from the corrosive media.

4. Conclusion

The inhibition efficiency of sodium tripolyphosphate (STPP) increases with the increase of the concentration up to 87% at 10^{-3} M.

(STPP) having a mixed type of inhibitor property and suppresses both anodic and cathodic processes.

(STPP) adsorbs on the mild steel surface according to the Langmuir adsorption isotherm.

UV–vis studies clearly reveal the formation of Fe-sodium tripolyphosphate (STPP) complex which may be also responsible for the observed inhibition.

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