

## Some triphosphates as corrosion inhibitors for mild steel in 3% NaCl solution

Suman Lata\* & R S Chaudhary

Department of Chemistry, M D University, Rohtak 124 001, India

Email: jakhar.suman@rediffmail.com

*Received 11 October 2007; revised 22 April 2008*

Inhibition of mild steel corrosion in 3% sodium chloride solution by sodium tripolyphosphate (STPP), sodium hexametaphosphate (SHMP) and adenosine triphosphate (ATP) in presence of 200 ppm zinc acetate has been investigated using weight loss, electrochemical polarisation and scanning electron microscopy techniques. Various corrosion parameters such as Tafel slopes, corrosion current density, heat of adsorption and activation energy value have been calculated to understand the inhibition mechanism. Inhibition efficiency increased with increase in concentration for STPP and SHMP whereas it decreased for ATP. However, inhibition efficiency decreased for all the three phosphates with increase in temperature. All the three phosphates acted as mixed inhibitors though anodic reactions are suppressed more in comparison to the cathodic reactions. STPP acted through chemisorption whereas SHMP and ATP are physically adsorbed over the surface of mild steel.

**Keywords:** Mild steel, Sodium chloride, Corrosion inhibitor, Phosphates

Mild steel, highly applicable and most widely used alloy of iron comes in contact with chloride ions very frequently under numerous conditions and circumstances in industries. Chloride ions are known to be aggressive towards mild steel and cause severe corrosion problems. Various inorganic compounds *viz.* nitrates, sulphates, silicates, chromates etc<sup>1</sup> have been reported as inhibitors for controlling corrosion of mild steel in water containing chloride ions but the inhibitive efficiency of such compounds when used alone was found to be very less. Zinc ions as inhibitor of the corrosion of steel in water have been known since 19<sup>th</sup> century. Many examples exist of their use in combination with other inhibitors to improve the protection of metals<sup>2-8</sup>. Many organic compounds containing nitrogen, sulphur, phosphorus atoms have also been examined as corrosion inhibitors for iron dissolution in acidic as well as in halide containing media<sup>9</sup>. Relatively low toxicity and ready availability of zinc salts have led to their wide use in practice. Compounds containing phosphorus like phosphonates and polyphosphates<sup>10</sup> have also been included among such inhibitors and in fact such compounds in combination with zinc ions<sup>11</sup> show synergistic effect and can provide high inhibitive efficiency towards

corrosion of mild steel in water containing chloride ions. In various industries, water being in great demand and the largest source of water is sea water which is at a peak in corrosivity due to the presence of approximately 3.5% NaCl. Moreover, mild steel, the cheapest as well as highly applicable material in industries gets attacked by chloride ions. So, it becomes a basic need to investigate various corrosion inhibitors for mild steel in about 3% NaCl solution.

### Experimental Procedure

Aqueous solution of 3% NaCl, zinc acetate and the three phosphates (STPP, SHMP and ATP) were prepared from AR grade reagents using doubly distilled water. Commercial mild steel sheets of percentage composition 0.14C, 0.03 Si, 0.032 Mn, 0.05S, 0.20P, 0.01 Ni, 0.01Cu, 0.01Cr were used in as received conditions. Mild steel specimens of size 3×1.5 cm were used for weight loss measurements. All the specimens were mechanically polished successively with the help of emery papers of grades 1/0, 2/0, 3/0 and 4/0 and then thoroughly washed with water and acetone. For weight loss measurements mild steel specimens were immersed in 200 mL test solution for a period of 10 days. All the experiments were carried out in an electronically controlled air thermostat with in an accuracy of  $\pm 1^\circ\text{C}$  in absence and presence of inhibitor.

\*Present Address: Department of Chemistry, Hindu Girls College, Sonapat 131 001, India

The electrochemical studies were carried out using potentiostat/galvanostat PGS 201 (Tacussel, France). Specimens used for electrochemical experiments had working area of 1 cm<sup>2</sup> and the remaining area was covered with lacquer. Platinum electrode was used as an auxiliary electrode and experiments were carried out in a 500 mL glass cell having three electrodes assembly.

All the potentials were measured against a pencil type saturated calomel electrode. The specimen was left in the test solution until a constant open circuit potential (OCP) was attained. Linear polarisation resistance (LPR) measurements were carried out galvanostatically by scanning through a potential range of 14 mV above and below the OCP value in steps of 2 mV. The resulting current was plotted against the potential and slope of the line was measured. The anodic and cathodic Tafel slopes  $\beta_a$  and  $\beta_c$  respectively were measured after recording anodic and cathodic polarization curves of the specimen upto a maximum shift of  $\pm 140$  mV from OCP value in steps of 10 mV.

The corrosion current density  $I_{corr}$  is related to the corrosion rate by the equation.

$$\text{Corrosion rate (C.R.) (mpy)} = \frac{0.1288 \times I_{corr} \times Eq.Wt}{D} \quad \dots(1)$$

where Eq. wt. = Gram equivalent weight of metal/alloy

$$D = \text{Density of metal (g/cm}^3\text{)}$$

$$I_{corr} = \text{Corrosion current density in } \mu\text{A/cm}^2$$

And

$$= \frac{\beta_a \times \beta_c}{2.303(\beta_a + \beta_c)} \times \frac{1}{R_p} \quad \dots(2)$$

where  $R_p$  is the linear polarization resistance (slope  $\frac{dE}{dI}$ ),  $\beta_a$  and  $\beta_c$  are anodic and cathodic Tafel slopes respectively. The percentage inhibition efficiency of the inhibitors was calculated using corrosion rate as:

$$\text{Percentage inhibition efficiency} = \frac{C.R.(Blank) - C.R.(Inhibitor)}{C.R.(Blank)} \times 100 \quad \dots(3)$$

where C.R. (Blank) = Corrosion rate of mild steel in 3% NaCl solutions

C.R. (Inhibitor) = Corrosion rate of mild steel in 3% NaCl solutions in presence of inhibitor

Morphology of corroded mild steel surface in absence and presence of various inhibitors was studied using scanning electron microscopy technique (SEM). Mild steel specimens were exposed to 3% NaCl solution at 50°C without and with inhibitor at 200 ppm concentration of STPP and SHMP and 50 ppm of ATP. 200 ppm of zinc acetate was also added to all the inhibitors. After completely polishing and cleaning the specimens, all the specimens were washed with doubly distilled water and then with acetone, dried and kept in a desiccator over silica gel till they were transferred to SEM chamber for surface investigations at  $\times 2000$  magnification.

## Results and Discussion

Initially, experiments were performed to get information about the corrosion of mild steel in 3% NaCl solution as a function of time upto 10 days by weightloss method. Figure 1 shows the plot of weightloss of mild steel specimens versus time of

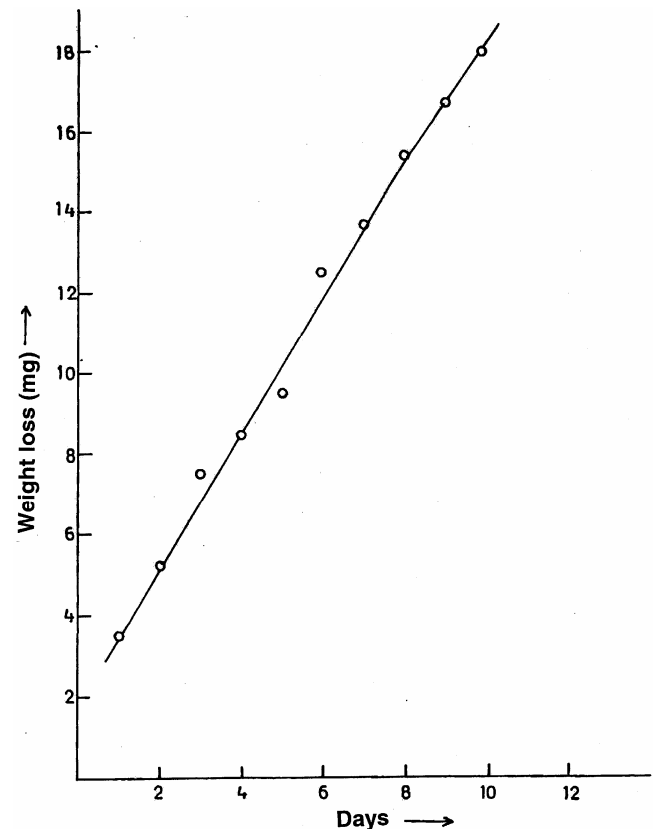


Fig. 1—Weight loss of mild steel in 3% NaCl solution versus time of exposure at 40°C

exposure in 3% NaCl solution at 40°C. It was observed that rate of corrosion increases linearly with time of exposure.

To estimate the inhibitive power of phosphates when used alone, each inhibitor was examined at 200 ppm concentration at 30°C. The results have been recorded in Table 1. Percentage inhibition efficiency was very less or even negative for mild steel in 3% NaCl solution at 30°C. Hence, in further experiments, Zn ions in the form of zinc acetate were added to the corrosion system alongwith each phosphate at 30°C. Zinc increases the rate of formation of the protective film and the concentration needed for effective protection is less than polyphosphate alone<sup>11</sup>. From Table 2, it is clear that 200 ppm of zinc acetate has shown better inhibitive effects out of its four different concentrations tested (50, 100, 200 and 300 ppm), therefore 200 ppm of zinc acetate was used to get better synergistic effects alongwith different concentrations of each inhibitor.

STPP, SHMP, ATP have been investigated at 25, 50, 100 and 200 ppm concentration of each phosphate as corrosion inhibitors for mild steel in 3% sodium chloride solution alongwith 200 ppm zinc acetate for enhancing inhibitive effect of each inhibitor at 30, 40 and 50°C. During weight loss experiments, all the mild steel specimens were exposed for 10 days under static conditions and all the three inhibitors have been studied in detail using weight loss method, galvanostatic polarization and scanning electron microscopy.

#### STPP, SHMP and ATP as inhibitors

The results obtained from various experiments performed for STPP, SHMP and ATP as inhibitors are shown in Tables 3, 4 and 5 respectively at 30, 40 and 50°C and concentrations 25, 50, 100 and 200 ppm of each inhibitor. It was observed that the percentage inhibition efficiency decreased with increase in temperature whereas it increased with increase in concentration of STPP and SHMP inhibitors but decreased again with increasing concentrations of ATP. With STPP and SHMP inhibitors, the inhibition efficiency was greater than 85% at 30°C and 200 ppm concentration of each inhibitor alongwith 200 ppm zinc acetate. ATP also showed greater than 70% inhibitor efficiency but giving a peculiar behaviour with increasing concentrations. ATP showed best inhibition efficiency at 25 ppm.

Cathodic and anodic polarization curves of mild steel in 3% sodium chloride solution in absence and presence of 25, 50, 100 and 200 ppm STPP, SHMP as well as ATP alongwith 200 ppm zinc acetate at 40°C have been shown in Fig. 2(a-c). It was also observed that the OCP shifted slightly towards anodic direction which indicated that all the three inhibitors may be considered as anodic in nature. However, a clear conclusion could not be drawn about the mechanism of inhibitor from OCP variation only. From the polarisation diagrams shown in Fig. 2 (a-c), it is evident that the inhibitors suppressed both, cathodic and anodic reactions and these may be considered as a mixed type though suppressing anodic reaction to greater extent. The percentage inhibition efficiency was found in good agreement with that obtained by galvanostatic polarization for all the three phosphates.

#### Mechanism of inhibition

Sodium tripolyphosphate (STPP, molecular formula  $\text{Na}_5\text{P}_3\text{O}_{10}$ ), has the following molecular structure:

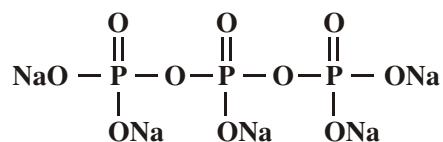


Table 1—Percentage inhibition efficiency by weight loss method of STPP, SHMP and ATP (200 ppm each) for mild steel in 3% sodium chloride solution

Exposure time = 10 days; Temperature = 30°C

S. no.	Inhibitor	Percentage inhibition efficiency
1	STPP	26.2
2	SHMP	12.8
3	ATP	-18.6

Table 2—Percentage inhibition efficiency by weight loss method of zinc acetate at different concentrations for mild steel in 3% sodium chloride solution

Inhibitor = zinc acetate; Exposure time = 10 days;  
Temperature = 30°C

S. No.	Concentration of zinc acetate (ppm)	Percentage inhibition efficiency
1	50	12.6
2	100	23.4
3	200	35.8
4	300	27.8

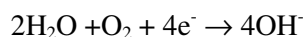
Table 3—Various corrosion parameters calculated from electrochemical experiments for mild steel in 3% sodium chloride solution in absence of different concentrations of STPP and 200 ppm zinc acetate at 30, 40 and 50°C

Concentration of inhibitor (ppm)	Temperature (°C)	OCP (mV)	$\beta_a$ mV/decade	$\beta_c$ mV/decade	$R_p$ (Ohms $\times 10^3$ )	$I_{corr}$ $\mu\text{A}/\text{cm}^2$	Corrosion rate (mpy)	% Inhibition efficiency by LPR	% Inhibition efficiency by weight loss
Blank	30	-652	78	334	1.16	24.5	10.9	-	-
	40	-672	80	340	0.78	37.5	16.5	-	-
	50	-690	86	348	0.62	45.0	22.0	-	-
25	30	-592	108	260	6.13	5.4	2.4	77.6	75.9
50	30	-586	104	262	7.77	4.0	1.9	82.7	80.8
100	30	-581	100	252	7.99	4.0	1.8	83.8	85.4
200	30	-578	94	246	12.78	2.3	1.0	90.4	92.3
25	40	-628	120	282	3.99	9.0	4.2	75.6	72.4
50	40	-622	112	270	4.04	8.5	3.9	77.4	76.5
100	40	-616	106	266	4.45	7.4	3.4	80.3	79.4
200	40	-602	102	260	6.14	5.2	2.4	86.2	86.8
25	50	-638	138	298	2.95	13.8	6.3	69.2	70.3
50	50	-632	132	288	3.01	13.0	6.0	71.0	72.0
100	50	-622	128	290	3.15	12.0	5.6	72.8	74.0
200	50	-618	126	284	3.78	10.0	4.6	77.8	79.4

Table 4—Various corrosion parameters calculated from electrochemical experiments for mild steel in 3% sodium chloride solution in absence and presence of different concentrations of SHMP and 200 ppm zinc acetate at 30, 40 and 50°C

Concentration of inhibitor (ppm)	Temperature (°C)	OCP (mV)	$\beta_a$ mV/decade	$\beta_c$ mV/decade	$R_p$ (Ohms $\times 10^3$ )	$I_{corr}$ $\mu\text{A}/\text{cm}^2$	Corrosion rate (mpy)	% Inhibition efficiency by LPR	% Inhibition efficiency by weight loss
Blank	30	-652	78	334	1.16	24.5	10.9	-	-
	40	-672	80	340	0.78	37.5	16.5	-	-
	50	-690	86	348	0.62	45.0	22.0	-	-
25	30	-624	84	284	4.33	6.5	2.98	72.9	73.2
50	30	-614	80	274	6.40	4.2	1.92	82.6	79.5
100	30	-608	80	262	7.39	3.6	1.65	85.1	82.1
200	30	-582	78	258	7.32	3.5	1.63	85.2	85.9
25	40	-636	98	298	2.87	11.0	5.11	70.3	70.8
50	40	-628	96	290	4.21	7.4	3.41	76.8	75.9
100	40	-611	94	282	5.02	6.0	2.80	83.8	78.9
200	40	-586	88	266	5.00	5.7	2.63	84.7	81.8
25	50	-648	106	312	2.27	15.0	6.94	66.4	65.6
50	50	-634	102	306	2.51	13.2	6.07	70.6	70.7
100	50	-627	98	288	2.69	11.8	5.41	73.8	74.6
200	50	-620	94	264	2.67	11.2	5.16	75.0	76.7

Here,  $\text{Zn}^{2+}$  ions can bind to any two favourable oxygen atoms giving zinc complex ( $\text{Na}_3\text{ZnP}_3\text{O}_{10}$ ). The following reactions may take place during corrosion of mild steel in 3% NaCl solution<sup>12,13</sup> and its inhibition by  $\text{Zn}^{2+}$  ions and STPP. Hydroxide ions which are produced as a result of following cathodic reaction



may attack the mild steel surface as:

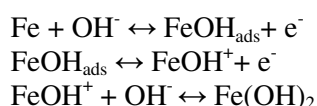


Table 5—Various corrosion parameters calculated from electrochemical experiments for mild steel in 3% sodium chloride solution in absence and presence of different concentrations of ATP and 200 ppm zinc acetate at 30, 40 and 50°C

Concentration of inhibitor (ppm)	Temperature (°C)	OCP (mV)	$\beta_a$ (mV/decade)	$\beta_c$ (mV/decade)	$R_p$ (Ohms $\times 10^3$ )	$I_{corr}$ ( $\mu\text{A}/\text{cm}^2$ )	Corrosion rate (mpy)	% Inhibition efficiency by LPR	% Inhibition efficiency by weight loss
Blank	30	-652	78	334	1.16	24.5	10.9	-	-
	40	-672	80	340	0.78	37.5	16.5	-	-
	50	-690	86	348	0.62	45.0	22.0	-	-
25	30	-538	100	316	5.26	6.2	2.8	73.9	74.0
50	30	-545	106	318	5.19	6.6	3.0	72.2	73.5
100	30	-550	108	322	5.14	6.6	3.1	72.2	72.2
200	30	-593	110	328	4.33	8.2	3.8	65.6	67.5
25	40	-600	108	320	3.17	11.0	5.0	70.5	71.2
50	40	-607	112	324	3.14	11.5	5.2	69.2	69.6
100	40	-610	114	328	3.13	11.7	5.4	68.7	68.6
200	40	-627	118	331	2.83	13.3	6.7	60.6	61.8
25	50	-618	110	324	2.52	14.0	6.5	68.6	68.9
50	50	-622	112	326	2.36	15.3	7.0	66.1	67.8
100	50	-625	114	330	2.00	18.3	8.4	63.6	62.1
200	50	-629	114	336	1.85	19.9	9.1	55.7	55.5

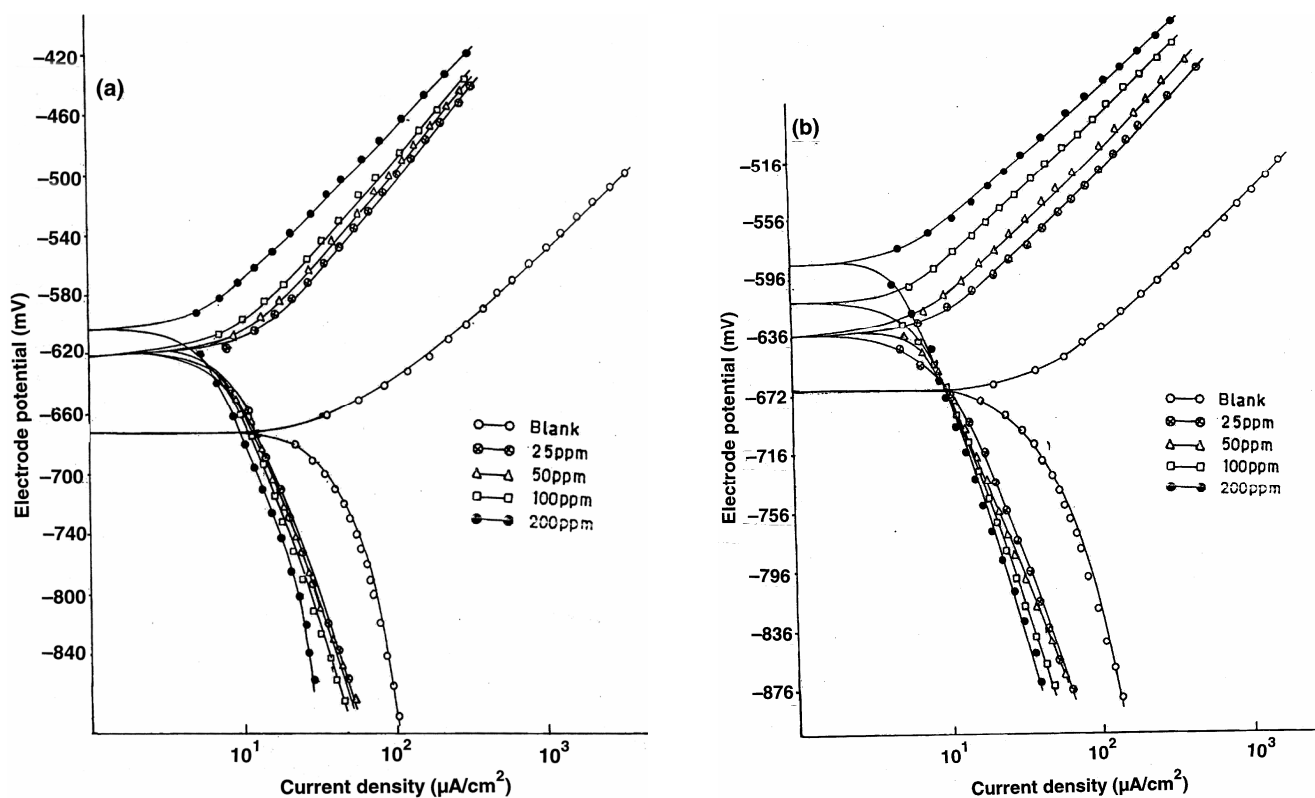


Fig. 2—(a & b) Cathodic and anodic polarization curves of mild steel in 3% NaCl solution in absence and presence of: (a) STPP and (b) SHMP (25, 50, 100 and 200 ppm) alongwith 200 ppm zinc acetate.

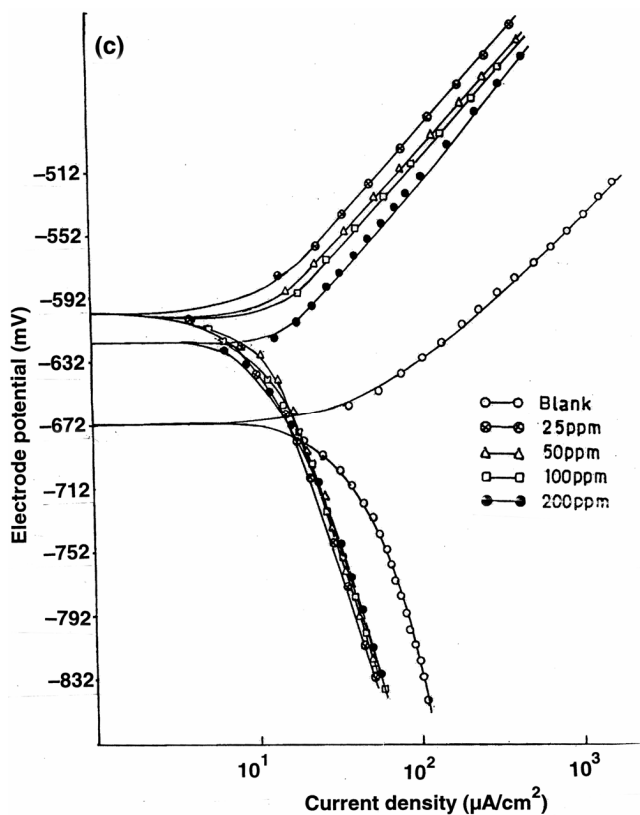
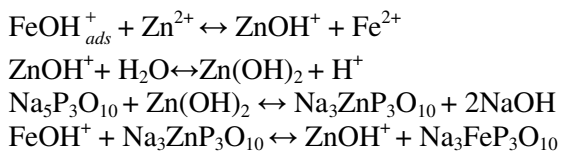
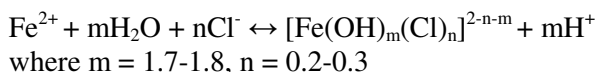


Fig. 2c—Cathodic and anodic polarization curves of mild steel in absence and presence of ATP (25, 50, 100 and 200 ppm) alongwith 200 ppm zinc acetate.

In presence of  $Zn^{2+}$  the following reactions may occur:



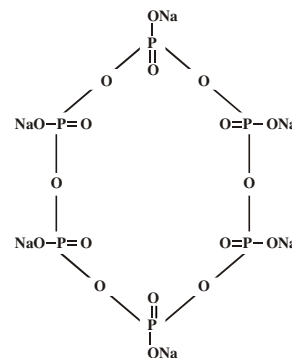
It has been reported that in chloride medium, formation of chloro complex may also occur as<sup>14</sup>:



As already stated  $Na_3ZnP_3O_{10}$ , a complex of zinc is formed in the course of reaction which may further change to  $Na_3FeP_3O_{10}$ , a stable complex of iron ( $Fe^{2+}$ ). Inhibition may be caused by the stabilisation of the surface film formed as a result of sodium iron polyphosphate ( $Na_3FeP_3O_{10}$ ) formation because complexes of iron are more stable than that of zinc<sup>15</sup>.

This complex of iron provides anodic protection whereas formation of  $ZnOH^+$  provides cathodic protection but conversion of soluble  $ZnOH^+$  to insulated precipitation film of  $Zn(OH)_2$  may also provide cathodic protection. Hence STPP shows mixed mode of inhibition but preferentially more anodic. The concept of complex formation of used polyphosphate with zinc ions and then replacement of  $Zn^{2+}$  ions by  $Fe^{2+}$  or  $Fe^{3+}$  ions which are usually more stable is also supported by Kuznetsov<sup>2</sup> who used HEDP and  $Zn^{2+}$  ions for controlling the corrosion of mild steel. A similar type of inhibition mechanism for mild steel by  $Zn^{2+}$  and HEDP has also been reported by Awad and Turgoose<sup>16</sup> for 2:1 Zn: HEDP complex at lower concentrations of zinc ions.

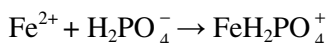
Molecular formula of SHMP is  $Na_6P_6O_{18}$ . It is a cyclic polyphosphate and may have the following molecular structure:



This compound is water soluble existing as anion in aqueous solution which has six equivalent negatively charged oxygen atoms after dissociation. This anion can form complex with  $Zn^{2+}$  ions or  $Fe^{2+}$  ions from any two negatively charged adjacent oxygen atoms. However,  $Fe^{2+}$  complexes formed are more stable in comparison to that of  $Zn^{2+}$  complexes<sup>15</sup>. Consequently,  $Zn^{2+}$  ions will be free to form  $ZnOH^+$  and/or  $Zn(OH)_2$  to afford cathodic protection. SHMP -  $Fe^{2+}$  complexes are adsorbed on anodic sites. Thus SHMP and  $Zn^{2+}$  ions in combination act as a mixed inhibitor.

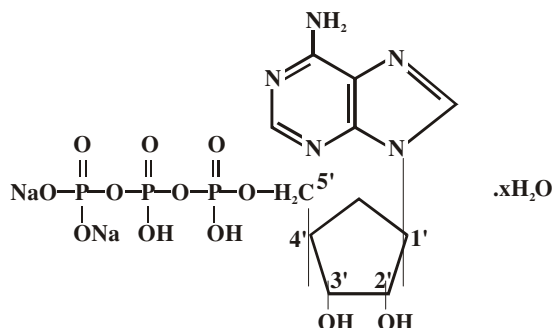
STPP and SHMP may partially amalgamate with the films appearing on the metal surface and improve their protective properties. Since, these invisible protective films mainly consist of  $\gamma-Fe_2O_3$ , they do not hamper the heat transfer and they protect the metal against corrosion by filling the voids and discontinuities with the help of ions and accelerate film growth<sup>10</sup>. Moreover, X-ray diffraction studies

on the oxides of iron revealed the presence of  $\gamma\text{-Fe}_2\text{O}_3$  in solutions at all pH levels irrespective of the nature of the iron substrate<sup>17</sup>.

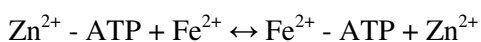


Film break down by  $\text{Cl}^-$  ions is a function of  $\text{Cl}^-$  ion concentration but film repair will depend upon  $\text{PO}_4^{3-}$  level<sup>18</sup> and competitive adsorption of the inhibitor anions in preference to the adsorption of aggressive  $\text{Cl}^-$  anions would occur. Similar results have been reported for low and high concentration of  $\text{Cl}^-$  ions<sup>19</sup>.

$\text{C}_{10}\text{H}_{14}\text{N}_5\text{Na}_2\text{O}_{13}\text{P}_3 \cdot x\text{H}_2\text{O}$  is the molecular formula of adenosine-5'-triphosphoric acid (disodium salt) (ATP  $\text{Na}_2$ ). Its molecular structure is:



As ATP is water soluble, it exists in ionic form in aqueous medium. Considering the structure of ATP molecule, there are various active sites present in the molecule such as nitrogen atom in the rings,  $-\text{NH}_2$  group and negatively charged oxygen atoms. Out of all these active sites available for adsorption of ATP molecule, the most preferred active sites are negatively charged oxygen atoms which may form complex with  $\text{Zn}^{2+}$  ions present in the system giving  $\text{Zn}^{2+}$  - ATP complex which will rapidly change to  $\text{Fe}^{2+}$  - ATP complex as  $\text{Fe}^{2+}$  complexes are more stable than  $\text{Zn}^{2+}$  complexes<sup>15</sup>.



Due to formation of  $\text{Fe}^{2+}$  - ATP complex,  $\text{Zn}^{2+}$  ions will be again available in the solution to form  $\text{ZnOH}^+$  or insoluble  $\text{Zn}(\text{OH})_2$  precipitations. The formation of  $\text{ZnOH}^+$  or insulated precipitation film of  $\text{Zn}(\text{OH})_2$  will

be adsorbed on cathodic sites and polarise the local cathodes.  $\text{Fe}^{2+}$  - ATP complex will be adsorbed on anodic sites, and suppress the anodic reaction. As both, anodic as well as cathodic reactions are appreciably retarded in presence of ATP with  $\text{Zn}^{2+}$  ions, it may be surmised that the inhibitor is functioning in mixed mode of inhibition. It also explains the shift in anodic and cathodic polarisation curves in presence of inhibitor. As ATP is large in size, there is a probability that after adsorption of  $\text{Fe}^{2+}$  - ATP complex has occurred; the adjacent electron rich atoms or groups may repel each other at higher concentrations of the inhibitor. This repulsion may lead to desorption of the inhibitor molecule from the surface of mild steel and in turn results in lower inhibition efficiency at higher concentrations of the inhibitor. It is also evident from the value of heat of adsorption at 200 ppm concentration of the inhibitor which is very low (-4.7 Kcal/mol). It also explains the results of weight loss and electrochemical polarisation experiments where it is observed that ATP provides higher protection at lower concentration and its efficiency decreases with increase in its concentration.

Figures 3 (a), (b) and (c) give plots of  $\log \theta/1-\theta$  versus  $\log C$  at 30, 40 and 50°C for STPP, SHMP and ATP respectively where  $\theta$  = surface coverage and  $1-\theta$  is uncovered surface. From these plots it seems that Langmuir adsorption isotherm mechanism is obeyed throughout the measured concentration range of these three inhibitors, as a result of which these inhibitors become significant to consider that these get adsorbed on the metal surface. ATP plots showed a different behaviour than that of STPP and SHMP.

With the help of  $\log \theta/1-\theta$  versus  $\log 1/T$  plots, heat of adsorption,  $\Delta H$  was calculated as shown in Fig. 4(a-c) for STPP, SHMP and ATP.  $\Delta H$  for STPP was maximum (-10.98 Kcal/mol) followed by SHMP (-6.2 Kcal/mol) and ATP (-4.7 kcal/mol). Hence it is clear that STPP shows strong adsorption on the metal surface amounting to nearly chemisorption but for SHMP and ATP it is physisorption. The thermodynamic parameters also indicate stronger interactions between the metal and each inhibitor.

Using Arrhenius plots as shown in Fig. 5(a-d), the energy of activation  $E_a$  for corrosion process in blank as well as in the presence of 200 ppm of each of the three inhibitors respectively (each with 200 ppm zinc

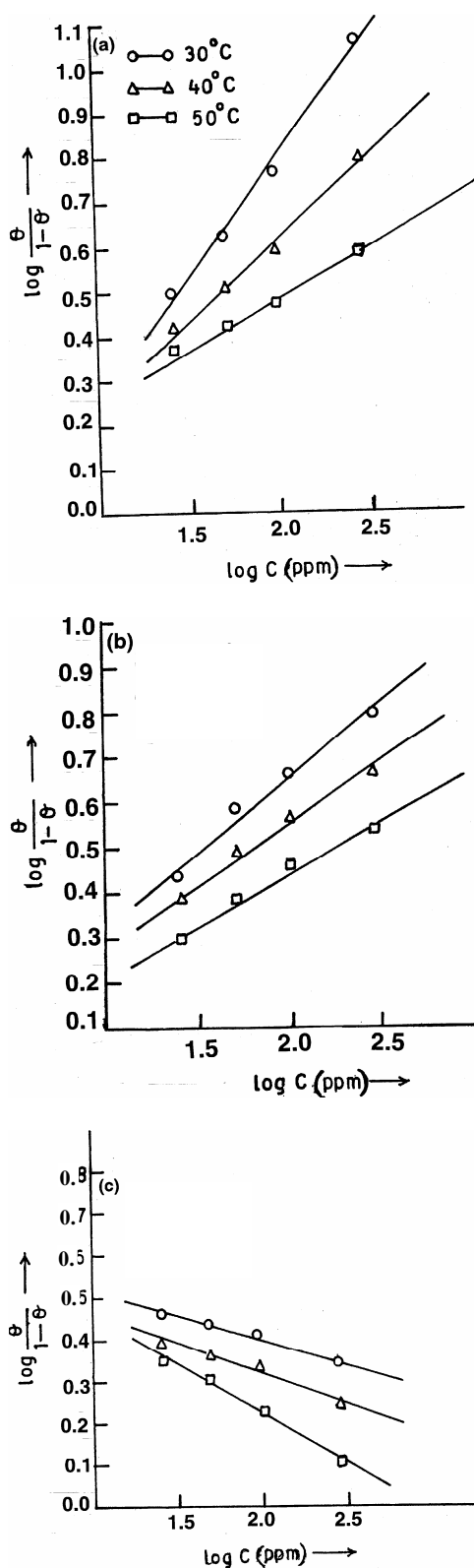


Fig. 3—Langmuir adsorption isotherm plots of: (a) STPP, (b) SHMP and (c) ATP, for mild steel in 3% NaCl solution along with 200 ppm zinc acetate.

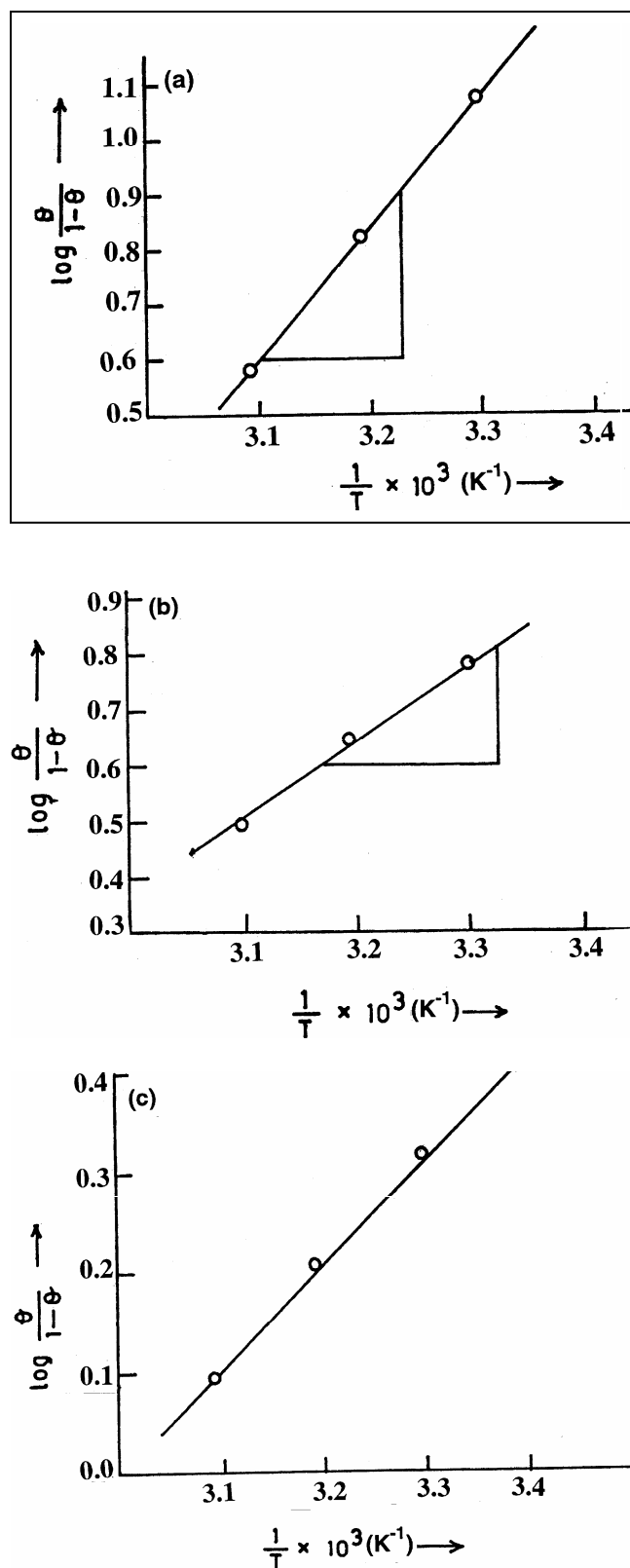


Fig. 4—Plots for heat of adsorption of: (a) STPP, (b) SHMP and (c) ATP each at 200 ppm concentration along with 200 ppm zinc acetate for mild steel in 3% NaCl solution.



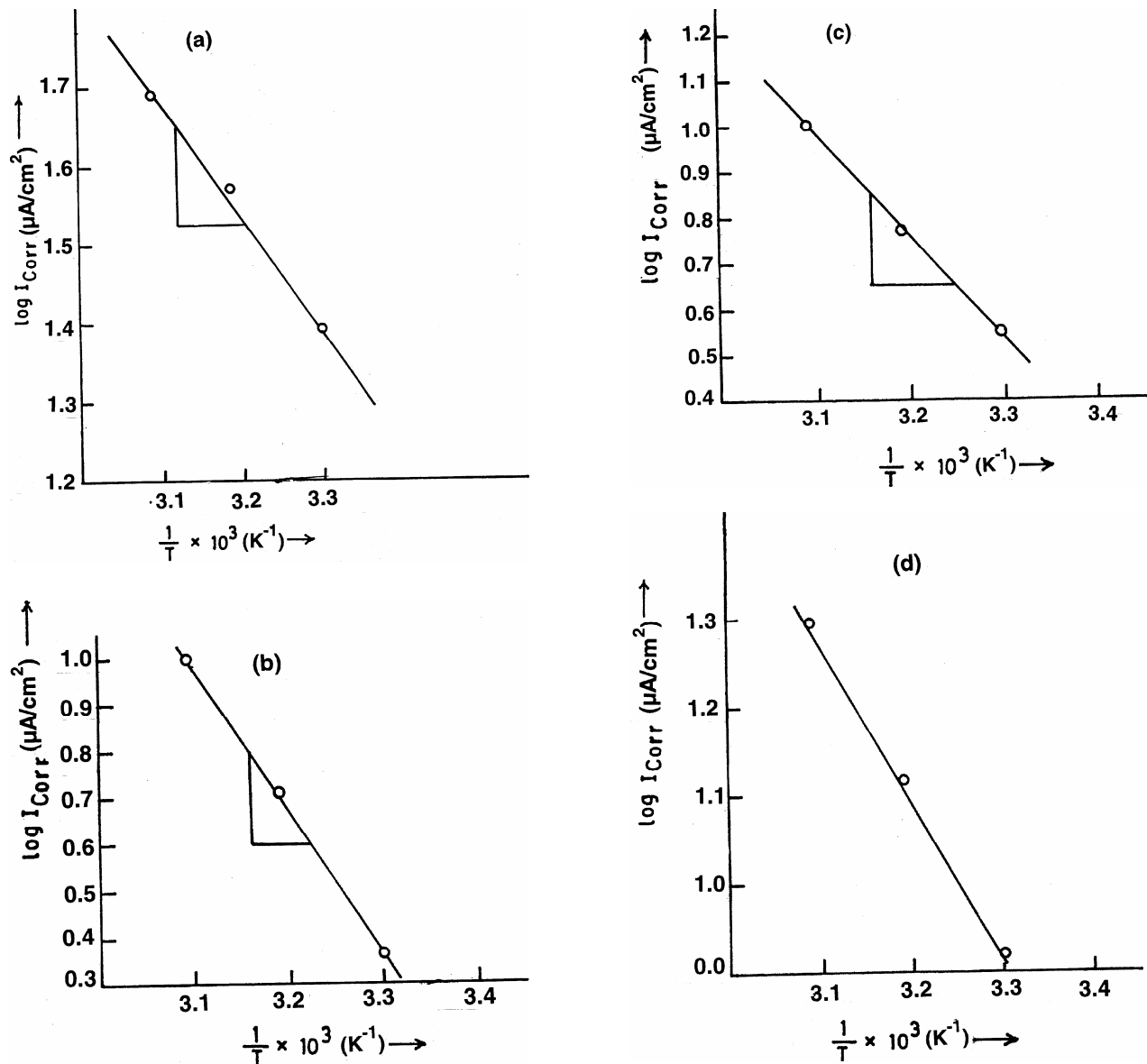


Fig. 5—Arrhenius plot of (a) Blank specimen, (b) STPP, (c) SHMP and (d) ATP each inhibitor at 200 ppm concentration along with 200 ppm zinc acetate for mild steel in 3% NaCl solution.

acetate) for mild steel specimens was computed using equation:

$$E_a = 2.303 \times 1.987 \times \left[ \frac{d \log I_{\text{corr}}}{d \left( \frac{1}{T} \times 10^3 \right)} \right] \text{Kcal/mol.} \quad \dots(4)$$

The values of activation energy  $E_a$  calculated were found to be 6.7 Kcal/mol for blank specimen, 14.1

Kcal/mol for STPP, 10.1 Kcal/mol for SHMP and 8.07 Kcal/mol for ATP. From these activation energy  $E_a$  values, it is clear that there is considerable shift in  $E_a$  value for STPP and SHMP at their 200 ppm concentration from  $E_a$  value of blank specimen which shows that these two inhibitors are quite good. ATP at 200 ppm concentration shows a little shift from that of blank specimen which shows that ATP gives poor inhibition at higher concentration. It is observed that the energy of activation is increasing by addition of inhibitors and it indicates that adsorption of inhibitor on to the surface of mild steel takes place.

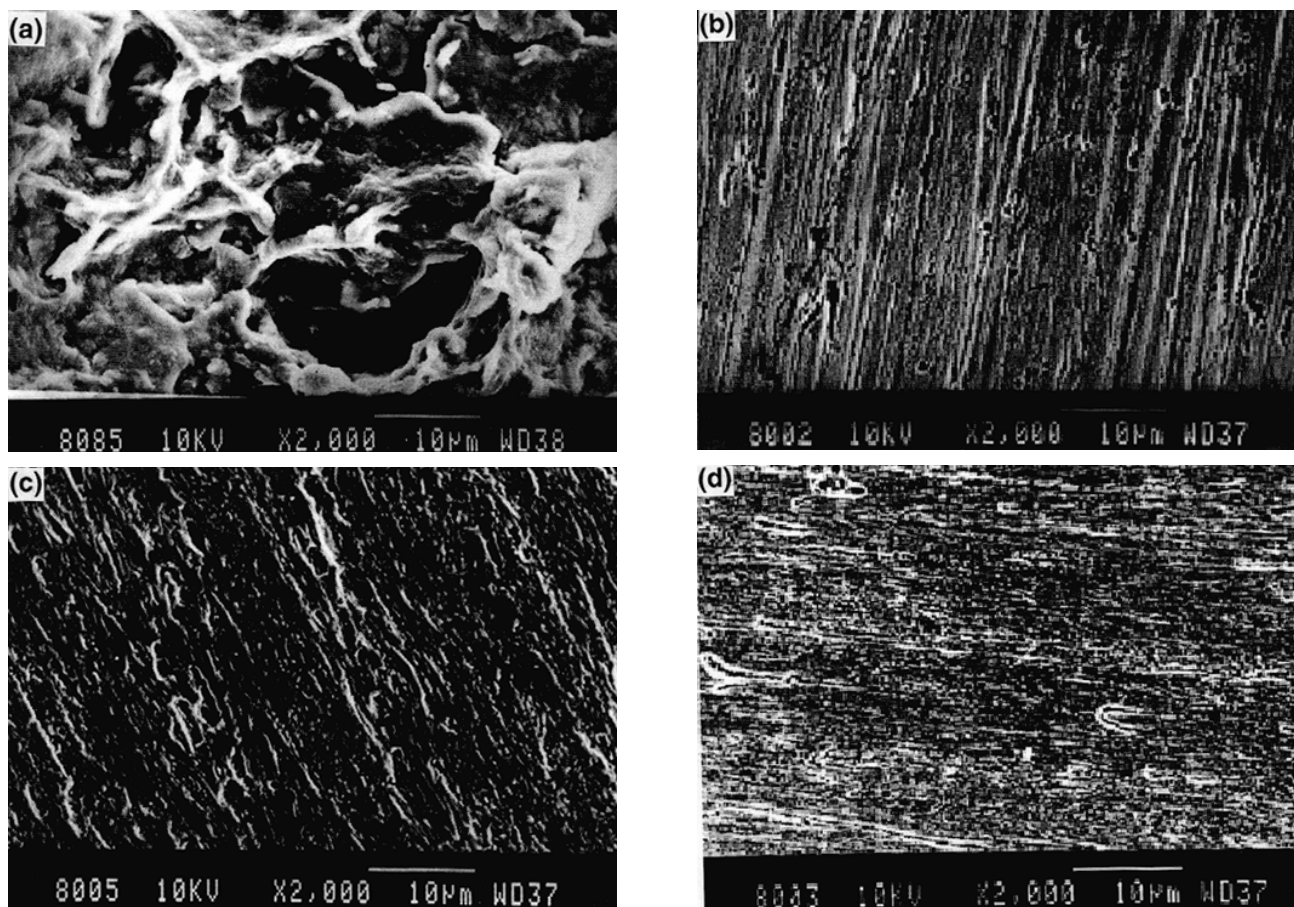


Fig. 6—Scanning electron micrograph of mild steel surface of: (a) Blank specimen, in the presence of (b) STPP, (c) SHMP and (d) ATP along with zinc acetate in 3% NaCl solution.

Figure 6 (a-d) shows scanning electron micrographs of mild steel surfaces in 3% NaCl solution in blank and with 200 ppm each of STPP and SHMP but with 50 ppm ATP respectively along with 200 ppm zinc acetate. All the specimens were kept for 10 days exposure at 50°C. On comparing inhibitive micrographs with that of blank, it is very clear that the inhibition provided by STPP is quite good, similarly for SHMP too, mild steel surface was smooth whereas remarkable smoothness is observed for 50 ppm ATP which also confirms that ATP shows good inhibition at lower concentration. From all these micrographs it appears that the protective film of adsorbed inhibitor molecule is present on the surface of mild steel, which acts as barrier for the access of aggressive ions to bare surface, in turn decreases the corrosion rate.

### Conclusion

From the study following conclusions may be drawn:

The percentage inhibition efficiency of all the phosphates is very high and is in the following order: STPP > SHMP > ATP

STPP and SHMP show an increase in percentage inhibition with increase in concentration whereas ATP shows a gradual decrease in inhibition efficiency with increase in concentration.

When temperature is increased, percentage inhibition efficiency decreases in all the three inhibitors.

All the three phosphates act as mixed inhibitors though anodic reactions are suppressed more in comparison to the cathodic reactions.

STPP acts through chemisorption whereas SHMP and ATP are physically adsorbed over the surface of mild steel.

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