

## Investigation of adsorption and inhibitive effect of phosphite on corrosion of mild steel in hydrochloric acid media

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### ABSTRACT

The inhibition behaviour of a phosphite compound:  $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$  (abbr. PhMg) on C38 steel in 1 M HCl solutions was investigated at 25 °C using electrochemical and weight loss methods. The results indicated that the title compound inhibited the corrosion of steel and the extent of inhibition increased with its concentrations. A mixed-inhibition mechanism is proposed for the inhibitive effect of PhMg. Effect of temperature is investigated in the (313-353 K) range. The determination of activation and adsorption parameters indicated that the inhibition action in the presence of PhMg is due to physical adsorption.

**Key words:** Corrosion, Mild steel, Corrosion inhibitors, Acid, phosphite.

### INTRODUCTION

In practice, corrosion can never be stopped but hindered to a reasonable level. Among various methods of corrosion control and prevention, organic or mineral inhibitors are the most frequently used. Organic compounds are widely used as inhibitors and act through a process of surface adsorption, so the efficiency of an inhibitor depends on the<sup>1-3</sup>.

1. chemical structure of the organic compound,
2. surface charge of the metal, and
3. type of interactions between the organic molecule and metal surface.

Literature reveals most inhibitors act by adsorption on the metal surface through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur, double bonds, triple bonds or aromatic rings which tend to form stronger coordination bonds. Compounds with p-bonds generally exhibit

good inhibitive properties, the electrons for the surface interaction being provided by the p-orbitals<sup>4,5</sup>. The search for new and efficient corrosion inhibitors requires the clarification of interactions between inhibitor molecules and the metal surfaces. Near the organic inhibitors widely used, limited numbers of inorganic compounds were used. Molybdate, vanadate, cerium and phosphate derivatives provide good to excellent inhibition properties<sup>6-12</sup>. The efficient inhibiting effect obtained recently by phosphonates, e.g., sodium methyl dodecylphosphonate and sodium methyl (11-methacryloyloxyundecyl) phosphonate<sup>13</sup> and phosphites like  $\text{NaCo}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ <sup>14</sup> on the corrosion inhibition of steel in molar HCl solution was a good argument for us to continue testing such materials. We report in this paper on the results of  $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$  on the corrosion of steel in similar conditions. The study is conducted by polarisation and gravimetric measurements. Effect of temperature is also studied and adsorption

thermodynamic data are deduced.

### EXPERIMENTAL

Crystals of tris(dihydrogenphosphite) monohydrate  $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$  have been re-synthesized as previously reported in Ref. 15 (Fig. 1).

C38 carbon steel cut from rectangular sheets was used as the test material for these experiments and has the chemical composition (0.09% P; 0.38% Si; 0.01% Al; 0.05% Mn; 0.21% C; 0.05% S and the remainder iron). The coupons were degreased with acetone, air dry, is embedded in polytetrafluoroethylene (PTFE). The exposed surface of the electrode (of area  $1 \text{ cm}^2$ ) was wet polished with silicon carbide abrasive paper up to 1200 grits, rinsed with ethanol and air dried. This was used as the working electrode during the electrochemical test.

A three-electrode polarization cell was used for all electrochemical measurements. Saturated calomel electrode (SCE) was used as reference and a platinum wire was used as the counter electrode.

The polarisation ( $E-I$ ) curves were recorded using a potentiostat (Potentio-Galvanostat EG&G model 273) connected with a personal computer. The measurements were carried out by sweeping linearly the potential from the starting potential ( $-0.800 \text{ V}$ ) into the positive direction at a given scan rate ( $1 \text{ mVs}^{-1}$ ) till anodic potential value. Before recording the polarisation curves, the steel electrode is polarised at  $-0.800 \text{ V}$  for 10 min.

Polarisation experiments were undertaken in deaerated  $1 \text{ M HCl}$  solutions in the absence and presence of different concentrations of inhibitor.  $1 \text{ M HCl}$  was prepared by dilution of analytical grade  $37\% \text{ HCl}$ .

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was  $60 \text{ ml}$ . The steel sheet was cut into coupons of dimension  $2 \text{ cm} \times 2 \text{ cm} \times 0.5 \text{ cm}$ . The immersion time for the weight loss was  $6 \text{ h}$  at  $308 \text{ K}$  and  $1 \text{ h}$  at

other temperatures. After the corrosion test, the specimens of steel were carefully washed in double-distilled water, dried and then weighed. Triplicate experiments were performed in each case and the mean value of the weight loss is reported. Weight loss allowed us to calculate the mean corrosion rate as expressed in  $\text{mg.cm}^{-2} \text{ h}^{-1}$ .

### RESULTS AND DISCUSSION

#### Polarisation study

The polarisation curves of steel in  $1 \text{ M HCl}$  in the absence and presence of PhMg is investigated. Fig. 2 shows the voltammograms obtained and the deduced parameters are gathered in Table 1. The inhibition efficiency ( $E_w \%$ ) was obtained using the following relation:

$$E_i \% = \frac{i_{\text{corr}} - i'_{\text{corr}}}{i_{\text{corr}}} \times 100 \quad \dots(1)$$

where  $i_{\text{corr}}$  and  $i'_{\text{corr}}$  are the corrosion current density of steel, respectively in the absence and presence of the inhibitor.

We notice that both cathodic and anodic current densities decrease in the presence of PhMg. The inhibitor exhibits more effect on cathodic than at anodic branch, but it may be classified as a mixed type inhibitor. The predominantly character of inhibitor on cathodic domain occurs by a slight displacement of  $E_{\text{corr}}$  toward cathodic values. Moreover, Table 1 shows that the Tafel cathodic slopes are modified in the presence of PhMg. This indicates that PhMg adsorb on the metal surface, causing modification of the mechanism of the reduction of hydrogen ion at the steel surface.

#### Weight loss tests

Gravimetric measurements of steel were investigated in  $1 \text{ M HCl}$  in the absence and presence of various concentrations of PhMg at  $6 \text{ h}$  of immersion and at  $308 \text{ K}$ . The inhibition efficiency ( $E_w \%$ ) was estimated by the following relation:

$$E_w \% = \frac{W_{\text{corr}} - W_{\text{corr (inh)}}}{W_{\text{corr}}} \times 100 \quad \dots(2)$$

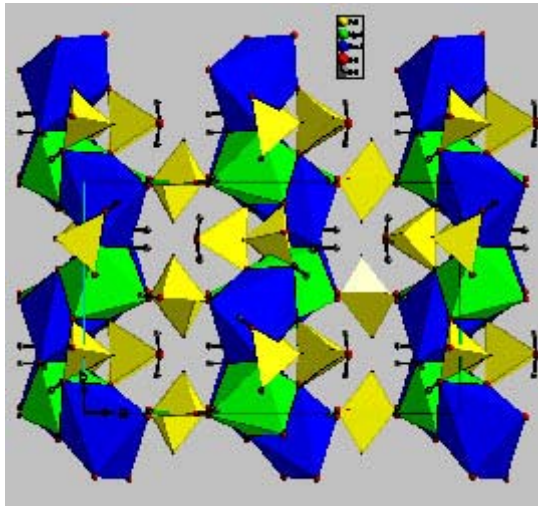


Fig. 1: A projection of the structure of  $\text{NaMg}(\text{H}_2\text{PO}_3)_3 \cdot \text{H}_2\text{O}$ . Octahedra colours as corresponding atoms. Atomic positions and cell parameters from 15.

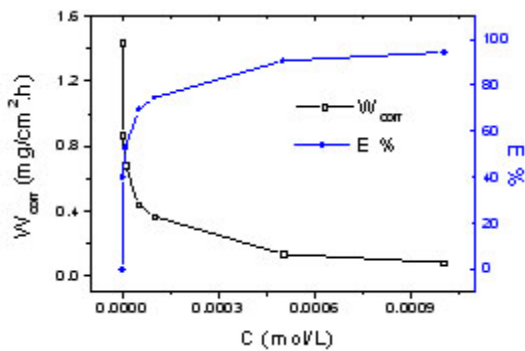


Fig. 2: Variation of corrosion rate of steel and efficiency of PhMg in molar HCl with concentration at 6h and 35°C.

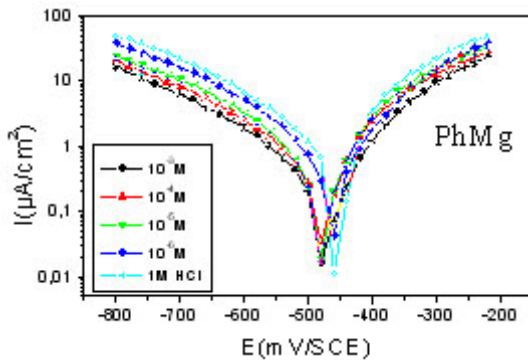


Fig. 3: Polarisation curves of steel in 1 M HCl at different concentrations of PhMg

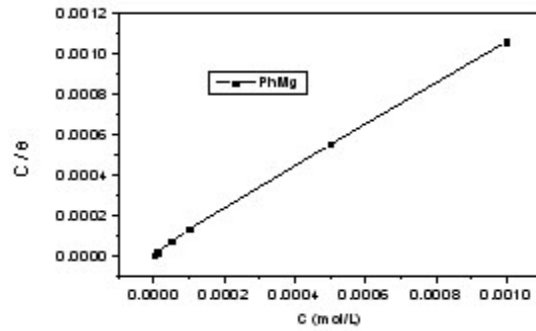


Fig. 4: The relationship between  $C/\theta$  and  $C$  of PhMg.

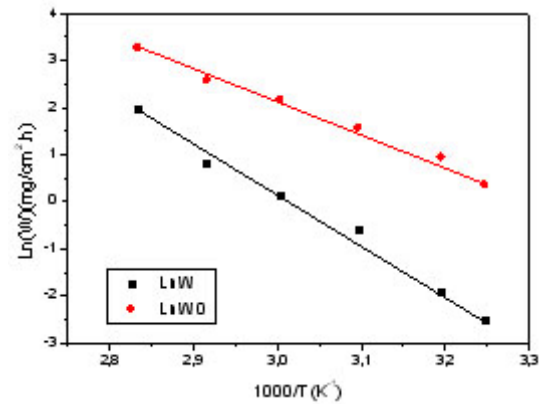


Fig. 5: Arrhenius plots of steel in 1M HCl with and without  $10^{-4}\text{M}$  PhMg

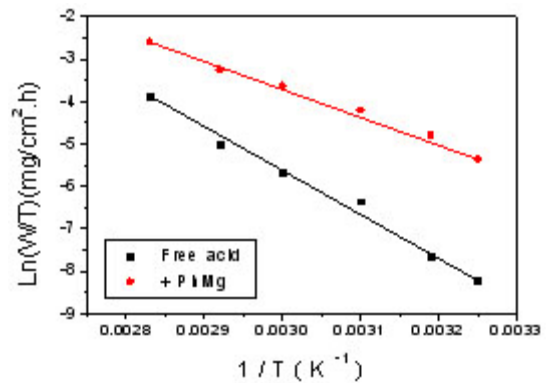


Fig. 6: Variation of  $W_{\text{corr}}/T$  against  $T^{-1}$  of steel in free acid and added of  $10^{-4}\text{M}$  PhMg

where  $W_{\text{corr}}$  and  $W_{\text{corr(inh)}}$  are the corrosion rates (CR) of steel, respectively in the absence and presence of the inorganic inhibitor.

The evolution of both the corrosion rates and the inhibition efficiencies evaluated from weight loss measurements for different PhMg concentrations in 1M HCl is illustrated in Figure 3. The addition of PhMg diminished the corrosion rate and hence inhibited steel corrosion in acid solution. The decrease in CR with increasing inhibitor

concentration suggests that the inhibiting action was concentration dependent. The inhibition efficiency ( $E_w$  %) attained its maximum (94.3%) at  $10^{-3}$ M. On the basis on the polarisation study, the inhibitive action of PhMg on the corrosion process may be interpreted by the action on both cathodic and anodic sites of the metal surface.

#### Adsorption isotherm and thermodynamic parameters

The dependence of the covered surface  $q$

**Table 1: Gravimetric results of steel in acid, at 6h and 308 K, with and without PhMg's addition**

concentration	$E_{\text{corr}}$ (mV/SCE)	$b_c$ (mV/ dec)	$I_{\text{corr}}$ ( $\mu\text{A}/\text{cm}^2$ )	E%
1M HCl	-475	171	1239	-
$10^{-6}$ M	-478	180	906	27
$10^{-5}$ M	-505	179	612	51
$10^{-4}$ M	-502	173	464	63
$10^{-3}$ M	-497	175	250	80

**Table 2: Effect of temperature on corrosion of steel in 1M HCl at  $10^{-4}$ M PhMg at 1h**

Temperature (K)	Concentration (M)	W ( $\text{mg}/\text{cm}^2.\text{h}$ )	Ew (%)	$\theta$
313	Blanc	2.604	-	-
	$10^{-3}$	0.148	94.3	0.943
323	Blanc	4.834	-	-
	$10^{-3}$	0.564	88.3	0.883
333	Blanc	8.7815	-	-
	$10^{-3}$	1.159	86.8	0.868
343	Blanc	13.235	-	-
	$10^{-3}$	2.294	82.7	0.827
353	Blanc	26.552	-	-
	$10^{-3}$	7.286	72.6	0.726

**Table 3: Some activation parameters as function of PhMg concentration**

C(M)	A ( $\text{mg}/\text{cm}^2.\text{h}$ )	$E_a$ (kJ/mol)	$\Delta H_a^\circ$ (kJ/mol)	$\Delta S_a^\circ$ (J/mol.K)	$E_a - \Delta H_a^\circ$ (kJ/mol)
Blanc	15,27591	55.276	52.538	-70.592	2.738
$10^{-3}$	24,59767	86.82	83.869	-18.15	2.95

fraction, obtained by the ratio  $E/100$  as function of the concentration ( $C$ ) of inhibitor, was tested graphically by fitting it to various isotherms. Langmuir's isotherm assumes that the solid surface contains a fixed number of adsorption sites and each site holds one adsorbed species. The ratio  $C/\theta$  versus  $C$  is plotted linearly, showing that the adsorption obeys to Langmuir isotherm:

$$\frac{C}{\theta} = \frac{1}{k} + C \quad \dots(3)$$

where  $C$  is the concentration of inhibitor,  $k$  the adsorptive equilibrium constant, and  $\theta$  the surface coverage.

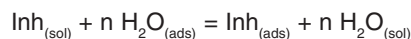
The values of linear regression between  $C/\theta$  and  $C$ , and the parameters of adsorption are determined from Fig. 4. The obtained slope 1.05 close to unity indicates that inhibitor adsorption agrees well that of Langmuir with a coefficient correlation  $R^2 = 0.9997$ . The obtained constant equilibrium is 64226.1. The standard adsorption free energy ( $\Delta G_{\text{ads}}^\circ$ ) is obtained according to the following equation:

$$K = \frac{1}{55.5} \exp\left(-\frac{\Delta G^\circ}{RT}\right) \quad \dots(4)$$

The negative values of  $\Delta G_{\text{ads}}^\circ = -38.6$  kJ/mol, indicates that the PhMg adsorbs spontaneously onto the steel surface. Moreover,  $-38.6$  kJ/mol reveals that the mineral inhibitor act by physical adsorption onto the metal surface.

For this kind of isotherm, a heat of adsorption is supposed independent of coverage and therefore of the electrode charge. Also the surface should also be completely homogeneous (no dislocations, steps, etc.) and all the sites should have the same energy. However, because it addresses the fundamental adsorption step, the Langmuir isotherm is used as starting point in the derivation of many other complex isotherms [16]. Adsorption of an inhibitor is regarded as a substitutional adsorption process between the inhibitor specie in the aqueous medium,  $\text{Inh}_{(\text{sol})}$ , and

the water molecules adsorbed on the metallic surface,  $\text{H}_2\text{O}_{(\text{ads})}$  [17]:



where  $X$  is the size ratio, representing the number of water molecules replaced by one molecule of inhibitor. heat of adsorption will be evaluated after studying the effect of temperature.

### Effect of temperature

The corrosion process and protectiveness of an inhibitor are significantly dependent on the temperature. In this optic, effect of temperature is conducted in the absence and presence of PhMg studied at  $10^{-4}\text{M}$ , in the range [313-353 K], during 1 hour of immersion. The data collected in Table 2, clearly show an increase of corrosion rate ( $W$ ) at different temperatures. The increase is more pronounced for uninhibited acid. The values of inhibition efficiency obtained from the weight loss at various temperatures show that the inhibition efficiency decreases rapidly with increasing temperature indicating that higher temperature dissolution of steel predominates on adsorption of PhMg at the surface.

The activation kinetic parameters such as energy ( $E_a$ ), enthalpy ( $\Delta H_a^\circ$ ) and entropy ( $\Delta S_a^\circ$ ) may be evaluated from the effect of temperature using Arrhenius law (eq. 5) and its alternative formulation (eq. 6):

$$W = A \exp\left(-\frac{E_a}{RT}\right) \quad \dots(5)$$

$$W = \frac{RT}{Nh} \exp\left(\frac{\Delta S_a^\circ}{R}\right) \exp\left(-\frac{\Delta H_a^\circ}{RT}\right) \quad \dots(6)$$

where  $W$  refers to the corrosion rate,  $R$  the gas constant,  $T$  the absolute temperature,  $A$  the pre-exponential factor,  $h$  is Plank's constant and  $N$  is Avogrado's number.

Figs. 6 and 7 show the plots of  $\ln(W)$  and

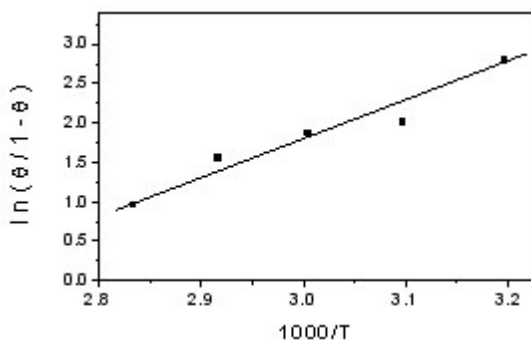
$\ln(W/T)$  versus  $1/T$ , respectively. Straight lines are obtained with a slope of  $(-DH_a^0/R)$  and an intercept of  $(\ln(R/Nh) + DS_a^0/R)$  from which the values of  $DH_a^0$  and  $DS_a^0$  are calculated (Table 3).

Higher values for the activation energy ( $E_a$ ) were found in the presence of inhibitor comparing with the ones reported in the literature<sup>18-20</sup>. Other studies indicated lower  $E_a$  in the presence of inhibitor<sup>21-23</sup>. It is clear that the values of  $E_a$  (108.89 kJ mol<sup>-1</sup>) in the presence of the PhMg are higher than that in the uninhibited acid solution (55.27 kJ mol<sup>-1</sup>), see Table 3. The decrease in inhibition efficiencies with increasing temperature and the increase of  $E_a$  in the presence of the inhibitor indicate the physical adsorption mechanism<sup>24</sup>.

Table 3 indicates on the other hand that both  $E_a$  and  $A$  increase in the presence of PhMg. Effectively, one notices the same variation of  $E_a$  and the pre-exponential factor  $A$ . From Eq. (5), it can be seen that at a given temperature, the value of the steel corrosion rate is jointly decided by the activation energy and pre-exponential factor. The steel corrosion rate basically decreases with an increase in concentration of PhMg<sup>25</sup>.

The positive sign of the enthalpy ( $DH_a^0$ ) reflects the endothermic nature of the steel dissolution process (Table 3). This result allows verifying the thermodynamic relation between  $E_a$  and  $DH_a^0$  as shown also in Table 3:

$$E_a - \Delta H_a^0 = RT \quad \dots(7)$$



**Fig. 7: Variation of  $\ln(\theta / (1-\theta))$  against  $T^{-1}$  of steel in acid added of  $10^{-4}M$  PhMg.**

The calculated values are too close to the one of the product  $RT$ , which is of 2.56 kJ/mol at 308 K.

The increase in entropy ( $DS_a^0$ ) in the presence of an inhibitor implies that the activated complex in the rate-determining step represents association rather than dissociation, indicating that an increase in disorder takes place on going from reactants to the activated complex<sup>26-28</sup>.

These data reveal that the inhibition of the corrosion reactions is affected without the mechanism changing. The entropy of activation in the presence and absence of the inhibitors is large and negative. This implies that the activation complex in the rate-determining step represents association rather than dissociation, indicating that a decrease in disorder takes place on going from reactants to the activated complex<sup>29</sup>.

The Langmuir isotherm supposing monolayer physical adsorption of the formed complex is given by the equation [30]:

$$\frac{\theta}{1-\theta} = AC \exp\left(-\frac{\Delta H_{ads}}{RT}\right) \quad \dots(8)$$

Where  $A$  is a temperature independent constant,  $C$  the inhibitor concentration and  $DH_{ads}$  is the adsorption heat.

The linear plot of  $\ln(\theta / (1-\theta))$  against the reciprocal of temperature shown in Fig. 7 helps to get  $DH_{ads}$  value ( $DH_{ads} = -37.88$  kJ/mol). The nature of the adsorption process can be clarified further if the heat of adsorption  $DH_{ads}$  value is known. It has been shown<sup>31,32</sup> that for  $DH_{ads} < 10$  kJ/mol the adsorption is most probably physical in character, while for  $DH_{ads} > 10$  kJ/mol chemisorption is proceeding. They are relatively high which verifies the chemisorptive character of the adsorption. The value of  $DH_{ads}$  is different for the different inhibitors which show that their structure affects the formation of the covalent bond with the metal. This bond is most probably formed between the unpaired electrons of the active centre and the positive active centres of the metal surface. However, the negative sign represents that the adsorption process is of

exothermic nature, so physical adsorption for the studied compound on mild steel surface in molar HCl solutions is more probable. Physical adsorption processes on mild steel surface were reported for various N-containing organic inhibitors which have been characterized with cations formation in acid media [33-35].

### CONCLUSION

From the above results and discussions, the following conclusions might arise:

NaMg(H<sub>2</sub>PO<sub>3</sub>)<sub>3</sub>.H<sub>2</sub>O induces inhibiting effect on the corrosion of steel in 1M HCl. The inhibition efficiency increases with the inhibitor concentration.

Inhibitor acts both on cathodic and anodic reactions, with a cathodic predominance.

The adsorption of PhMg on the steel surface from 1M HCl follows the Langmuir adsorption isotherm. The adsorption process being a spontaneous process.

The inhibition efficiency of PhMg decreases in the temperature range [308-358 K].

### REFERENCES

- Noor, E.A., *Mater. Chem. Phys.*, **114**: 533 (2009).
- Abd El-Rahim, S.S., Refaey, S.A.M., Taha, F., Saleh, M.B. and Ahmed, *R.A.* **31**: 429 (2001).
- Kaddouri, M., Cheriaa, N., Souane, R., Bouklah, M., Aouniti, A., Abidi A., Hammouti B. and J. Vicens, *J. Appl. Electrochem*, **37**: 1253 (2008).
- Fouda A.S., Heakal F.E. and Radwan M.S., **39**: 391 (2009).
- Arslan T., Kandemirli F., Ebenso E.E., Love I. and Alemu, H., *Corros. Sci.*, **51**: 35 (2009).
- Lin B-L., Lu J-T., Kong G., *Corros. Sci.*, **50**: 962 (2008).
- Iannuzzi M. and Frankel G.S., *Corrosion Science* **49**(5): 2371-2391 (2007).
- Addi E.H.A., Bazzi L., Elhilali M., Salghi R., Hammouti B. and Mihit, M., *Applied Surface Science* **253**: 555 (2006).
- Salghi R., Bazzi L., Hammouti B., Kertit S., Bouchart A. and El Alami Z., *Ann. Chim. Sci. Matér.*, **25**: 593(2000).
- Li X., Deng S., Fu H. and Mu G., *Corros. Sci.*, **50**: 3599 (2008).
- Alaoui L.M., Kertit S., Bellaouchou A., Guenbour A., Benbachir A. and Hammouti B., *Port. Electrochim. Acta* **26**: 339 (2008).
- Wei Z., Xinchun L., Yuhong L., Guoshun P. and Jianbin L., *Appl. Surf. Sci.* **255**: 4114 (2009).
- Benabdellah M., Dafali A., Hammouti B., Aouniti A., Rhomari M., Raada A., Senhaji O. and Robin J.J., *Chem. Eng. Comm.*, **194**: 1328 (2007).
- Herrag, L., Hammouti, B., Elkadiri, S., El Bali, B., Lachkar, M. and Ouarsal, R., *Pigm. Resin Techn.* **37**: 167 (2008).
- R. Ouarsal, A. Alaoui Tahiri, M. Lachkar, M. Dusek, K. Fejfarova and B. El Bali, *Acta Cryst.*, **E59**: i33 (2003).
- Bokris J.O.M., Amulya K.N., Reddy M. and Gamboa-Aldeco, *Modern Electrochemistry Fundamentals of Electrodeics*, 2<sup>nd</sup> Edition, Vol. 2A, Kluwer Academic Publishers, NY. 914 (2000).
- Bokris J.O.M. and Swinkels D.A.J., *J. Electrochem. Soc.* **111**: 736 (1964).
- Ferreira E.S., Giacomelli C., Giacomelli F.C. and Spinelli, A., *Mater. Chem. Phys.*, **83**: 129 (2004).
- Elachouri M., Hajji M.S., Salem M., Kertit S., Aride J., Coudert R. and Essassi, E., *Corrosion*, **52**: 103 (1996).
- Elkadi L., Mernari B., Traisnel M., Bentiss F. and Lagrenée M., *Corros. Sci.*, **42**: 703 (2000).
- Cai Q.H., Shan Y.K., Lu B. and Yuan, X.H., *Corrosion*, **49**: 486 (1993).
- Banerjee S.N. and Misra S., *Corrosion*, **45**: 780 (1989).
- Quraishi M.A., HariomSharma K., *Mater. Chem. Phys.*, **78**: 18 (2003).
- Popova A., Sokolova E., Raicheva S. and

- Christov M., *Corros. Sci.*, **45**: 33(2003).
25. Mu G.N., Li X. and Li F., *Mater. Chem. Phys.*, **86**: 59 (2004).
26. Abd El Rehim S.S., Ibrahim M.A.M. and Khalid K.F., *Mater. Chem. Phys.*, **70**: 268 (2001).
27. Abd El-Nabey B.A., Khamis E., Thompson G.E. and, Dawson J.L., *Surf. Coat. Techn.*, **28**: 83 (1986).
28. S.S. Abd El-Rehim, H.H. Hassan, M.A. Amin, *Mater. Chem. Phys.* **70**: 64 (2001).
29. Noor E.A. and Al-Moubaraki A.H., *Mater. Chem. Phys.*, **110**: 145 (2008).
30. Wahdan M.H., *Mater. Chem. Phys.*, **49**: 135 (1997).
31. A.E. Stoyonova, E.I. Sokolova, S.N. Raicheva, *Corros. Sci.*, **39**: 1995(1997).
32. Noor E.A., *Corros. Sci.*, **47**: 33(2005).
33. Nahlé A., Abu-Abdoun I. and Ibrahim Abdel-Rahman, *Anti-Corrosion Methods and Materials*, **55**:217 (2008).
34. Benabdellah M., Tebbji K., Hammouti B., Touzani R., Aouniti A., Dafali A. and El Kadiri S., *Phys. Chem. News*, **43**: 115 (2008).
35. Quraishi M.A. and Jamal D., *Mater. Chem. Phys.* **78**: 608 (2003).