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A pyrrolidine phosphonate derivative as corrosion inhibitor for steel in H_2SO_4 solution

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ABSTRACT

A new corrosion inhibitor, namely diethyl 2-(2-oxopyrrolidin-1-yl) ethyl phosphonate (P1) was synthesized and its action on the corrosion of steel in 0.5 M H_2SO_4 solution has been studied. Weight loss measurements, potentiodynamic polarisation and linear polarisation resistance (Rp) and impedance spectroscopy (EIS) methods have been used. The inhibition efficiency increases with the concentration of P1 to attain 86% at 5.10^{-3} M. We have noted a good agreement between gravimetric and electrochemical methods (potentiodynamic and Rp polarisation and impedance spectroscopy (EIS)). Polarisation measurements show also that the pyrrolidone derivative acts essentially as a cathodic inhibitor. The cathodic curves indicate that the reduction of proton at the steel surface is an activating mechanism. P1 adsorbs on the steel surface according to Langmuir adsorption model. Effect of temperature is also studied in the 298-353 K range.

Key words: Pyrrolidone, Phosphonate, Inhibition, Corrosion, Steel, Acid, Langmuir.

INTRODUCTION

Corrosion inhibitors are substances that minimize or prevent corrosion if they are added at low concentrations in an aggressive environment. Selection of effective corrosion inhibitors is very important for an application in which inhibitors are needed regarding what kind of metal or alloy and corrosive environment are used. Effectiveness of the organic inhibitors depends on their adsorption rates and covering capabilities on metal surfaces [1*]. It has been reported by many authorities that adsorption depends on the molecular structure, surface charge of a metal and type of electrolytes [2,3*]. Inhibitors are adsorbed by the metal surface immersed in an aqueous phase replacing water molecules adsorbed by the surface. Electrostatic interaction between an inhibitor molecules and a metal are prominent during this action of inhibitors. Electron densities of different functional group or groups, polarizability and electronegativity are main factors in this interaction. The use of inhibitors is the most practical methods of protection against corrosion, especially in acidic solutions. Their addition is necessary to secure the attack of metal from corrosiveness media such chemical cleaning and pickling generally used to remove mill scales (oxide scales) from the metallic surface. Also inhibitors should be effective even under severe conditions in concentrated acid (20%) and temperatures ranging from 60 to 95°C [1]. Compounds containing heteroatoms such as: sulphur, nitrogen and oxygen containing compounds exhibit the most efficient corrosion inhibition. Survey of literature reveals that pyrrolidone [2-6], pyridine [7-13] and phophonate [14-16] compounds are effective corrosion inhibitors up to 80°C. The synthesis of new organic molecules offers various molecular structures containing several heteroatoms and substituents. Their adsorption is generally explained by the formation of an adsorptive film of a physical and/or chemical character on the metal surface. In continuation of our work on development of organic compounds as acid inhibitors, we have chosen an organic inhibitor namely diethyl2-(2-oxopyrrolidin-1-yl)ethylphosphonate (P1) with a view to study its inhibiting properties on corrosion of steel in 0.5 M H_2SO_4 in the 298-353 K range. The presence of the pyrrolidone ring and the phosphonate group are the active centers through which they can adsorb readily on the metal surface. Moreover, phosphonic compounds possessing hydrolytic stability, scale inhibiting and ability to form complexes with metal cation, have been used as corrosion inhibitors [15,16].

In the present work, first we have synthesized and characterized diethyl2-(2-oxopyrrolidin-1-yl) ethylphosphonate, Fig.1 and second we investigate the corrosion of steel in 0.5 M H_2SO_4 in the presence of this inhibitor. Weight loss tests and electrochemical techniques (potentiodynamic and Rp polarisation and impedance measurements) have been used to study the effect of addition of this compound on the corrosion of steel in sulphuric acid solution.

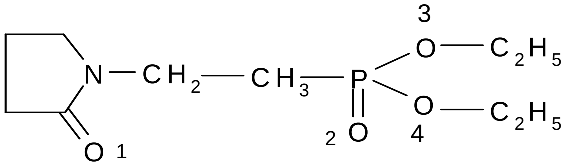


Fig. 1. Molecular structure of the pyrrolidone derivative: Diethyl-2-(2-oxopyrrolidin-1-yl)ethylphosphonate

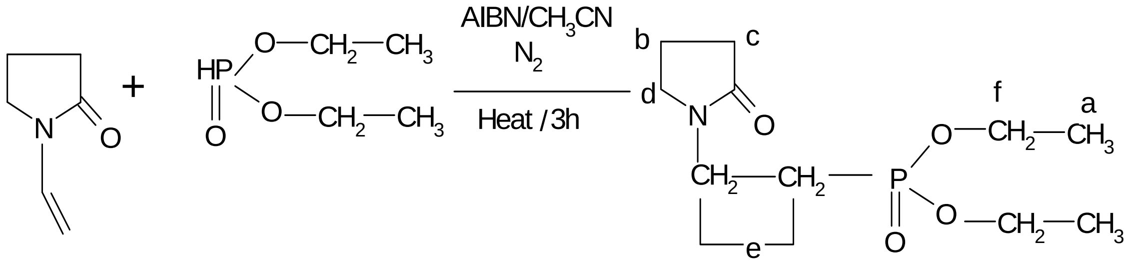
MATERIALS AND METHODS

2. Experimental

All chemicals used are of analytical grade and acquired form Aldrich Chemical. Co. All of them are used without previous purification; the solvents were distilled before use. Distilled and deionized water was used for all solutions preparations. The telomere diethyl2-(2-oxopyrrolidin-1-yl) ethylphosphonate (P1) was synthesized in our Lab. using the telomerisation reaction in acetonitril at 68°C with stirring in an argon atmosphere using AIBN as initiator as shown in Scheme 1. In a round bottom flask of 250 ml, we introduce 3.73g of diethyl phosphite (2.7 10^{-2} mol), 20 ml of CH_3CN and 3 10^{-2}g of the AIBN, then, 3g of 1-vinyl-2-pyrrolidone (2.7 10^{-2} mol) was added dropwise over a period of 30 min from a dropping funnel. After 3 h of agitation to backward flow, the mixture was concentrated dry; the principal product was separated by chromatography on column. This product is a viscous liquid with yellow color and is soluble in water, CH_2Cl_2, $CHCl_3$ and other organic solvents. The yield of the synthesis is 77%.

FT- IR spectra were recorded on a Shimadzu Fourier transform infrared FTIR- 8400 S spectrometer using a KBr disc containing 2% finely ground samples (spectra resolution, 4 cm^{-1}; number of scans 20). ^1H and ^{13}C N.M.R spectra were measured in $CDCl_3$ on a Bruker 200 MHZ spectrometer using TMS as internal standard. Elemental Analyses were carried out at technical scientific research national centre at Rabat- Morocco.

The compound was characterised by N.M.R and F.T.I.R spectroscopies and element analysis before use. ^{1}H-NMR ($CHCl_3$) (δ ppm): 1.50 (t, 6Ha), 2.12 (m, 2Hb), 2.49 (m, 2Hc), 3.4 (m, 2Hd), 3.50 (m, 4He); 3.9 (q, 4Hf). These previous methods have confirmed the purity of the pyrrolidone derivative P1.



Scheme 1.

Prior to all measurements, the steel samples (0.09 % P; 0.38 % Si; 0.01 % Al; 0.05 % Mn; 0.21 % C; 0.05 % S and the remainder iron) were ground with different emery paper up to 1000 grade, washed thoroughly with bidistilled water degreased and dried with acetone. The aggressive solution (0.5 M H_2SO_4) was prepared by dilution of analytical grade 98% H_2SO_4 with bidistilled water.

Gravimetric measurements were carried out in a double walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 60 cm^3. At the conclusion of a run the coupons were washed with de-ionized water and acetone, dried and immediately weighed. The steel specimens used had a rectangular form (2 cm x 2 cm x 0.05 cm).

Electrochemical measurements were carried out in a conventional three electrode electrolysis cylindrical pyrex glass cell. The working electrode (W.E) had the form of a disc cut form the steel sheet. The area exposed to the corrosive solution was 1cm^2. A saturated calomel electrode (SCE) and a disc platinum electrode were used respectively as reference and auxiliary electrode. The temperature was thermostatically controlled at 298 ± 1 K.

Polarisation curves were recorded with a potentiostat (EG&G 273A) at a scan rate of 1 mV/s. Before recording the polarisation curves the test solution was de-aerated and magnetically stirred for 30 min in the cell with nitrogen. The steel electrode, kept at its open circuit value for 30 min, was pre-polarised at -800 mV for 10 min. The potential of the electrode was then swept to anodic potentials. Gas bubbling was maintained throughout the experiments. Linear polarisation resistance is determined from i-E plots in the vicinity of E_{corr} at ±10 mV.

Electrochemical impedance spectroscopy (EIS) was carried out with a Voltalab electrochemical system at E_{corr}. The circular surface of steel exposing of 1cm^2 to the solution was used as working electrode. After the determination of steady-state current at a given potential, sine wave voltage (10 mV) peak to peak, at frequencies 10^5 to 10^{-2} Hz was superimposed on the rest potential. Computer programs automatically controlled the measurements performed at rest potentials after 30 min of exposure in solution without bubbling. The impedance diagrams are given in the Nyquist and Bode representations.

RESULTS AND DISCUSSION

3.1. Weight loss tests

The effect of addition of pyrrolidone derivative (P1) at different concentrations on the corrosion of steel in 0.5 M H_2SO_4 solution was studied by weight-loss at 298 K after 6 hours of immersion. Inhibition efficiency (E_w%) is calculated using equation (1):

$$E_w\% = \left(1 - \frac{W_{corr}}{W^{o}_{corr}}\right).100 \qquad (1) ;$$

with W_{corr} and $W°_{corr}$ are the corrosion rates of steel with and without organic compound, respectively. Table 1 collects the results of weight loss of steel in 0.5 M H_2SO_4 with and without the addition of various concentrations of the pyrrolidone compound (P1). It is clear that the corrosion rate decreases with increasing the concentration of compound tested. For the comparison, similar results are obtained by Ramesh et al. [14] with phosphonates compounds in water medium.

Table1 Effect of pyrrolidone derivative (P1) concentration on corrosion data of steel in 0.5 M H_2SO_4 (298 K & 6h)

Concentration (M)	W_{corr} (mg/ cm^2.h)	E_W%
Blank	1.608	-
$5x10^{-3}$	0.233	86
$2.5x10^{-3}$	0.361	78
10^{-3}	0.552	66
$5x10^{-4}$	0.739	54
$2.5x10^{-4}$	0.938	42
10^{-4}	1.216	24

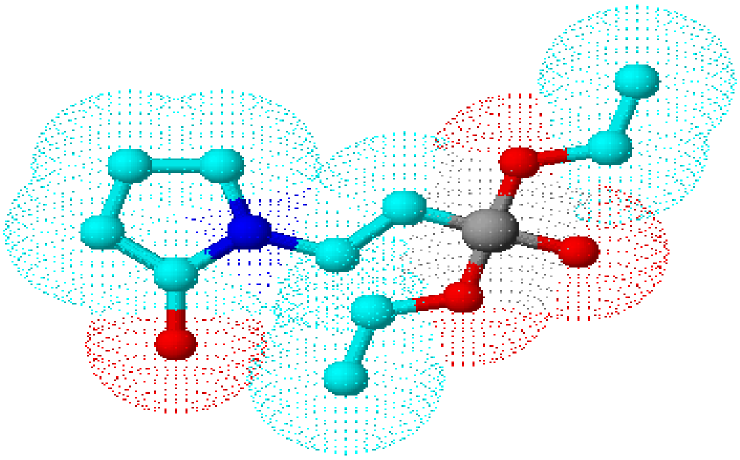


Fig.2. Optimized structural of P1

It is known that the inhibition efficiency should follows in the sequence O < N < S < P [17,18]. In theory the phosphoric products are excellent corrosion inhibitors [19-21] but this products although it contains a phosphorus atom their efficiency does not exceed 86% to 5 10^{-3} mol/l and this is to justify by calculates partial atomic charges (table 5). It is noted that the load partial total of phosphorus is positive equal (0.3331e), consequently it is not adsorbed on the surface of metal. The P presence may reinforce the adsorption of N and O atoms as shown in the optimal structure of the molecule (Figure 2).

Table 2. Partial atomic charges calculated by PETRA program [22]

atoms	O_1	O_2	O_3	O_4	N	P
Calculation of Partial atomic charges (e)	-0.4417	-0.4376	-0.2196	-0.1296	-0.1029	0.3331

3.2. Polarisation results.

Fig. 3 shows the influence of P1 concentration on the cathodic and anodic polarisation curves of steel in 0.5 M H_2SO_4. The potentiodynamic polarisation values of corrosion current (I_{corr}), corrosion potential (E_{corr}), cathodic Tafel slope (b_c) are regrouped in Table 3. In this case, the relation (2) gives the inhibition efficiency (E_I%):

$$E_I\%=\left(1-\frac{I_{corr}}{I^o_{corr}}\right).100 \qquad (2)\ ;$$

with $I°_{corr}$ and I_{corr} are the uninhibited and inhibited corrosion current densities, respectively, determined by extrapolation of cathodic Tafel lines to corrosion potential.

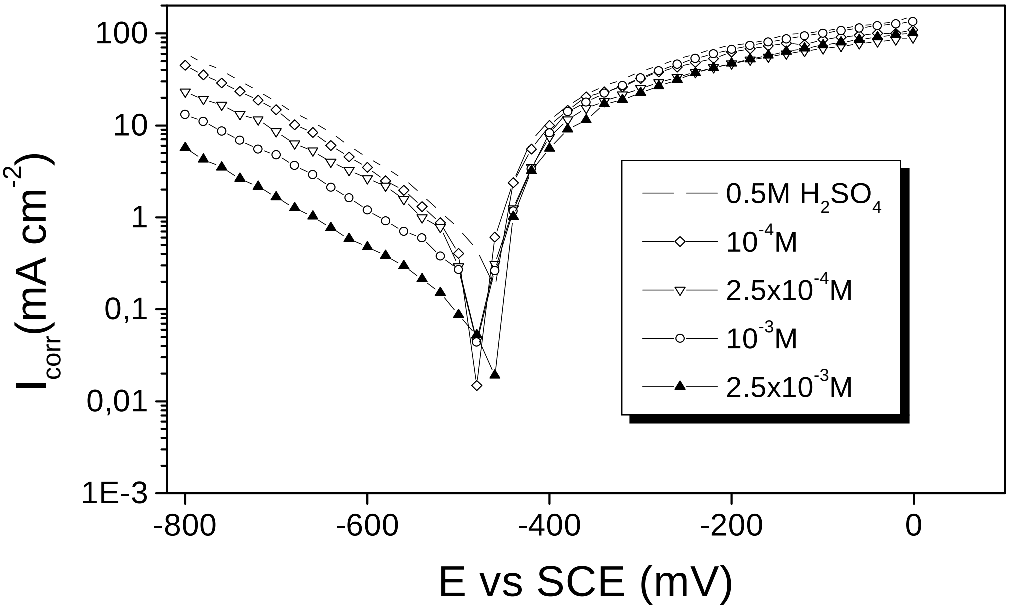


Fig. 3. Polarisation curves of steel in 0.5 M H_2SO_4 for various concentrations of P1

As it is shown in Fig. 3 and table 3, cathodic polarisation curves rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled. Thus the presence of pyrrolidone compound does not affect the mechanism of this process. The addition of pyrrolidone derivative causes a decrease of the current density. The values of corrosion potential (E_{corr}) and cathodic Tafel slope (b_c) remain almost constant upon the addition of inhibitor concentration. The results demonstrate that the hydrogen reduction is inhibited and that the inhibition efficiency increases with inhibitor concentration to attain 79% at 2.5 10^{-3} M.

The anodic curves obtained indicate that the inhibition mode of P1 depends upon electrode potential. It seems that after potential corrosion, the presence of P1 does not change the current versus potential characteristics. This result indicates that P1 acts essentially as a cathodic inhibitor.

Table 3 Electrochemical parameters and the corresponding inhibition efficiency of steel in 0.5 M H_2SO_4 in the presence of pyrrolidone derivative at various concentrations

Concentration (M)	E_{corr} (mV/SCE)	b_c (mV dec^{-1})	b_a (mV dec^{-1})	I_{corr} (μA cm^{-2})	R_p (Ω cm^2)	E_I (%)	E_R (%)
Blank	-463	184	36	542	31	-	-
10^{-4}	-470	176	41	401	39	26	21
$2.5x10^{-4}$	-469	187	38	309	51	43	39
10^{-3}	-467	180	45	168	91	69	66
$2.5x10^{-3}$	-461	182	53	114	124	79	75

The linear i-E plots determined at ± 10 mV around E_{corr} leads to evaluate the linear polarisation resistance (R_P). The corresponding R_P values of steel in 0.5 M H_2SO_4 in the presence and absence of different concentrations of the inhibitor are also given in Table 3, for comparative purposes. The inhibition efficiency E_R% is calculated using the equation (3):

$$E_R\ (\%) = 100\ .\ (\ 1 - R_p\ /\ R_p')\qquad (3);$$

where R'_P and R_P are the polarisation resistance with and without the inhibitor, respectively.

We remark that R_P increases with increasing of inhibitor concentration. This in turn leads to a decrease in I_{corr} values. E% increases with the product content and attains 75% at 2.5 10^{-3} M.

3.3. Electrochemical impedance spectroscopy (EIS)

More information about the corrosion behaviour of steel, in acidic solutions with and without pyrrolidone compound may be get using electrochemical impedance spectroscopy (EIS) measurements. The charge-transfer resistance (R_t) values are calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al [23]. The double layer capacitance (C_{dl}) and the frequency at which the imaginary component of the impedance is maximal ($-Z_{max}$) are found as represented in equation (4):

$$C_{dl} = \left({}^{1}\!/_{\omega.R_t} \right) \quad \text{where} \quad \omega = 2\pi f_{max} \qquad (4);$$

the inhibition efficiency got from the charge transfer resistance is calculated by: E (%) = 100 .

$$(\ 1 - R_t\ /\ R_{t/inh}\ )\qquad (5);$$

where R_t and $R_{t/inh}$ are the charge transfer-resistance values with and without inhibitor, respectively.

The impedance parameters derived from these investigations are mentioned in Table 4. As we notice, Fig. 4, the impedance diagrams consists of large capacitive loops. In fact, the presence of pyrrolidone compounds enhances the value of R_t in acidic solution indicating a charge transfer process mainly controlling the corrosion of steel. Values of double layer capacitance are also brought down to the maximum extent in the presence of pyrrolidones. The decrease in C_{dl} is due to the adsorption of this compound on the metal surface leading to the formation of film from acidic solutions [24].

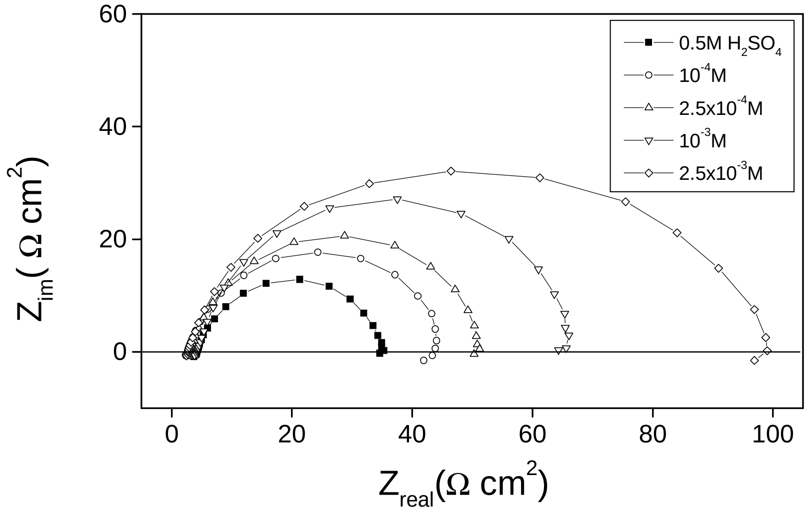


Fig. 4. Nyquist plots of steel in 0.5 M H_2SO_4 containing various concentrations of P1

Table 4. EIS parameters of steel in 0.5 M H_2SO_4 with P1 at various concentrations.

Concentration (M)	R_s (Ω.cm^2)	R_t (Ω.cm^2)	F_{max} (Hz)	C_{dl} (µF/ cm^2)	E%
blank	4.86	30	51.50	103	-
10^{-4}	2.68	42	40.15	94.38	28
$2.5x10^{-4}$	3.22	48	40.15	82.58	37
10^{-3}	4.34	63	39.75	63.54	52
$2.5x10^{-3}$	2.78	97	30.07	54.55	69

Fig. 5 shows the Bode plots [26,27] on the electrodes made of these samples. The EIS results for the liquid- and steam-treated samples can be explained by the simple equivalent Randles circuit [25], Fig. 6, which consists of a solution resistance R_s in series with a component composed of parallel film capacitance C_{dl} and transfer resistance R_t [27].

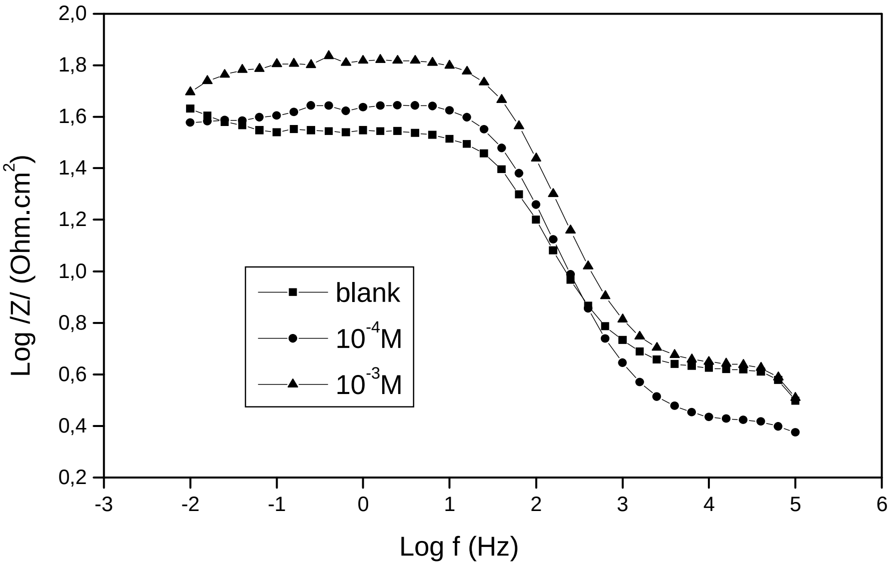


Fig. 5. Bode plots of steel in 0.5 M H_2SO_4 containing various concentrations of P1.

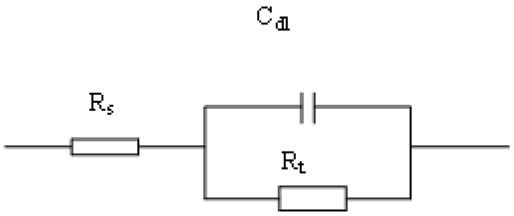


Fig. 6. A simple Randles-type equivalent circuit for EIS measurements.

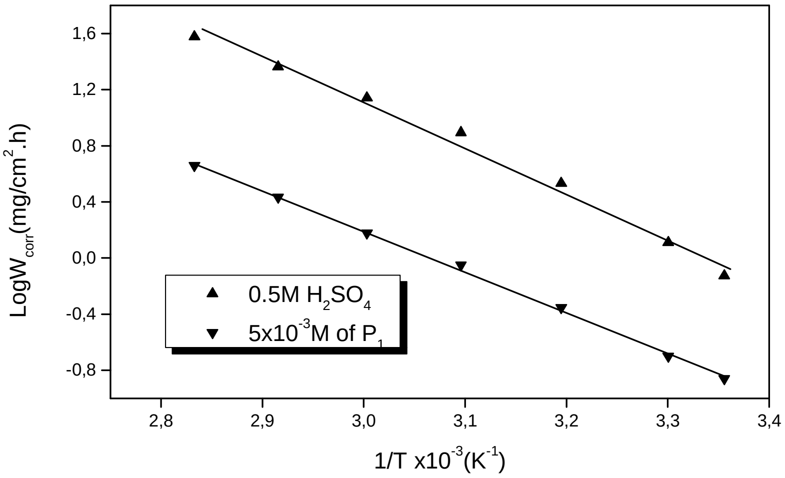
3.5. Effect of temperature

The effect of temperature on the corrosion rate of steel in free acid and acidic solutions with 5 10^{-3} M of P1 at 1 hour immersion period is investigated from 298 to 353 K as shown in Table 5. It is clear that the increase of corrosion rate is more pronounced with the rise of temperature for blank solution. In the presence of the tested molecule, corrosion phenomena is highly reduced. Hence, we note that the efficiency depends on the temperature and increases with the rise of temperature from 298 to 353 K. This can be explained by the increase of the strenght of adsorption process at elevated temperature and suggested a chemisorption mode.

Table 5. Effect of temperature on steel corrosion in free acid and at 5 10^{-3} M of P1 at 1 h

Temperature (K)	W^0_{corr} (mg/ cm^2.h)	W_{corr} (mg/ cm^2.h) (P1)	***E%***
298	0.7455	0.1377	82
303	1.2913	0.1990	85
313	3.4075	0.4429	87
323	7.8478	0.8897	89
333	13.841	1.5014	89
343	23.00	2.7048	88
353	37.72	4.5486	88

Fig. 7. Arrhenius plots of corrosion rate for mild steel in 0.5 M H_2SO_4 in the absence and presence of P1.



The logarithm of the corrosion rate of steel W_{corr} can be represented as a straight-line function of 1000/T (Arrhenius equation, Fig.7), where T is the temperature in Kelvin:

$$W°_{corr} = k \exp(-E_a/RT) \text{ and } W_{corr} = k' \exp(-E_a'/RT) \quad (6);$$

$W°_{corr}$ and W_{corr} are the corrosion rates of steel in free acid and acidic solutions with inhibitor P1, respectively. The corresponding activation calculated from the slopes of Arrhenius plots. E_a = 62.2 kJ/mol and E'_a=55.6 kJ/mol are the activation energy without and with the inhibitor, respectively.

It's observed that the E_a value decreases in the presence of inhibitor indicating the high performance of the pyrrolidone compound at higher temperatures. This decrease of activation energy may be attributed to the process of **chemisorption** of P1 on the steel surface [1, 28].

3.6. Adsorption isotherm

Several adsorption isotherms were assessed and the Langmuir adsorption isotherm [29] was found to be the best description of the adsorption behaviour of the studied inhibitor:

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

$$K = \frac{1}{55.5}\exp\left(-\frac{\Delta G°_{ads}}{RT}\right) \qquad (8) ;$$

C is P1 concentration, θ the fraction of the surface covered determined by E/100, K the equilibrium constant and $\Delta G°_{ads}$ the standard free energy of adsorption reaction.

Fig. 8 shows the dependence of the ratio C/θ as function of C. The obtained plot is linear with a slope 0.91 to close to unity. The regression coefficient is R = 0.9996. The intercept permit the calculation of the equilibrium constant K which is 3086.4. This result leads to evaluating ΔG° = -29.9 kJ/mol.

The Langmuir's isotherm involves the assumption of no interaction between the adsorbed species on the electrode surface [30]. Also this kind of isotherm is generally regarded as to indicate physical adsorption [31]. This result confirms those obtained by E_a and E% determinations.

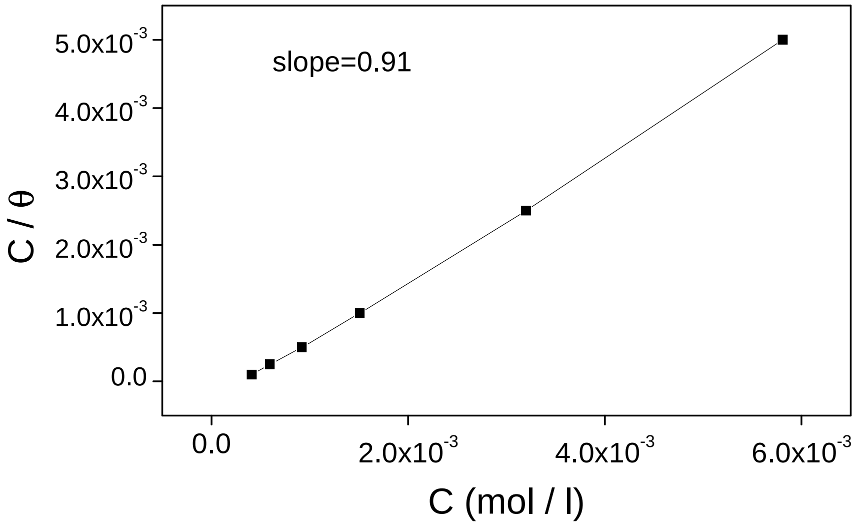


Fig. 8. Langmuir isotherm adsorption of pyrrolidone on steel in 0.5 M H_2SO_4.

CONCLUSION

1. The pyrrolidone derivative (P1) studied is a better inhibitor for steel in 0.5M H_2SO_4.
2. The inhibition efficiency of P1 increases with the increase of inhibition concentration to reach 86% at 5 10^{-3} M.
3. P1 essentially acts as a cathodic-type inhibitor without modifying the mechanism of hydrogen evolution.
4. The inhibition efficiency of P1 increases with the temperature.
5. P1 adsorbs on the steel surface according to the Langmuir adsorption isotherm.

REFERENCES

[1] A. Yildirim, M. Cetin, *Corros. Sci*. 50 (**2008**) 155.
[2] E.E. Oguzie, Y. Li, F.H. Wang, *J. colloid Interface Sci*. 310 (**2007**).
[3] A. Fiala, A. Chibani, A. Darchen, A. Boulkamh, K. Djebbar, *Appl. Surf. Sci*. 253 (**2007**) 9347.
[4] Sayed S. Abdel Rehim, Omar A. Hazzazi, Mohammed A. Amin, Khaled F. Khaled, *Corros. Sci*. 50 (**2008**) 2258.
[5] K.F. Khaled, *Electrochim. Acta*, 55 (**2010**) 5375.
[6] R. Annand, R. Hurd, N. Hackerman. *J. Electrochem.* 112 (**1965**) 138.
[7] Y. Xiao-Ci, Z. Hong, L. Ming-Dao, R. Hong-Xuan and Y. Lu-An *Corro. Sci*. 42 (**2000**) 645.
[8] A. Aouniti, B. Hammouti, S. Kertit. *Bull. Electrochem.* 14 (**1998**) 193.
[9] S.A. Abd El-Maksoud, *J. Electroanal. Chem*. 565 (**2004**) 321.
[10] Y. Abed, B. Hammouti, S. Kertit, K. El Kacemi, A. Mansri, *Bull. Electrochem*. 17 (**2001**) 105.
[11] Y. Abed, Z. Arrar, A. Aouniti, B. Hammouti, S. Kertit, A. Mansri, *J. Chim. Phys*. 95 (**1999**) 1347.
[12] A. Chetouani, K. Medjahed, K. E. Benabadji, B. Hammouti, S. Kertit, A. Mansri, *Prog. Org. Coat.* 46 (**2003**) 312.
[13] Chetouani, K. Medjahed, K.E. Sid-Lakhdar, B. Hammouti, M. Benkaddour, A. Mansri, *Corros. Sci*. 46 (**2004**) 2421.
[14] S. Ramesh, S. Rajeswari, S. Maruthamuthu, *Appl. Surf. Sci*. 229 (**2004**) 214.
[15] T. Hohrvath, E. Kalman, G. Kutsan, A. Rasusher, *Br. Corros. J.* 29 (**1994**) 215.
[16] J.L. Fang, Y. Li, X.R. Ye, Z.W. Wang, Q. Liu, *Corrosion* 49 (**1993**) 266.
[17] E. McCafferty, Corrosion control by coating, H. Leidheiser Editor, Science Press, Princeton, JJ, (**1979**) 279.
[18] J.G.N. Thomas, Proc. 5th European Symposium on Corrosion Inhibitors, Ann. Univ. Ferrara.
[19] X.H.To, N. Pebere, N. Pelaprat, B. Boutevin, Y. Hervaud. *Corros. Sci* 39 (**1997**) 1925.
[20] S. Rajendran, B.V. Apparao, N. Palaniswamy, V. Periasamy, G. Karthikeyan. *Corros. Sci* 43 (2001) 1345.
[21] G. Gunasekaran, R. Natarajan, N. Palaniswamy. *Corros.sci* 43 (**2001**) 1615.
[22] W.-D. Ihlenfeldt, J. Gasteiger, *J. Comput. Chem*, **8** (**1994**) 793.
[23] T. Tsuru, S. Haruyama, B. Gijutsu, *J. Jpn. Soc. Corros. Eng*. 27 (**1978**) 573.
[24] F. Bentiss, M. Lagrenée, M. Traisnel, J.C. Hornez. *Corros. Sci*. 41 (**1999**) 789.
[25] G.W. Walter, *Corros. Sci*. 26 (**1986**) 681.
[26] G.D. Zhou, Y. Feng, A. Fujishima, B.H. Loo, *Bull. Chem. Soc. Jpn*. 65 (**1992**) 2315.
[27] K. Hladky, L.M. callow, J.L. Dawson, *Br. Corros*. J. 15 (**1980**) 20.
[28] T. Szauer, A. Brandt, *Electrochim. Acta* 22 (**1981**) 1209.
[29] I. Langmuir, J. Amer. Chem. Soc. 39 (**1947**) 1848.

[30] A.J. Bard, L.R. Faulkner, Electrochemical methods, John Wiley & Sons, N.Y. **1980**, 517.
[31] M. Benabdellah, R. Touzani, A. Aouniti, A. Dafali, S. El Kadiri, B. Hammouti, M. Benkaddour, *Mater. Chem. Phys.* 105 (**2007**) 373.
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