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N,N-Dipropynoxy methyl amine trimethyl phosphonate as corrosion inhibitor for iron in sulfuric acid

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The corrosion inhibition of iron in 0.5 M sulfuric acid by *N, N*-dipropynoxy methyl amine trimethyl phosphonate has been investigated by means of the potentiodynamic polarization and electrochemical impedance spectrum (E.I.S) techniques. *N,N*-dipropynoxy methyl amine trimethyl phosphonate was studied in concentrations from 40 ppm to 320 ppm at a temperature of 298 K. The results show that the inhibition mechanism of *N,N*-dipropynoxy methyl amine trimethyl phosphonate is mixed controlled. It is also found that this inhibitor obeys the Frumkin adsorption isotherm and Flory-Huggins isotherm based on a substitutional adsorption process.

1. Introduction

Inhibition is one of the most important applications in corrosion protection. Inhibitors protect the metal by adsorbing onto the surface and retard metal corrosion in aggressive environment. Selecting the appropriate inhibitor for a specific environment and metal is of great importance, since an inhibitor that protects one particular metal may accelerate the corrosion of another.

Amines and their derivatives are well-known corrosion inhibitors [1]. The presence of a heteroatom in an organic compound with unsaturated bonds causes an adsorption process on the metal surface, which reduces metal dissolution [2]. *N,N*-dipropynoxy methyl amine and quaternary salt have been used in oil exploitation industry successfully owing to their high inhibition efficiency. The adsorption and desorption of this series compounds have already been investigated [3]. According to Hoar and Holiday [4, 5], inhibitor molecules adsorb to a different extent at different types of surface sites and influence the anode and cathode reactions unequally and the adsorption of inhibitor molecules reduces the number of electrode reaction sites, and thus, inhibition becomes more predominant when the surface is covered with a monolayer of the inhibitor. However, the degree of coverage of the metal surface by adsorbed inhibitor is often less than a monolayer, with the rate of the process reduced by several orders of magnitude. It has been proposed that organic inhibitor adsorbed on the metal surface would change the double-layer structure and affect kinetics of the electrochemical reactions, thereby partly insulating the metal from attack of the corrosive medium and make it more difficult for the metal ion atoms to pass from the lattice to solutions [5].

The effectiveness of different corrosion inhibitors has been studied as a function of the electron density of the donor atom in the inhibitor molecule [6] and of the molecular structure and size of the inhibitor [7].

Recently, we synthesized a new inhibitor by using *N,N*-dipropynoxy methyl amine and trimethyl phosphoric acid and obtained the compound of *N,N*-dipropynoxy methyl amine trimethyl phosphonate. The present investigation deals with the corrosion inhibition of iron and adsorption mechanism of *N,N*-dipropynoxy methyl amine trimethyl phosphonate in sulfuric acid by means of potentiodynamic polarization and E.I.S techniques.

2. Experimental

Coupons for electrochemical measurements are cut from pure iron (99.99%) rode with a surface area of 0.785 cm^2. The sides of the working electrode were coated with epoxy leaving only the polished surface at the top to the solution. The specimens were mechanically polished with different grades of emery paper (down to 800), cleaned with distilled water and acetone. The blank solution is 0.5 M H_2SO_4.

The inhibitor used was a newly synthesized compound with the linear molecular formula of $[C_6H_6N(CH_2OC{\equiv}CH)_2]^+[C(H_2PO_3)_3]^-$, in concentrations of 40 ppm, 80 ppm, 160 ppm and 320 ppm.

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Electrochemical measurements were conducted by using the normal three-electrode cell with a platinum auxiliary electrode and a saturated calomel reference electrode (SCE). The E.I.S measurements were done by using EG&G PARC M378 system with the frequency from 100 KHz to 0.03 Hz. The polarization curves were measured by using EG&G PARC M342 system with a scanning rate of 0.1 mV/s. The E.I.S results were analyzed by PARC "EQUIVCRT.PAS" software. In all experiments, the specimens were immersed in the studied solution for 2 hours to stabilize the electrode surface before measurements. The solutions were deoxygenated by bubbling nitrogen gas before and during the experiment. All the experiments were done at 298 K.

3. Results and discussions

3.1. Electrochemical characteristic of *N,N*-dipropynoxy methyl amine phosphonate in sulfuric acid

The polarization curves of pure iron in sulfuric acid with different concentration of *N,N*-dipropynoxy methyl amine trimethyl phosphonate are shown in Fig. 1. Both of the anode and cathode reactions were inhibited and the corrosion potential moved to the negative direction slightly (see Table I). Table I shows the electrochemical parameters obtained from the polarization curves. Here E_{corr} is corrosion potential, I_{corr} is corrosion current, ba and bc are the anodic and the cathodic Tafel slopes, respectively, the inhibition efficiency P was calculated from the following relation:

$$P = \left(1 - I_{\mathrm{corr}}/I^0_{\mathrm{corr}}\right) * 100\% \qquad (1)$$

Here I^0_{corr} is corrosion current in the blank solution. The inhibition efficiency reaches 84% even with 40 ppm addition of the inhibitor and reaches 96% with 320 ppm addition. If the inhibition effect is only caused through the surface coverage by inhibitor molecules, the corrosion potential will remain unchanged [8, 9]. The data in Table I show that the corrosion potential moves slightly toward negative direction and it is still in the experimental error range. So the inhibition mechanism can be considered mainly as a surface coverage mechanism.

The E.I.S is a very powerful technique to investigate the electrode reaction process. At corrosion potential, the anodic and cathodic reactions occurred concurrently. Normally for iron in acid solution, the cathodic reaction is the hydrogen ion reduction to form hydrogen gas, while the anodic reaction is the iron dissolution. The E.I.S at corrosion potential corresponds to these two processes. Fig. 2 shows the measured E.I.S of the iron electrode in 0.5 M H_2SO_4 solution and with 160 ppm inhibitor. As can be seen, the Nyquist plot always appears as a capacitive semicircle in the high to intermediate frequency range and an inductive semicircle in the low frequency range. The equivalent circuit for this system is shown in Fig. 3, where R_s is the solution resistance between the reference and working electrodes, R_t is the transfer resistance and C_{dl} is the interfacial capacitance of the Helmholtz double-layer, L is the inductance. The impedance (Z) of this system can be written as:

$$Z(jw) = R_s + \frac{R_t(R + jwL)}{R_t + R_0 + jw(L + R_0R_tC_{dl}) - w^2LR_tC_{dl}} \qquad (2)$$

TABLE I Electrochemical parameters of iron in 0.5 M H_2SO_4 with different inhibitor concentrations

C(ppm)	0	40	80	160	320
E_{corr}(mV)	−470.5	−489.5	−490.6	−478.1	−472.0
Icorr(uA/cm^2)	219.1	36.0	20.8	11.6	10.2
Ba(mV)	63.4	52.3	50.9	48.6	52.4
Bc(mV)	126.5	114.2	117.3	105.4	129.0
P	/	83.5	90.5	94.7	95.6

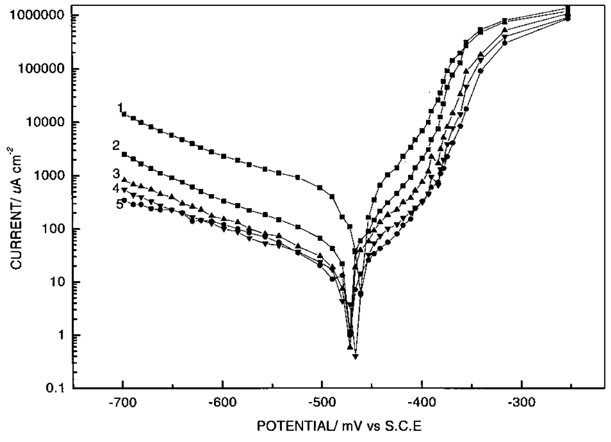

Figure 1 The polarization curves of the inhibitor in sulfuric acid. 1—blank solution, 2—40 ppm, 3—80 ppm, 4—160 ppm, 5—320 ppm.

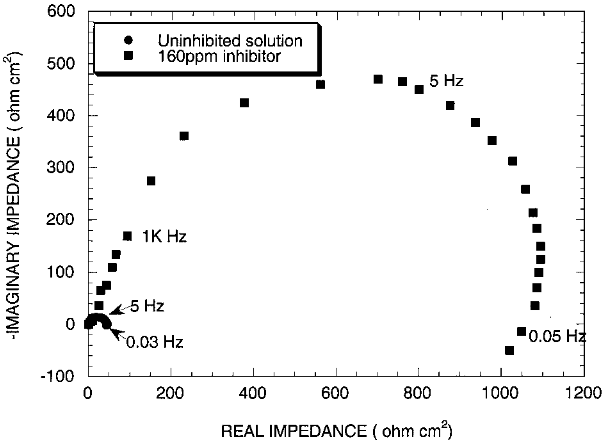

Figure 2 Electrochemical Impedance Spectroscopy (E.I.S) of iron in blank solution and 160 ppm inhibitor solution at corrosion potential.

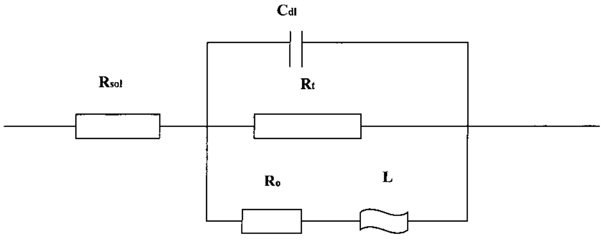

Figure 3 The equivalent circuit of the system.

TABLE II Electrochemical parameters of R_t and C_{dl} with different inhibitor concentrations

C(ppm)	0	40	80	160	320
R_t(ohm/cm^2)	46.2	620.1	789.7	1118.7	1205.4
C_{dl}(uF/cm^2)	182.7	63.1	25.5	19.4	17.6

At the high frequency range, the impedance can be simplified as:

$$Z(jw) = R_s + \frac{R_t}{1 + jwR_tC_{dl}} \tag{3}$$

The state of the adsorbed inhibitor species and the inhibition mechanism can be reflected by the change of capacitance and resistance after addition inhibitors. Table II shows the electrochemical parameters calculated from the E.I.S measurement with different inhibitor concentrations. The electron transfer resistance continues to increase as the increase of inhibitor concentration, while the interfacial capacitance continues to decrease with the increase of inhibitor concentration.

The inhibitor molecules adsorbed on the electrode surface and formed an adsorption layer through nitrogen atom, oxygen atoms and unsaturated bonds of the inhibitor, which acts as hindrance to the sulfuric acid solution and enhances the protection of the metal surface. The adsorption of an organic adsorbate on the surface of iron electrode is regarded as a substitutional adsorption process between the organic compound in the aqueous phase (Org_{aq}) and the water molecules adsorbed on iron surface (H_2O_{ams}):

$$Org_{aq} + xH_2O_{ams} \Leftrightarrow Org_{ams} + xH_2O_{aq} \tag{4}$$

Where x is the size ratio, i.e. the number of water molecules replaced by one adsorbate molecule.

3.2. The adsorption and desorption performance of *N,N*-dipropynoxy methyl amine trimethyl phosphonate

(i) Frumkin isotherm [10]:

$$Kc = [\theta/(1-\theta)]\exp(-2a\theta) \tag{5}$$

where c is the inhibitor concentration, and a is the interaction term parameter ($a > 0$ lateral attraction and $a < 0$ repulsion between adsorbed organic molecules), k is the equilibrium constant of the adsorption reaction given by: $k = (1/55.5)[\exp(-\Delta G^0_{ads}/RT)]$, the value 55.5 is the concentration of water in the solution in mol/l, R is the gas constant, T is the absolute temperature, and ΔG^0_{ads} is the adsorption energy, θ is surface coverage by organic molecules and can be calculated from the inhibitor efficiency relationship [11]:

$$\theta = 1 - R_t/R_{ti} \tag{6}$$

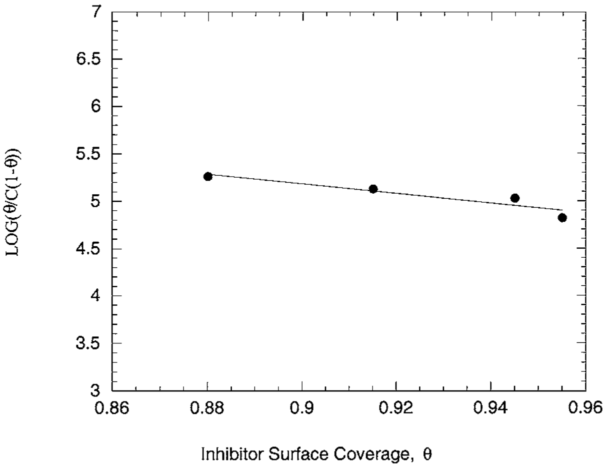

Figure 4 Frumkin isotherm plot.

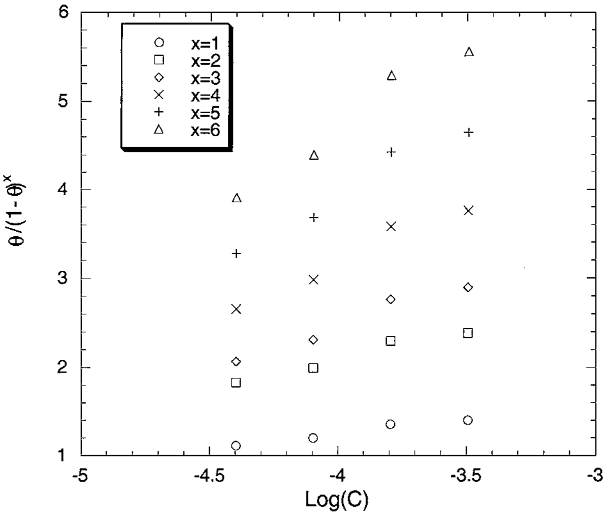

Figure 5 Flory-Huggins isotherm.

where R_t is the transfer resistance in blank solution, R_{ti} is the transfer resistance in solution with addition of inhibitor. Fig. 4 shows the relationship between $\log(\theta/c(1-\theta))$ and θ; a linear relationship was obtained and the regression coefficient is about 0.98. From the slope of this line, we got $a = -0.612$. This means that the force between adsorbed inhibitor molecules is repulsion.

(ii) Flory-Huggins isotherm [12]:

$$Kc = \theta/(x(1-\theta)^x) \tag{7}$$

where x is the number of water molecules replaced by one molecule of organic adsorbate. This isotherm takes account of the water molecule replaced by adsorbed inhibitor molecule. The above isotherms have the form $f(\theta, x)\exp(-a\theta) = kc$, where $f(\theta, x)$ is the configurational term, which depends essentially on the physical model, and $\exp(-a\theta)$ is the interaction term, which depends on the strength of the interaction. Fig. 5 shows a Flory-Huggins isotherm plot for x values up to 6. Table III summarizes meaningful parameters as a function of the number of water molecules being replaced by adsorbed inhibitor molecule. It can be seen from the slopes in Fig. 4 and the correlation coefficient (R) in Table III, that the slope for $x = 3$ remains constant, close to unity. A value of x equal to 3 means that one molecule of N,N-dipropynoxy methyl amine

TABLE III Adsorption isotherm parameters for inhibitor onto iron in 0.5 M sulfuric acid

x	slope	log(k)	R
1	0.3372	2.6012	0.9809
2	0.6568	4.8551	0.9809
3	0.9764	7.2339	0.9810
4	1.296	9.6639	0.9810
5	1.6156	12.122	0.9809
6	1.9352	14.598	0.9809

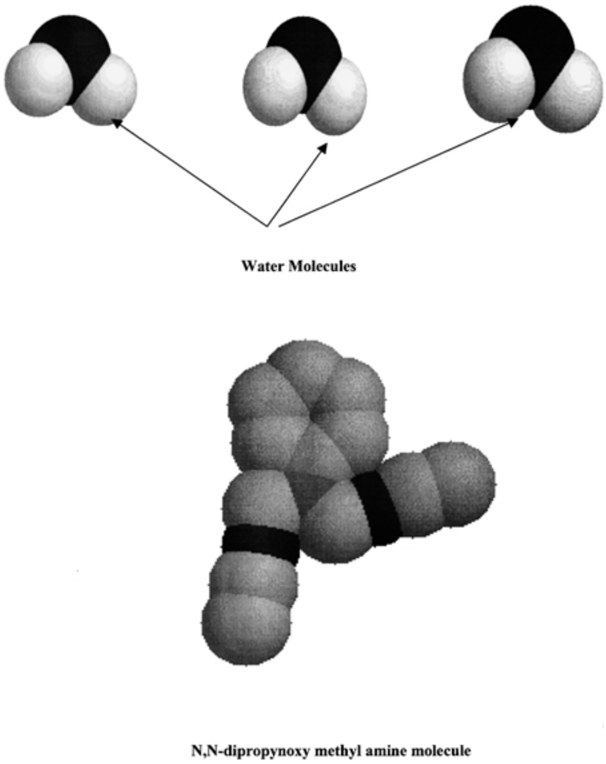

Figure 6 Molecular configuration of water and N,N-dipropynoxy methyl amine.

trimethyl phosphonate replaces 3 molecules of water on the iron surface. Fig. 6 shows that the area occupied by horizontal-oriented N,N-dipropynoxy methyl amine trimethyl phosphonate molecules is about 30Å^2 (the projected area of a triangle surrounding a molecule), the area occupied by an adsorbed water molecule is in the range from 8.3Å^2 to 12Å^2 [13, 14]. From Flory-Huggins isotherm, it can be seen that one inhibitor molecule can displace 3 water molecules, thus it can be inferred that the adsorbed inhibitor molecule is horizontal-oriented.

In Fig. 1 when the applied anodic potential approached the desorption potential (80 mV to 100 mV) relative to the corrosion potential, the corrosion current increased rapidly and inhibitor molecules on the iron electrode surface began to escape. This phenomenon occurs due to the large repulsion force among inhibitor molecules when the anodic potential is near to the desorption potential. Fig. 7 shows the E.I.S of iron electrode at different anodic polarization (relative to corrosion potential) with the addition of 160 ppm inhibitor. The low frequency inductance semicircle began to increase and more than two time constants appeared.

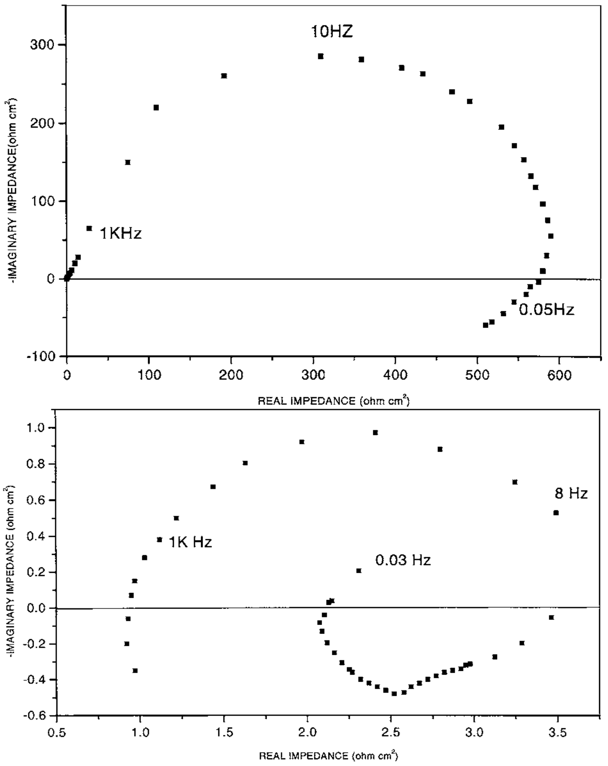

Figure 7 E.I.S of iron in solution with 160 ppm inhibitor at different anodic potential relative to corrosion potential. 1—$\Delta E = 40$ mV, 2—$\Delta E = 80$ mV.

Fig. 7b is similar to that of iron electrode in blank solution at the same polarization. This means that at this potential, most of the adsorbed inhibitor molecules have been desorbed from the electrode surface.

3.3. The inhibition mechanism of *N,N*-dipropynoxy methyl phosphonate

N,N-dipropynoxy methyl amine trimethyl phosphonate can be dissolved in sulfuric acid in the form of N,N-dipropynoxy methyl amine cation (CHPOMA$^+$) and trimethyl phosphonate anion (NTMP$^-$). According to Ye [15], there are excess positive charges on iron surface at free corrosion potential. Without the strong adsorbed anion, it is unfavorable for the adsorption of CHPOMA$^+$. In our experiment, the NTMP$^-$ is a kind of surfactant; it is very easy to adsorb on the electrode surface giving rise to a negative excess charges. Thus it is beneficial for CHPOMA$^+$ adsorption. Moreover, according to molecular structure, there are five active adsorption centers on CHPOMA$^+$, two tri-bond and three heteroatoms of N and O, all of them can contribute to the strong adsorption between inhibitor molecule and iron surface.

4. Conclusions

The inhibition mechanism for pure iron in 0.5 M sulfuric acid in the presence of N,N-dipropynoxy methyl amine trimethyl phosphonate seems to be that of selective adsorption at active sites. N,N-dipropynoxy methyl amine trimethyl phosphonate was chemically adsorbed on the iron surface according to

Flory-Huggins isotherm, with one molecule replacing 3 molecules of water. The inhibition efficiency of *N*,*N*-dipropynoxy methyl amine increases with inhibitor concentration. It is also inferred from projected molecular area method that the adsorbed inhibitor molecule is horizontal-oriented on the iron surface.

References

1. J. M. BASTIDAS, J. L. POLO, E. CANO and C. L. TORRES, *J. Mater. Sci.* **35** (2000) 2637.
2. A. SRHIRI, M. ETMAN and F. DABOSI, *Electrochim. Acta* **41** (1996) 429.
3. T. DU, J. CHEN and D. CAO, *Bulletin of Electrochemistry* **13** (1997) 13.
4. T. P. HOAR, in "Int. Conf. Surface Reactions" (Pittsburgh Corrosion Publishing Co., Pittsburgh, PA, 1948) p. 127.
5. T. P. HOAR and R. D. HOLIDAY, *J. Appl. Chem.* **3** (1952) 502.
6. R. C. AYERS and N. HACKERMAN, *J. Electrochem. Soc.* **110** (1963) 507.
7. P. DUPIN, A. DE SAVIGNA and A. LATTES, *Werhst. Korros.* **33** (1982) 203.
8. C. CAO, *Corros. Sci* **38** (1996) 2073.
9. *Idem., Electrochim. Acta* **35** (1990) 841.
10. S. MURALIDHARAN, K. L. N. PHANI, S. PITCHUMANI, S. RAVICHANDRAN and S. V. K. IYER, *J. Electrochem. Soc.* **142** (1995) 1478.
11. R. ZVAUYA and J. L. DAWSON, *J. Appl. Electrochem.* **24** (1994) 943.
12. T. DU, C. CAO, J. YU and H. LIN, *Br. Corros. J.* **32** (1997) 301.
13. R. PARSONS, R. PEAT and R. M. REEVES, *J. Electroanal. Chem.* **62** (1975) 151.
14. B. G. ATEYA, B. E. EL-ANADOULY and F. M. EL-NIZAMI, *Corros. Sci.* **24** (1984) 509.
15. K. YE, *Materials Protection (in Chinese)* **23** (1990) 37.

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