

# Phosphonium iodine as nickel corrosion inhibitor in 1 M sulfuric acid medium

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Received: 9 February 2006 / Accepted: 26 February 2007 / Published online: 18 July 2007  
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**Abstract** The inhibiting action of alkyltriphenylphosphonium iodine salt  $((C_8H_{17})Ph_3P^+, I^-)$  towards the corrosion behaviour of nickel in 1 M  $H_2SO_4$  solution has been studied. This compound was found to retard both anodic and cathodic reactions of nickel corrosion. At constant temperature, the corrosion rate decreases with increasing inhibitor concentration. On the other hand, the increase in temperature leads to an increase in the corrosion rate. The activation energy,  $\Delta E_a$ , were calculated. They were found  $19.3 \text{ kJ mol}^{-1}$  and  $71.1 \text{ kJ mol}^{-1}$ , respectively for the uninhibited solution and in the presence of  $10^{-3} \text{ M}$  of phosphonium salt. The inhibitor adsorption was identified to occur according to Langmuir isotherm. The equilibrium constant,  $k$ , as well as the free energy of adsorption,  $\Delta_{ads}G^\circ$ , for inhibitor process were then calculated. Phosphonium iodine exhibited a singular behaviour for  $T \geq 318 \text{ K}$  where inhibitor desorption increases.

## Introduction

Phosphonium salts are considered as excellent corrosion inhibitor, especially in acidic media. In fact, Morad [1] used six organic phosphonium compounds of the structure  $YTP^+, X^-$ , ( $T = \text{phenyl}$ ,  $X = Br^-$  or  $Cl^-$  and  $Y = \text{propyl}$ , propargyl, cyclopropyl, allyl, 1,3-dioxolanyl and cinnamyl) to inhibit the corrosion of mild steel in aerated 0.5 M  $H_2SO_4$  solution. Khaled [2] evaluated the inhibiting action of (chloromethyl) triphenyl phosphonium chloride, triphenyl (phenylmethyl) phosphonium chloride and tetraphenyl phosphonium chloride on the corrosion of iron in 1 M HCl solution. In previous works [3], we tested tetraphenyl phosphonium bromide as nickel corrosion inhibitor in sulfuric acid medium. Recently, we have evaluated the effect of  $R^+, X^-$  ( $R^+ = (C_8H_{17})Ph_3P^+$  or  $K^+$ ,  $X^- = I^-$  or  $Br^-$  or  $Cl^-$ ) salts addition on the corrosion behaviour of nickel in 1 M  $H_2SO_4$  medium [4]. The results achieved allowed us considering that phosphonium iodine addition modifies the interface behaviour due to the interaction between the molecule and the material surface.

Thus, in this research program we studied phosphonium iodine salt adsorption on nickel when immersed in 1 M sulphuric acid medium.

## Experimental

Electrochemical experiments were conducted in a classical three-electrode cell. Saturated calomel electrode was used as reference and a platinum wire as counter electrode.

Working electrodes were prepared from high purity nickel (>99.99 wt%). Before use, they were embedded in a chemically inert resin and mechanically polishing up to 2500 SiC grade. Their active area is equal to  $1 \text{ cm}^2$ .

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An aerated 1 M H<sub>2</sub>SO<sub>4</sub> aqueous solution, prepared from ultra pure reagent, was used as corrosive electrolyte. The halide salt was C<sub>8</sub>H<sub>17</sub>Ph<sub>3</sub>P<sup>+</sup>I<sup>-</sup> and it was prepared in the laboratory by adding triphenylphosphine to heptane iodine.

The electrochemical instrumentation consisted of a Taccussel potentiostat-galvanostat PGP 201. Voltmaster 1 software was employed for instrumentation control and data treatment.

**Results and discussion**

Figure 1 shows anodic and cathodic polarization curves for nickel electrode immersed for 1 h at open circuit potential in 1 M sulphuric acid aqueous media, in the absence and presence of 10<sup>-3</sup> M of the iodine alkyl triphenyl phosphonium. The scan rate has been fixed at 8.33 mV/s and the temperature at 298 K.

In absence of the halide salt and independently on the temperature, one notes the presence of four regions on the polarization curves. The region I represent the cathodic domain characterized by a charge transfer process. It can be assigned to the strong concentration of acid (1 M) and the mobility of the H<sup>+</sup> ion that conceals the contribution of the oxygen in the global kinetics of the cathodic reaction. In the region II the electrochemical process at the Nickel–H<sub>2</sub>SO<sub>4</sub> interface is controlled by activation kinetic. The extrapolation of this part to the potential of corrosion permits us calculating the material corrosion rate. The region III is characterized by the presence of two oxidation peaks (1a) and (2a) corresponding to the electrochemical generation of nickel oxides and/or sulfates. Then, the current falls (region IV). A surface steady state appeared indicating that the

corrosion products formed at the electrode surface allowed a pseudo-passivation of the material.

When the inhibitor is added, we observed an increase of the cathodic current density especially for region I. Then, the current density tends to a plateau. Thus, the cathodic reaction is limited by oxygen diffusion. Finally, the current density increases corresponding to H<sup>+</sup> reduction.

One can conclude that the organic halide salt denotes an inhibition activity for the cathodic reaction taking place at the surface of nickel in 1 M H<sub>2</sub>SO<sub>4</sub>.

For the anodic domains (regions II, III and IV), one can notes that the corrosion potential tends to more anodic value. Indeed, only the second activation peak is observed. Furthermore, the steady state current decreased for the entire over potential interval considered.

Hence, one can conclude that organic iodine salt acts as mixed inhibitor. The observed inhibitive action could be due to an adsorption phenomenon at the surface of nickel making a barrier for charge and mass transfer between the metal and its environment.

To characterize the nickel interfacial behaviour, we carried out the voltammetric investigation at various temperatures ranging from 308 K to 328 K. The polarization curves obtained are reported in Fig. 2.

We have measured the corrosion potential (*E*<sub>corr</sub>) and the corrosion current densities (*j*<sub>corr</sub>) from the points of intersection of the extrapolated anodic and cathodic Tafel regions. Then, the Inhibition Efficiency percentage (IE%) and the degree of surface coverage (*θ*) were calculated as follow:

$$IE\% = 100 \frac{j_0 - j_1}{j_0} \tag{1}$$

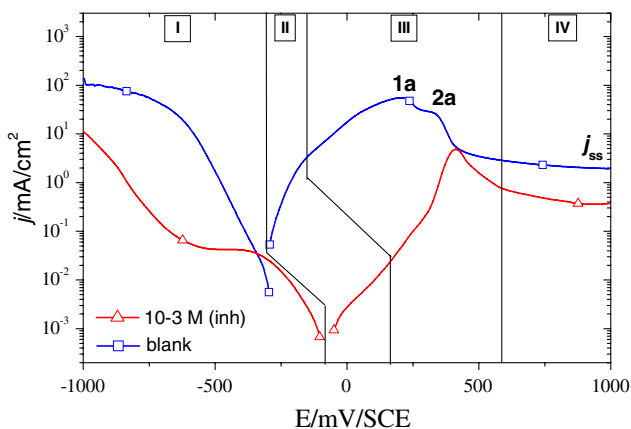
$$\theta = \left( \frac{j_0 - j_1}{j_0} \right) \tag{2}$$

where *j*<sub>0</sub> and *j*<sub>1</sub> are the corrosion current densities obtained in the absence and the presence of the inhibitor.

The results obtained are gathered in Table 1.

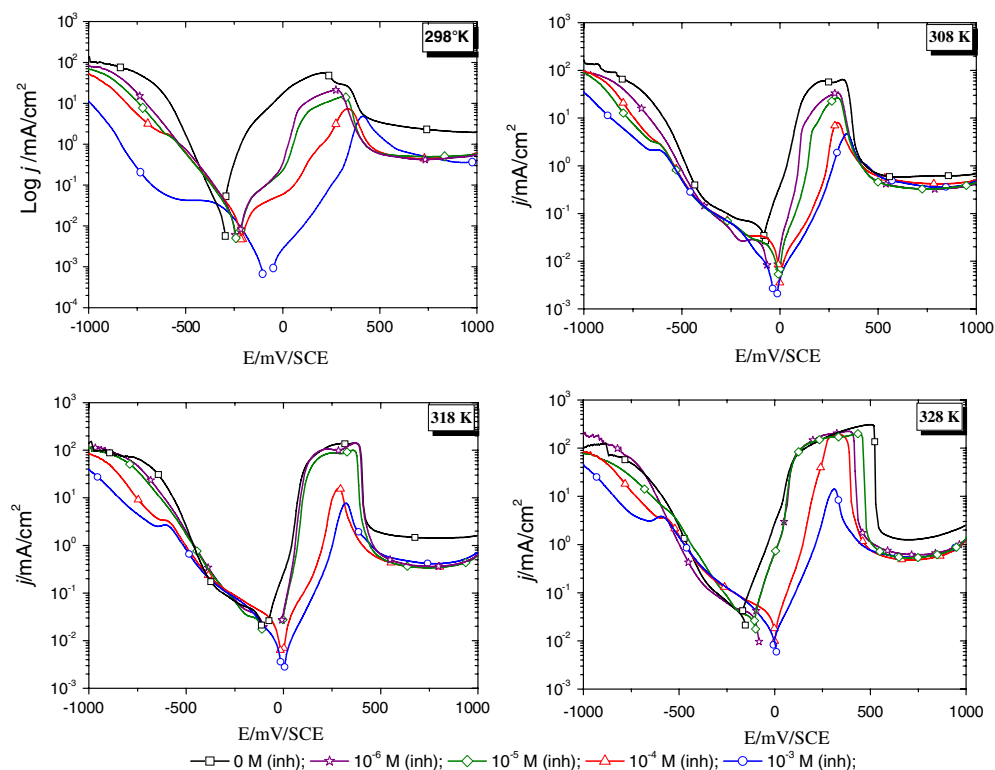
From the data of Table 1, the following conclusions can be made:

- (1) at constant temperature, IE% increases with the increase in the concentration of the studied inhibitor. Such behaviour could be explained on the basis of increased adsorption of the inhibitor on the metal surface;
- (2) in the presence of the same concentration of each inhibitor, IE% decreases with the rise in temperature due to the enhanced effect of temperature on the dissolution process of nickel in H<sub>2</sub>SO<sub>4</sub> solution and; or the partial desorption of the inhibitor from the metal surface.



**Fig. 1** Polarization curves of nickel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without 10<sup>-3</sup> M phosphonium iodine salt

**Fig. 2** Polarization curves of nickel in 1 M H<sub>2</sub>SO<sub>4</sub> at different phosphonium iodine concentrations for various temperatures ranging from 298 K to 328 K



**Table 1** Corrosion potentials  $E_{corr}$ , corrosion current densities  $j_{corr}$ , percentage inhibition efficiencies ( $\% \eta$ ), and the degree of surface coverage  $\theta$  at different temperatures for nickel electrode immersed in 1 M sulphuric acid medium with and without  $10^{-3}$  M phosphonium iodine salt

T/K	[inh]/mol/L	$E_{corr}$ /mV/SCE	$j_{corr}$ /μA/cm <sup>2</sup>	$\% \eta$	$\theta$
298	0	-296	28	–	–
	$10^{-6}$	-243	13	54	0.54
	$10^{-5}$	-235	11	61	0.61
	$10^{-4}$	-224	5.4	81	0.81
	$10^{-3}$	-56	0.8	97	0.97
308	0	-82	35	–	–
	$10^{-6}$	-11	7	80	0.80
	$10^{-5}$	-1	6	83	0.83
	$10^{-4}$	-1	4	89	0.83
	$10^{-3}$	-14	1.5	96	0.96
318	0	-74	41	–	–
	$10^{-6}$	-3	12	71	0.71
	$10^{-5}$	-3	10	76	0.76
	$10^{-4}$	3	5	87	0.87
	$10^{-3}$	6	3	93	0.93
328	0	-153	59	–	–
	$10^{-6}$	-96	47	20	0.20
	$10^{-5}$	-96	46	22	0.22
	$10^{-4}$	0	25	57	0.57
	$10^{-3}$	-7	12	80	0.80

The dependence of the corrosion rate on temperature can be expressed by the Arrhenius equation:

$$\text{Log}j_{\text{corr}} = \text{constant} - \left( \frac{\Delta E_a}{2.303RT} \right) \tag{3}$$

where:

- $\Delta E_a$ : the activation energy of the corrosion reaction;
- $T$ : the absolute temperature;
- $R$ : the universal gas constant.

Figure 3 shows the Arrhenius plots for the corrosion rate of nickel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without the presence of 10<sup>-3</sup> M of phosphonium iodine slat.

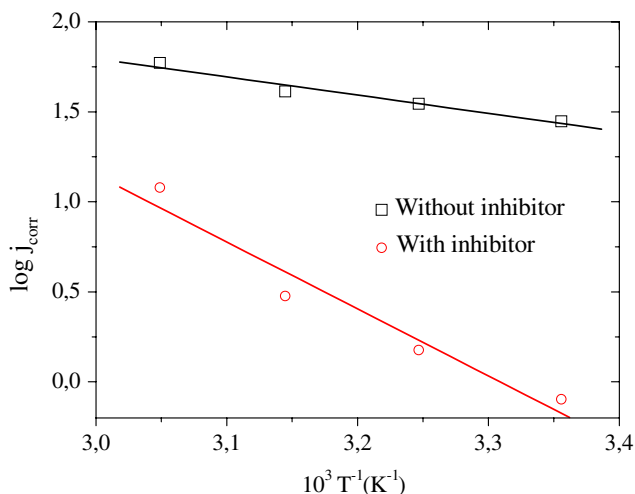
The results give rise to satisfactory straight lines from the slopes of which one can calculate the activation energy.  $\Delta E_a$  values were found to be 19.3 kJ mol<sup>-1</sup> for the uninhibited solution and 71.1 kJ mol<sup>-1</sup> in the presence of 10<sup>-3</sup> M of phosphonium salt. The value of  $\Delta E_a$  for the inhibited solution is higher than that for uninhibited one, indicating the greater tendency of such compound to react at the surface of nickel, in 1 M H<sub>2</sub>SO<sub>4</sub> electrolyte [5–7].

From the above mentioned results it is concluded that the inhibition of nickel corrosion in 1 M H<sub>2</sub>SO<sub>4</sub> solution occurs by adsorption of the additive used [8, 9].

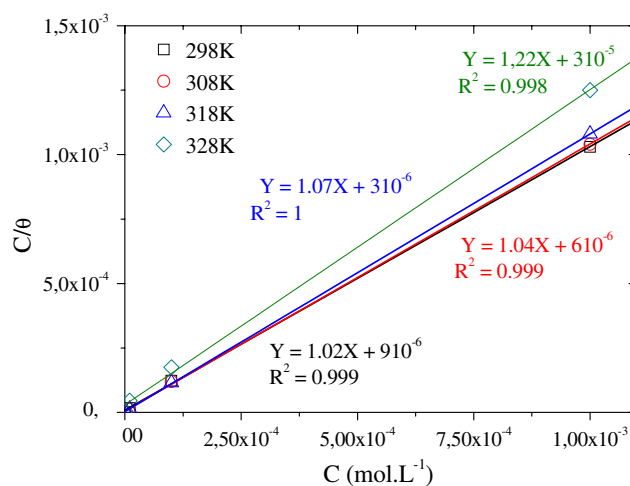
The most commonly used isotherms for studying the adsorption mechanism of an inhibitor on a metal electrode surface are listed in the literature [10–19].

In order to choose the appropriate isotherm model to describe the adsorption mechanism of phosphonium iodine at nickel surface, we plotted  $C/\theta$  versus concentration  $C$  (Fig. 4).

A linear relationship is obtained, independently on the temperature considered. To explain such result, we



**Fig. 3** Arrhenius plots for nickel in 1 M H<sub>2</sub>SO<sub>4</sub> with and without the presence of 10<sup>-3</sup> M of the phosphonium iodine slat



**Fig. 4** Langmuir adsorption isotherms on nickel in 1 M H<sub>2</sub>SO<sub>4</sub> solution with and without the presence of 10<sup>-3</sup> M of the phosphonium iodine slat

considered that the surface coverage ( $\theta$ ) of the inhibitor on the nickel specimen is related to the concentration ( $C$ ) of the inhibitor in the bulk of the solution according to Langmuir adsorption isotherm:

$$\theta = \left( \frac{kC}{1 + kC} \right) \tag{4}$$

where  $k$  is the equilibrium constant for the adsorption process.

Rearranging Eq. 4:

$$C/\theta = \left( \frac{1}{k} \right) + C \tag{5}$$

One can conclude that the absorption of phosphonium iodine salt on nickel surface in 1 M sulphuric acid medium occurs according to the Langmuir adsorption isotherm.

From the intercepts of the straight lines on the  $C/\theta$  axis,  $k$  values could be calculated (Table 2).

Furthermore, the equilibrium constant ( $k$ ) for the adsorption process of the inhibitor could also be related to the free energy of adsorption  $\Delta_{\text{ads}}G^\circ$  by the relationship:

$$k = \frac{1}{55.5} \exp\left( -\frac{\Delta_{\text{ads}}G^\circ}{RT} \right) \tag{6}$$

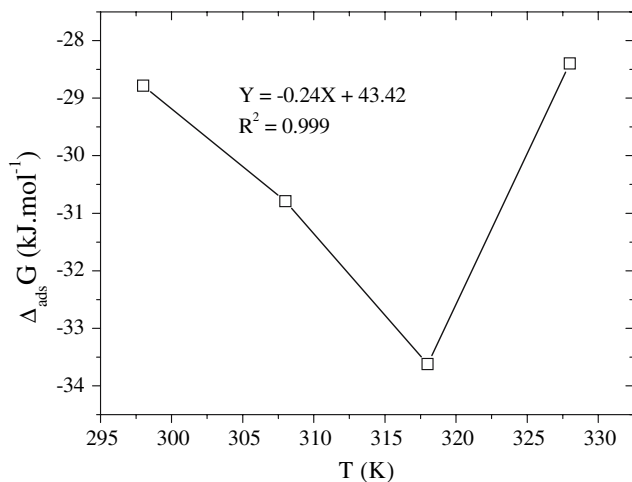
The calculated values are gathered in Table 2. Then, we plotted  $\Delta_{\text{ads}}G^\circ$  against temperature (Fig. 5).

Independently on the temperature considered, negative values are obtained for  $\Delta_{\text{ads}}G^\circ$  indicating the spontaneous interaction between phosphonium iodine and nickel surface.

However, the free energy decreases from -28.8 kJ mol<sup>-1</sup> at 298 K to -33.6 kJ mol<sup>-1</sup> at 318 K. A linear relationship

**Table 2** Values of  $k$  and  $\Delta_{\text{ads}}G^\circ$  for the adsorption of the phosphonium iodine salt on the nickel surface in the temperature domain 298–328 K

$T$	$k$ ( $\text{kJ mol}^{-1}$ )	$\log k$	$\Delta_{\text{ads}}G^\circ = -RT \log k$ ( $\text{kJ mol}^{-1}$ )
298	111	11.62	-28.8
308	167	12.02	-30.8
318	333	12.72	-33.6
328	33.3	10.41	-28.4



**Fig. 5** Adsorption standard free energy ( $\Delta_{\text{ads}}G^\circ$ ) versus temperature could be used to describe  $\Delta_{\text{ads}}G^\circ$  variation versus  $T$  in this interval. Then, other thermodynamic functions can be calculated through the following equation:

$$\Delta_{\text{ads}}G = \Delta_{\text{ads}}H - T\Delta_{\text{ads}}S \quad (7)$$

where  $\Delta_{\text{ads}}H^\circ$  and  $\Delta_{\text{ads}}S^\circ$  the enthalpy and the entropy of adsorption. They were equal to  $+43.4 \text{ kJ mol}^{-1}$  and  $+240 \text{ J K}^{-1} \text{ mol}^{-1}$ , respectively.

In the temperature domain considered, both thermodynamic functions values are positive reflecting for phosphonium iodine adsorption on nickel surface:

- (1) an endothermic behaviour;
- (2) an increase of the molecular disorder.

Then, the free energy exhibited a singular behaviour. In fact, it increases reaching  $-28.4 \text{ kJ mol}^{-1}$ . Such result

could be attributed to the competition adsorption/desorption of the additive on nickel surface for  $T \geq 318 \text{ K}$ .

## Conclusion

The results of these experiments revealed that:

- (1) phosphonium iodine decreases the corrosion rate of nickel in 1 M  $\text{H}_2\text{SO}_4$  electrolyte;
- (2) at constant temperature, IE% increases with increasing inhibitor concentration;
- (3) at the same concentration, IE% decreases with increasing temperature;
- (3) inhibition occurs by adsorption according to the Langmuir isotherm;
- (4) inhibitor desorption increases for  $T \geq 318 \text{ K}$ .

**Acknowledgements** The authors would like to thank AUF (Agence Universitaire de la Francophonie) for financial support.

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