

Temperature Effects on the Thermodynamic Parameters of Tributylamine Adsorption on Carbon Steel as a Corrosion Inhibitor in Oil, Gas And Petrochemical Industries

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Received September 9, 2022, Accepted February 3, 2023

Abstract

Tributylamine was used as the corrosion inhibitor for carbon steel in highly corrosive environment saturated with carbon dioxide and the inhibitor concentration has been optimized. The effect of temperature on the thermodynamic parameters of the tributylamine adsorption on carbon steel in a corrosive solution (NACE) containing saturated CO₂ by using electrochemical tests is investigated. The experiments were conducted without inhibitor and in the presence of inhibitor with concentrations of 20, 50, 100 and 150 mg/L using electrochemical impedance technique. The optimal concentration of the inhibitor was 150 mg/L and the corresponding corrosion rate was 3.01 mpy, indicating an efficiency of 85.67%. Decrease in corrosion rate and increase in positive values of activation energy and entropy as well as negative values of enthalpy were observed at all tested temperatures. Adsorption isotherm of this inhibitor was fitted with Frumkin model. It is concluded that adsorption of inhibitor on the surface of carbon steel is physical.

Keywords: Corrosion; Tributylamine; Thermodynamic parameters; Carbon dioxide; Inhibitor; Impedance; Frumkin isotherm.

1. Introduction

Corrosion phenomenon is one of the most crucial factors in destruction of industrial instruments. Due to highly corrosive environments in oil, gas and petrochemical industries it is extremely important to study and manage the corrosion on these industries. Corrosion is defined as a chemical or electrochemical reaction between materials, usually metal with its surrounding, which leads to changes in the properties of the materials. From thermodynamic point of view, the oxidized materials have lower levels of energy than the materials on normal states. So, the tendency to reach the lower level of energy causes oxidation of metals. It can be concluded that, corrosion phenomena is inevitable and only by using some methods it is possible to delay or reduce its rate [1-5].

The presence of CO₂ in crude oil and other products can cause corrosion. CO₂ is considered as the most destructive corrosion agent of the steel. The corrosion process can be accelerated in the presence of water. Use of inhibitors is one of the most practical ways for protection against internal corrosion. Corrosion inhibitor can be added to the system in small quantities to slow or stop the corrosion reaction. The presence of one or more functional groups including P, S, O, or N atoms in the inhibitors structure enhances adsorption of inhibitor on the metal surface [6-11].

Inhibitors can be cathodic, anodic, and cathodic-anodic. Cathodic inhibitors can reduce the cathodic reactions rate or selectively precipitate on cathodic regions. They can occupy the cathodic sites and prevent the diffusion of reducing agents onto the surface. Anodic inhibitors or oxidizing agents create protective oxidized layers on the metal surface which occupy the anodic sites. Cathodic-anodic inhibitors precipitate on the surface and simultaneously occupy the anodic and cathodic sites, so they lead to reducing the corrosion rates [12-13].

The efficiency of organic inhibitors is related to their adsorption properties. Surface adsorption of these inhibitors is strongly influenced by various factors such as nature, metal surface charge, adsorption mechanism, chemical structure of inhibitor, reaction temperature and pressure, liquid velocity and corrosive environment. The adsorption of inhibitors performs by physical and chemical mechanisms. Physical adsorption is related to the electrostatic interaction between ions or dipoles on the adsorbate and the electrical charge at the surface between the metal and the solution. On the other hand, chemical adsorption corresponds to the bond formation or ion exchange between inhibitor and metal surface. The energy of chemical adsorption is more than physical adsorption. Physical adsorption is unstable at high temperatures but chemical adsorption is stable at elevated temperatures [12, 14]. According to a research conducted in 2009, the amino ethyl imidazoline derivative has been studied as a corrosion inhibitor in sour environment and the results showed that this derivative at concentration of 80 mg L⁻¹ and in the presence of 2000 mg L⁻¹ potassium iodide gives the best result [15]. 4-carboxy-phenyl benzoic acid was used as a corrosion inhibitor, and the best result was achieved in the inhibitor concentration of 2.41 mM [16]. In another study, for imidazoline and bis-imidazoline derivatives the best results were obtained in the concentration of 50 mg L⁻¹ and the corrosion rate reached to 0.06 and 0.51 microns per year (mpy), respectively on this concentration [17].

In this study, the Tafel and electrochemical impedance procedures were used to examine the corrosion rate of the carbon steel. Tributyl amine was used as the corrosion inhibitor for carbon steel in highly corrosive environment saturated with carbon dioxide and the inhibitor concentration has been optimized. The polarization resistance and amount of corrosion rate were obtained from the plots of Tafel and electrochemical impedance. The corrosion rate was calculated from the related equations and the performance of the inhibitors was evaluated by comparing of corrosion rate in the presence and absence of inhibitor.

2. Experimental

2.1. Materials

Carbon steel was supplied from Research Institute of Petroleum Industry (RIPI). Tributyl amine as corrosion inhibitor was purchased from Aldrich. NACE solution containing 9.62% NaCl, 0.305% CaCl₂, and 0.186% MgCl₂.6H₂O was prepared according to the standard of NACE 1D182. All other chemical reagents with high purity were obtained from Merck.

2.2. Electrochemical tests

The solution containing 500 mL of 10% salt solution was prepared according to the standard NACE 1D182, purged with nitrogen gas for 30 minutes, and then saturated with carbon dioxide for another 30 minutes. The pH of solution was fixed at 3.5 by continuous injection of CO₂ gas at atmospheric pressure. The experiments were performed in a glass cell with three electrodes (platinum, calomel and working electrode). The impedance test without the inhibitor and in the presence of inhibitor with concentrations of 20, 50, 100 and 150 mg L⁻¹, was conducted in the range of 0.01 to 100000 Hz in the open-circuit potential. In the next step 500 mL of solution according to previous procedure was added to the electrochemical double-layer cell. The electrodes were placed in the cell and then the solution was purged by nitrogen for 30 minutes. It was then saturated with carbon dioxide for another 30 minutes. The cell was saturated with continuous pumping of CO₂ gas at atmospheric pressure and the pH of the solution was fixed at 0.01 ± 3.5. The temperature of electrochemical cell was adjusted at desired temperature by the circulator. Finally, the rate of corrosion was measured using electrochemical impedance test in the presence and absence of the inhibitor with optimum concentration of 150 mg L⁻¹ at 30, 40, 50 and 60°C. All experiments were performed in 25°C and atmospheric pressure repeated for three times.

3. Results and discussions

The electrochemical parameters were achieved in 10% salt solution saturated by CO₂ for carbon steel with and without inhibitors in various concentrations from electrochemical impedance test and they are represented in Table 1. These results were calculated using the following equations [16, 18-19].

$$CR = \frac{I_{corr} \cdot K \cdot EW}{A \cdot d} \tag{1}$$

$$\theta = 1 - \frac{R_{p \text{ uninhib}}}{R_{p \text{ inh}}} \tag{2}$$

where CR, I_{corr}, θ, R_{p inh}, R_{p uninhib}, EW, K, A and d are the corrosion rate, the corrosion current density, inhibition efficiency, polarization resistance in the presence of inhibitor, and polarization resistance in the absence of inhibitor, equivalent number, corrosion constant and surface and density of the sample, respectively [20-22].

The amounts of inhibition efficiency percentage (IE %) at different concentration of inhibitor are listed in Table 1.

Table 1. Results obtained from electrochemical impedance tests at ambient temperature

C (mg L ⁻¹)	R _p (Ω.cm ²)	CR (mpy)	θ	% IE
without inhibitor	97.7	21.01	-	-
20	111.8	18.50	0.1261	12.61
50	120.0	17.11	0.1858	18.58
100	172.4	11.91	0.4333	43.33
150	682.1	3.01	0.8568	85.68

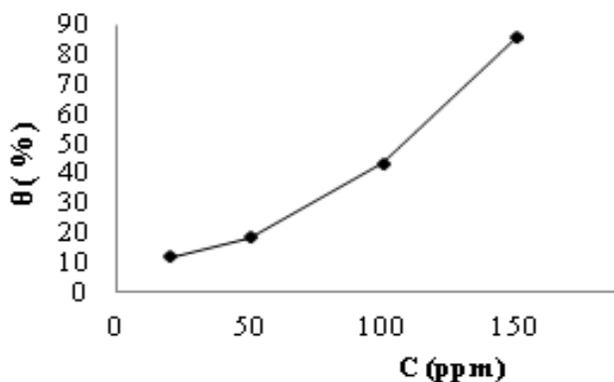


Figure 1 indicates that the efficiency of inhibitor is increased with increasing the concentration of inhibitor up to 150 mg L⁻¹. It was observed that the best efficiency was achieved in this concentration. Not shown here, it is to note that, above this concentration the efficiency did not change significantly. It can be concluded that the coating process of this inhibitor related to its concentration. Therefore, the concentration of 150 mg L⁻¹ was chosen as the optimal concentration for further investigations.

Figure 1. Effect of inhibitor concentration on the efficiency of inhibitor

3.1. Effect of temperature

In order to evaluate the effect of temperature in the thermodynamic parameters, the electrochemical impedance test was performed in the absence and presence of inhibitor with the optimum concentration (150 mg L⁻¹) at various temperatures of 30, 40, 50 and 60 °C.

Figures 2 and 3 show the Nyquist plots obtained from electrochemical impedance tests in the presence of inhibitor at concentration of 150 mg L⁻¹ and absence of inhibitor in the range of 30-60°C.

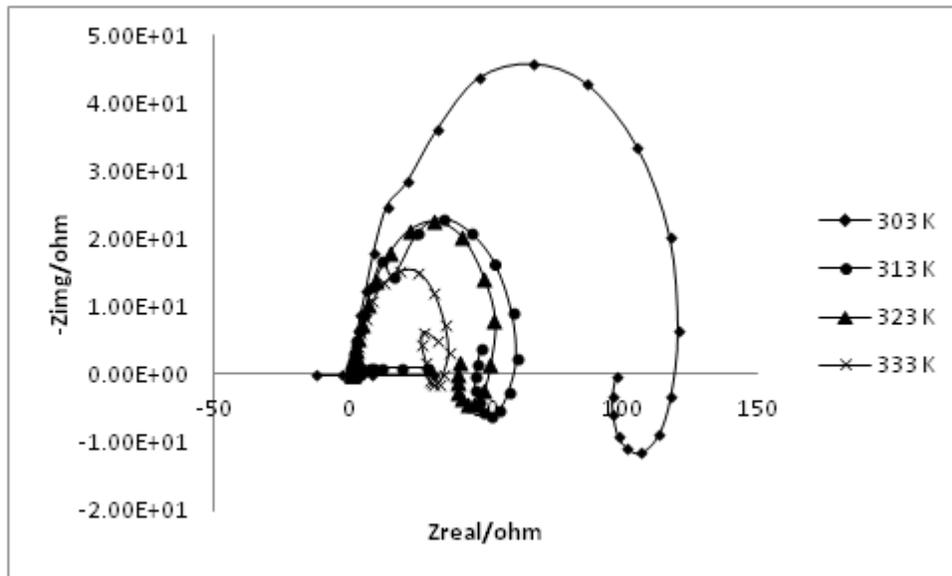


Figure 2. Nyquist plots obtained from electrochemical impedance test in the absence of inhibitor at different temperatures

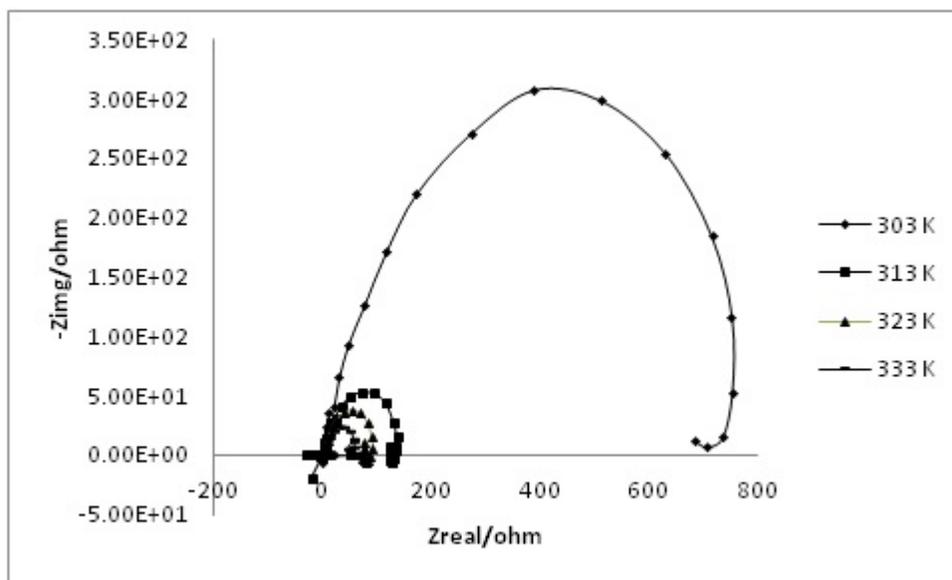


Figure 3. Nyquist plots obtained from electrochemical impedance test in the presence of inhibitor at different temperatures

Figures 4 and 5 show the Bode electrochemical diagrams with and without inhibitor in the range of 30-60°C in saturated NACE solution with CO₂ gas. The plot of the total impedance (Z) against logarithm of frequency in the absence of inhibitor is presented in Figure 4. The current density of corrosion and corrosion rate are obtained from R_p and equations 1 and 2. Figure 5 shows the diagram of impedance against logarithm of frequency in the presence of 150 mg L⁻¹ inhibitor.

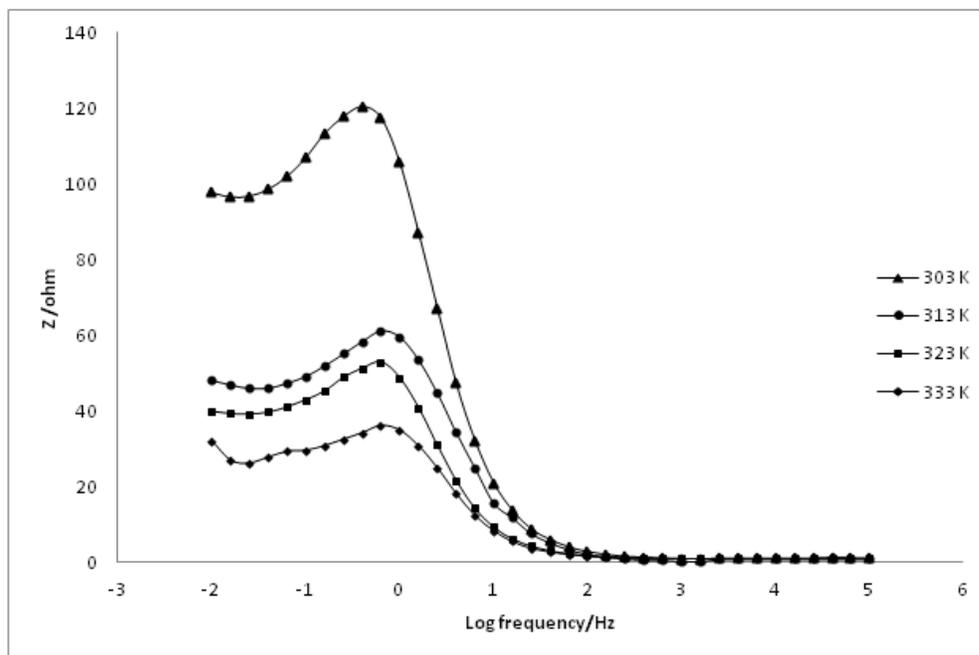


Figure 4. The Bode electrochemical diagrams in the absence of inhibitor at different temperatures

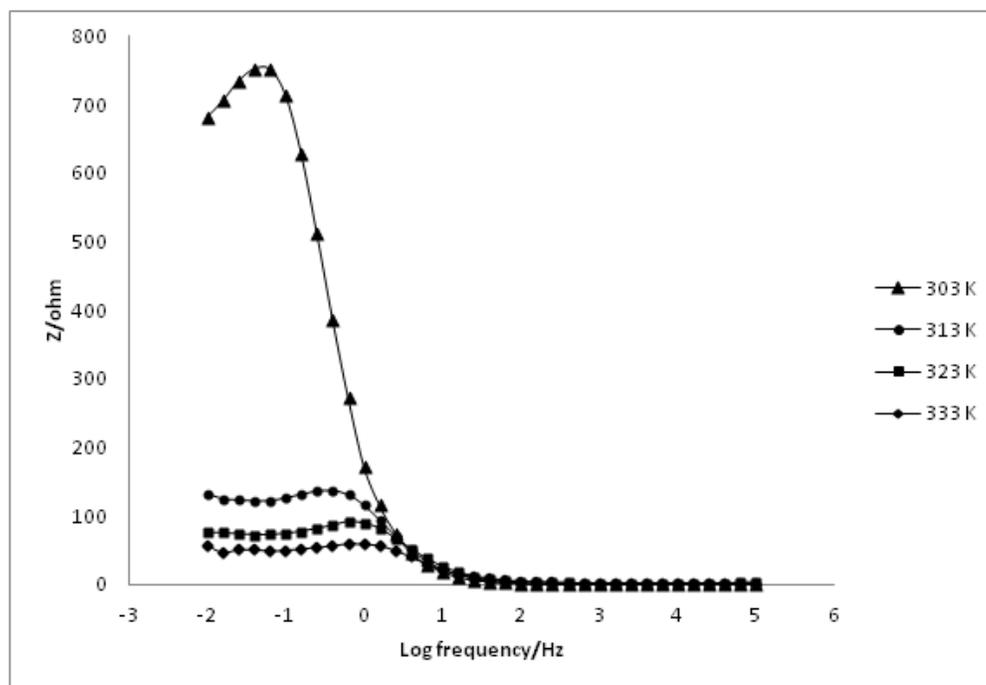


Figure 5. The Bode electrochemical diagrams in the presence of inhibitor at different temperatures

The results of electrochemical impedance test at different temperatures are shown in Table 2. As shown in this Table, corrosion rate increases with increasing temperature in the presence and absence of inhibitor. However, in the presence of the inhibitor, corrosion rates at all tested temperatures are significantly lower, which indicate the effect of inhibitor in corrosion process.

Table 2. Results of electrochemical impedance test at different temperatures

C (mg L ⁻¹)	I _{corr} (A)				CR (mpy)			
	303(K)	313(K)	323(K)	333(K)	303(K)	313(K)	323(K)	333(K)
without inhibitor	0.01088	0.0002046	0.0004219	0.0005147	21.01	42.6	51.34	63.98
150	0.00001327	0.0000635	0.0001555	0.0002296	3.01	15.49	27.06	36.1

Thermodynamic parameters were calculated using corrosion rate values for each concentration at different temperatures according to the Arrhenius equation [18,23-24].

$$I_{corr} = \frac{RT}{Nh} \exp\left(\frac{\Delta Sa}{R}\right) \exp\left(\frac{\Delta Ha}{RT}\right) \quad (3)$$

$$I_{corr} = A \exp\left(\frac{-E_a}{RT}\right) \quad (4)$$

$$\Delta G_a = \Delta H_a - T\Delta S_a \quad (5)$$

where I_{Corr}, h, R and N are the corrosion current density, Planck's constant, universal gas constant and Avogadro's constant, respectively. Thermodynamic parameters including enthalpy (ΔH_a) and entropy (ΔS_a) are obtained from the equation 3 and the values of activation energy (E_a) were calculated according to equation 4. Finally, the amount of Gibbs free energy (ΔG_a), for each temperature was obtained using the equation 5. The results are listed in Table 3.

Table 3. Thermodynamic parameters of the Arrhenius equation

C (mg L ⁻¹)	E _a (kj.mol ⁻¹)	ΔH _a (kj.mol ⁻¹)	ΔS _a (J.mol ⁻¹ .k ⁻¹)	ΔG _a (kj.mol ⁻¹)			
				303 (K)	313 (K)	323 (K)	333 (K)
without inhibitor	44.89	-42.151	29.43	-51.07	-51.36	-51.65	-51.95
150	75.65	-75.74	124.66	-113.51	-114.76	-116	-117.25

According to the results on this table, the significant increase in positive values of E_a, as well as negative values of enthalpy and positive values of entropy, indicate desired adsorption of inhibitor on the metal surface. On the other hand, adsorption process of inhibitor on the metal surface is predominate than metal corrosion process. The increase in positive values of E_a suggests the physical adsorption of inhibitor on the metal surface. Considerable increase in the amount of entropy in the presence of tributylamine as inhibitor indicates the increase of irregularities of the system. Negative values of Gibbs free energy at all tested temperatures indicate a spontaneous adsorption of inhibitor on the surface of the metal [18, 25-27].

3.2. Adsorption mechanism

The adsorption mechanism of tributylamine inhibitor on carbon steel surface was studied using the results presented in Table 1. In order to explain the adsorption mechanism of the inhibitor on the surface of carbon steel, adsorption data were evaluated by different isotherm models such as Langmuir, Temkin and Frumkin isotherm models [14,17, 28-29]. Frumkin isotherm model using the following equation showed better fit with the experimental data.

$$\text{Frumkin: } \text{Log}(\theta C_{inh})/(1-\theta) = \text{Log } K_{ads} + \alpha\theta \quad (6)$$

where θ, K_{ads}, C_{inh}, and α are degree of coverage, adsorption equilibrium constant, concentration of the inhibitor and interaction parameter, respectively. Adsorption isotherms were plotted according to the results on Table 1. As shown in Figure 6, experimental data calculated based on regression method were in good agreement with Frumkin model (R² =0.92).

Adsorption standard free energy (ΔG^o_{ads}) can be obtained from the following equation [14, 17].

$$\Delta G^o_{ads} = - RT \ln (55.5 K_{ads}) \quad (7)$$

where R is the universal gas constant (J mol⁻¹ K⁻¹) and T is the reaction temperature (K).

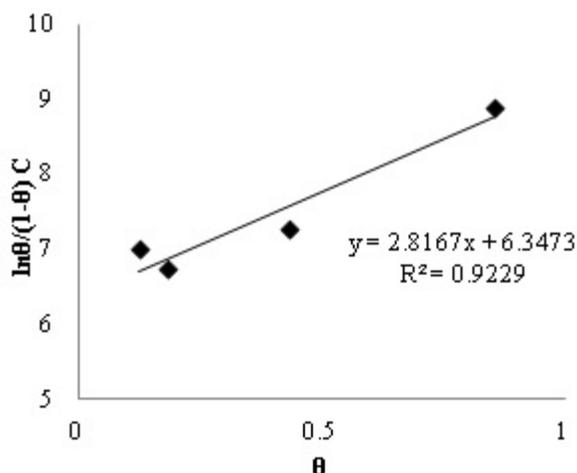


Figure 6. Inhibitor adsorption isotherm based on Frumkin model

The value of adsorption constant (K_{ads}) can be calculated using the slope of the isotherm diagram. Adsorption standard free energy for this inhibitor was found to be -26.35 kJ/mol. Negative value of ΔG°_{ads} indicates spontaneous adsorption of inhibitor on the surface. ΔG°_{ads} values less than -40 kJ/mol indicate physical adsorption of inhibitor. Therefore, adsorption of this inhibitor on the surface of carbon steel is physical that shows electrostatic interactions between the inhibitor and the charge on the surface [30-32].

4. Conclusions

In this study, tributylamine as an inhibitor was tested in corrosive media saturated with CO_2 . By increasing the concentration of the inhibitor, corrosion rate decreases and the degree of coverage and efficiency increases. The highest efficiency of this inhibitor ($\%85.68$) was achieved in 150 mg L^{-1} of inhibitor concentration. The corrosion rate in the presence of inhibitor at all tested temperatures was lower than the blank sample. The significant increase in positive values of E_a , negative values of ΔH_a and positive values of entropy in the presence of inhibitor represents appropriate and considerable progress of inhibitor adsorption on the surface of metal and also confirmed the physical adsorption mechanism. The significant increase in the amount of entropy in the presence of the inhibitor indicates that the system disorder has been increased and the negative values of Gibbs free energy at different temperatures indicate spontaneous adsorption on the surface of the metal. The adsorption mechanism of this inhibitor was fitted with Frumkin isotherm ($R^2 = 0.92$). The value of adsorption free energy (-26.35 kJ/mol) represents the physical adsorption of inhibitor and electrostatic interactions between the inhibitor and the charge on the surface.

Acknowledgments

This research was conducted at the Research Institute of Iran's oil industry. The authors would like to acknowledge the Research Institute of Petroleum Industry (RIPI) for support on this research work.

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