Study on Inhibition of N80 Carbon Steel in 0.5M KCl Solution Saturated with CO_2 by Gum Arabic

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Abstract

The effect of Gum Arabic (GA) on the corrosion of an N80 carbon steel pipeline in a CO_2-saturated chloride (0.5M KCl) solution was investigated through AC impedance and polarization curves. Potentiodynamic measurements showed that the corrosion current density decreased in the presence of inhibitors and that the inhibitor acts like a mixed-type inhibitor, with anodic predominance. The Nyquist diagrams showed an increase in polarization resistance values in the presence of the inhibitor, thus increasing inhibition efficiency. At higher temperatures, the inhibition efficiency decreased, implying that the inhibition action of GA occurred *via* the physical adsorption process. The activation parameters of the corrosion process such as activation energies, E_a, and the heat of adsorption, Q_{ads}, were calculated, respectively, by the obtained corrosion rate and inhibition efficiency at different temperatures. At higher temperatures, the increase in activation energy combined with the negative levels of the heat of adsorption further supported the physical adsorption nature of the process.

Keywords:

corrosion inhibition, gum arabic, carbon steel, electrochemical techniques

1. INTRODUCTION

Despite its relatively limited corrosion resistance, carbon steel is widely used in oil and gas industry infrastructures mainly due to its low cost. One of the most-practical methods to protect the metal dissolution from aggressive environments is the use of inhibitors. In particular, organic inhibitors provide more environmental benefits than the traditional toxic ones, meeting the stringent environment regulations that limit their consumption. Commercial gum arabic was selected for the present study. GA is a water-soluble and complex mixture of arabinogalactan, oligosaccharides, polysaccharides, and glucoproteins [1] and is biodegradable and readily available from renewable sources [2]. As witnessed by an increasing number of publications, GA is emerging as a promising candidate as a corrosion inhibitor of metal infrastructures [2–7]. It was reported that the inhibition process by GA is mainly attributed to the adsorption of the chain molecules via their functional group onto the metal surface (i.e., hydroxyl functional group (–OH), and carboxyl functional group (–COOH)) [2–8]. One of the most-frequent and aggressive environments found in the oil and gas industry are fluids with high concentrations of chlorides containing carbon dioxide [9, 10]. It is well-known that the presence of chloride ions leads to an autocatalytic process dissolution of the metal owing to the breakdown of the oxide layers on the metal surface by localized corrosion spots [11–13]. Moreover, the literature reports that the corrosion rate in chloride water is enhanced by a factor of around 16 by the presence of CO_2 [14]. Therefore, the objective of the research presented in this paper was to study the inhibition effect of GA on N80 carbon steel pipeline in CO_2-saturated chloride solutions for the first time.

The study was carried out using electrochemical techniques such as electrochemical impedance spectroscopy (EIS) and linear sweep voltammetry (LSV).

2. EXPERIMENTAL

The electrochemical experiments were performed by using three electrode cells connected to a Potentiostat/ Galvanostat Gamry reference 600. N80 carbon steel was used as a working electrode, a platinum electrode as an auxiliary electrode, and a saturated calomel electrode (SCE) as a reference electrode. All potentials reported were measured versus SCE. The electrical connection of the specimen to the potentiostat was achieved by spot welding an insulated copper wire onto an unexposed electrode surface. All of the experiments were conducted at 25 and 45°C in an unstirred solution consisting of a CO_2-saturated chloride (0.5M KCl) solution with and without the presence of the inhibitor gum arabic (GA) (e.g., 0.5 g/l). The solutions were prepared from analytical-grade material (SIGMA-ALDRICH) and distilled water with 0.055 $\mu S \cdot cm^{-1}$ of conductivity. The efficiency of the inhibitor was evaluated via linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Tafel curves were obtained at a scan rate of 1.0 $mV \cdot s^{-1}$. EIS measurements were performed under potentiostatic

conditions in a frequency range of 100 kHz to 0.01 Hz, with an AC signal with an amplitude of 10 mV. In both electrochemical techniques, the measure started after exposing the sample for 24 h in the tested solution. The data was then collected and fitted with a Gamry echem analyst in order to calculate inhibitor efficiency (*EI*%) and the corrosion rate (CR).

3. RESULTS AND DISCUSSION

3.1. EIS measurements

Nyquist plots of N80 pipe carbon steel in a 0.5M KCl solution saturated with CO_2 with the absence and presence of 0.5 g/l of GA performed at 25 and 45°C are shown in Figures 1a and b. The EIS results of these capacitive loops are simulated by an equivalent circuit containing a parallel combination of constant phase element (*Q*) with polarization resistance (R_p) and solution resistant (R_s) (e.g., $R_s(QR_p)$). It can be seen that, after the addition of GA, the impedance modulus of the system increased at both temperatures. The increase of polarization resistance (R_p) with respect to a blank 0.5M KCl solution as shown in Table 1 is attributed to the increase in resistance and adsorption of inhibitor molecules on the steel surface [2, 4, 6].
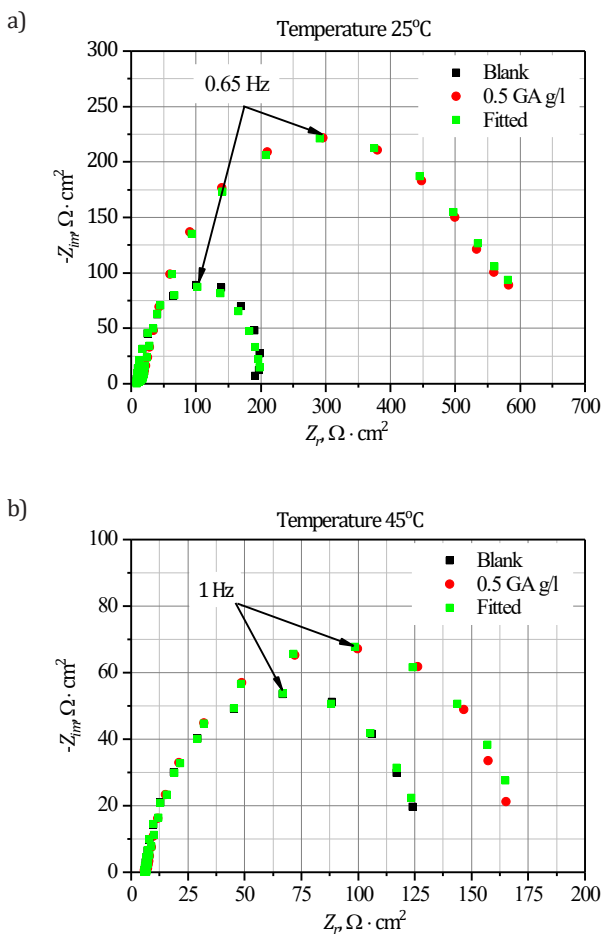
a)

b)

Fig. 1. Nyquist plots recorded at OCP after 24 hours of exposure for carbon steel (N-80) pipeline steel in CO_2-saturated chloride (0.5M KCl) solution in absence and presence of GA (0.5 g/l) within temperature range of 25°C (a) and 45°C (b)

Table 1
Electrochemical parameters obtained from EIS within temperature range of 25–45°C after 24 hours of exposure

C_{inh}, g · l⁻¹	R_s, Ω · cm²	R_p, Ω · cm²	CR, mm · yr⁻¹	EI, %
Temperature 25°C				
Blank	8.79	192.00	0.00157	–
0.5	9.23	561.00	0.00054	65.78
Temperature 45°C				
Blank	5.96	125.00	0.00248	–
0.5	6.77	170.00	0.00178	26.47

The inhibition efficiency was calculated using polarization resistance (R_p) as follows:

$$EI\% = \frac{R_p^i - R_p}{R_p^i} \cdot 100 \qquad (1)$$

where R_p^i band R_p are the values of the polarization resistance in the presence and absence of the inhibitor in the tested solution, respectively. Whereas, the corrosion rate (*CR*) is calculated from the following equation according ASTM Standard G 102 [15]:

$$CR = K \frac{i_{corr}}{\rho}(EW) \qquad (2)$$

where *K* (3272 mm A⁻¹ · cm⁻¹ · yr⁻¹) is a constant for converting units, i_{corr} is the current density (A · cm⁻²), ρ is the density of the corroded metal (steel: 7.85 g · cm⁻³), and *EW* (Fe: 27.93 g · eq.⁻¹) is the element equivalent weight.

The corrosion parameters obtained by EIS measurements at different temperatures are tabulated in Table 1. It can be clearly seen that the corrosion rate values decreased in the presence of GA. This decrease in *CR* is ascribed to the formation of a product layer promoted by the adsorption of the inhibitor onto the electrode surface. However, increases in temperature led to increasing the corrosion rate and decreasing the corrosion resistance of the steel in the tested solution. The *EI*% is also affected by increases in temperature; as a result, the *EI*% decreased from a value of 65.78% to 26.47%. In fact, the increase in temperature lead to the stimulation of the metal surface kinetic energy [16], which has an adverse effect on the adsorption process; i.e., the adsorption of the inhibitors is significantly reduced, a trend often attributed to the physical adsorption process [6]. The physisorption is consistent with the electrostatic interaction between charged molecules and a charged metal, while the chemisorption is consistent with charge sharing or transfer from the inhibitor components to the metal surface to form a co-ordinate type of bond [17]. The inhibition effect of Gum Arabic is attributed to the presence of hydroxyl functional group (–OH) and carboxyl functional group (–COOH) [2]. In an acid solution, the carbonyl oxygen (C=O) may be protonated, and the molecule exists as a polycation [18]. While in the presence of Cl⁻ anions, the metal surface can be

negatively charged by the adsorption of these anions on its surface. The adsorption, therefore, is the result of an electrostatic interaction between the GA molecules and mild steel surface [19, 20].

3.2. LSV measurements

Figures 2a and b show the polarization curves for N80 pipe carbon steel in the absence and presence of the inhibitor in the tested solution, performed respectively at 25 and 45°C. Table 2 contains all of the electrochemical corrosion kinetic parameters such as corrosion potential (E_{corr}), corrosion current density (i_{corr}), corrosion rate (CR), and inhibition efficiency ($EI\%$).

The inhibition efficiency was calculated using the corrosion current density as follows:

$$EI\% = \frac{i_{corr} - i_{corr}^i}{i_{corr}} \cdot 100 \qquad (3)$$

where i_{corr} and i_{corr}^i are the corrosion current densities in the absence and presence of inhibitor.

From Figure 2 and Table 2, it is can be seen that, by adding the inhibitor in the tested solution, the current density of both the cathodic and anodic branches markedly decreases towards lower values when compared to the blank solution at both temperatures due to the adsorption of the inhibitor on the metal surface [6]. However, by adding GA, the corrosion potential does not shift remarkably, suggesting that the inhibitor acts as a mixed-type inhibitor.
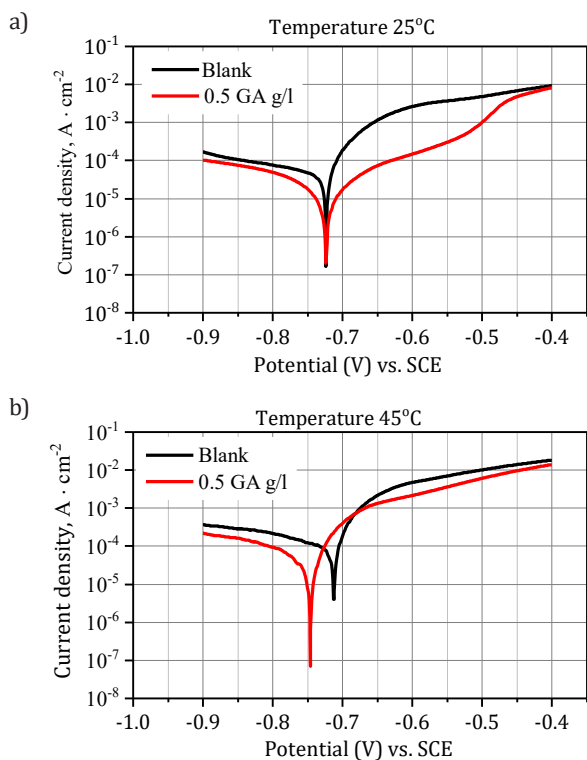
a)

b)

Fig. 2. Polarization curves recorded at OCP after 24 hours of exposure for carbon steel (N-80) pipeline steel in CO_2-saturated chloride (0.5M KCl) solution in absence and presence of GA (0.5 g/l) within temperature range of 25°C (a) and 45°C (b)

The findings were in well-agreement with those obtained from the EIS measurements, with the values of the $EI\%$ decreasing from 70.26 to 47.48 at the higher temperature.

Table 2
Potentiodynamic polarization parameters for carbon steel (N-80) pipeline steel in CO_2-saturated chloride (0.5M KCl) solution at different concentrations of GA after 24 hours of exposure

Temperature 25°C				
C_{inh}, g · l⁻¹	E_{corr}, V/SCE	i_{corr}, μA · cm⁻²	CR, mm · yr⁻¹	EI, %
Blank	−0.726	117.6	0.00137	–
0.5	−0.724	34.97	0.00041	70.26
Temperature 45°C				
C_{inh}, g · l⁻¹	E_{corr}, V/SCE	i_{corr}, μA · cm⁻²	CR, mm · yr⁻¹	EI, %
Blank	−0.713	156.60	0.00182	–
0.5	−0.746	82.25	0.00096	47.48

3.3. Effect of temperature

To understand the effect of the inhibitor on corrosion rates at different temperatures, the linearized Arrhenius equation of chemical kinetics was considered:

$$\log CR = \log A - \frac{E_a}{2.303 RT} \qquad (4)$$

Here, A is the frequency factor and E_a is the apparent activation energy, R is the gas constant (8.314 J · mol⁻¹ · K⁻¹), and T is the absolute temperature (K).

The Arrhenius equation can be rearranged in the following equation:

$$\log \frac{CR_2}{CR_1} = \frac{E_a}{2.303 R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right) \qquad (5)$$

where CR_1 and CR_2 are the values of the corrosion rates at temperatures T_1 (25°C) and T_2 (45°C), respectively.

The values of E_a (Tab. 3) were found to increase from 13.97 kJ · mol⁻¹ in the blank solution to 49.4875 kJ · mol⁻¹ and from 11.20 to 33.55 kJ · mol⁻¹ with the addition of GA at 25 and 45°C, respectively.

Table 3
Apparent activation energies and heat of adsorption calculated within temperature range of 25–45°C

EIS		
C_{inh}, g · l⁻¹	E_a, kJ · mol⁻¹	Q_{ads}, kJ · mol⁻¹
Blank	18.03	–
0.5	47.04	−66.07
LVS		
C_{inh}, g · l⁻¹	E_a, kJ · mol⁻¹	Q_{ads}, kJ · mol⁻¹
Blank	11.20	–
0.5	33.55	−48.16

Higher values of E_a in the presence of inhibitors can be correlated with an increasing thickness in the double layer, which enhances the E_a of the corrosion process [18]. Combined with the trend of decreased efficiency in the inhibition, such behavior confirmed the physical adsorption nature of the process [6, 21].

Another thermodynamic parameter that further describes the adsorption mechanism operative in the corrosion inhibition process is the heat of adsorption, Q_{ads}. The heat of adsorption is connected to the degree of surface coverage, θ ($EI\% = 100 \cdot θ$), through the following relationship [1]:

$$Q_{ads} = 2{,}303R \left[\log\left(\frac{θ_2}{1-θ_2} \right) - \log\left(\frac{θ_1}{1-θ_1} \right) \right] \cdot \left(\frac{T_1 \cdot T_2}{T_2 - T_1} \right) \quad (6)$$

where $θ_1$ and $θ_2$ are values of the degree of surface coverage at temperatures T_1 and T_2, respectively. Negative Q_{ads} values are consistent with physisorption, while positive values of Q_{ads} imply chemical adsorption. As can be seen from the calculated values of Q_{ads} shown in Table 3, they are all negative (which is consistent with the inhibition physisorption mechanism proposed) [22].

4. CONCLUSION

1. GA was found to be an efficient corrosion inhibitor for carbon steel in a CO$_2$-saturated chloride (0.5M KCl) solution.
2. GA acts as mixed-type inhibitor by promoting the formation of a product layer, thus lowering both cathodic and anodic current density.
3. At the higher temperature, the inhibition efficiency decreased and activation energy increased, indicating that the inhibition is endothermic in nature, and the adsorption process was more-favored at lower temperatures (physisorption).
4. The negative values of the heat of adsorption further support the physical adsorption nature of the process.

Acknowledgements

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