Influence of Temperature and Velocity of Fluid on The Rate of Corrosion of Mild Steel in Existence of NPK (Nitrogen, Phosphorus, and Potassium) Inhibitor in Tap Water System

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ARTICLE INFO	ABSTRACT
	The corrosion of using various concentrations of the NPK inhibitor on the mild steel in the tap water was investigated at various temperatures and 1.2 m/s fluid velocity. The results revealed that the efficiency of NPK inhibitors relies on the temperature and the concentration. The coverage ratio and efficiency increase due to the formation inhibitor's layer on the metals' surface; therefore, this stops the reaction of corrosion. The inhibitor's efficiency decreases for NPK concentration above 75 ppm once the temperature increased above 35 ℃. The type of adsorption is followed the Frumkin model. The increase inactivate energy (Ea) at a low concentration of inhibitor maybe understand as the physical adsorption. The negative value of the change in enthalpy reveals the exo-thermic nature of the dissolution of mild steels. Furthermore, the negative value of ($\Delta S°$) means increasing in disordering.

1. Introduction

Generally, a corrosion process assisted by mass transfer and chemical dissolution is called a flow accelerated corrosion (FAC) and it is different from the erosion-corrosion process. From the practical way, it assumed that there is some influence from the mechanical parameter leading to the collapse of the scale on the surface of the corroded material to become unfastened and flood out with the high speed of the fluid. Such a parameter could be auxiliary increased the overall flow accelerated corrosion; however, it is not considered as a parameter for thinning by itself. The initiation of the dissolution of the electrochemical process primarily leads to FAC and the establishment of a loosely held scale [1-4].

Corrosion Inhibitors are chemicals acting to mitigate or decrease the rate of corrosion of the surfaces of mild steels. Corrosion considers as an electro-chemical process happening because of anodic reactions and/or cathodic reactions. Mostly, oxidation of the metal ions is called the anodic

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reaction, and reduction of the hydrogen ions is called the cathodic reaction. Thus, the inhibitions of the anodic site are the inhibitors utilized to mitigate the anodic reactions. Also, the inhibition of the cathodic site used to prevent the cathodic reactions are known as the cathodic inhibitors. Anodic Inhibitions shape a protecting layer covering on anodic site of the metals where the surface of metals is vanished and therefore straightforwardly governor the corrosion rate by inhibiting the reaction that consequences in the corrosion process. The corrosion rate of any uncovered sites on the surface of the metal will be increased as much as compared to the covered areas. Thus, such a factor might result in a localized or pitting attack of the uncovered sites on the surface of the mild steel [5].

Cathodic Inhibitors develop a protecting film covering on the cathodic metal areas of the metal where the metal's surface does not vanish. Therefore, they are indirectly mitigated the corrosion rate interfering with the flow of current needed for electrochemical reaction to progress between the anodic and cathodic metal [6].

NPK (nitrogen (10)-phosphorous (52)-potassium (10)) fertilizer is mostly comprised of three core components which are 1- Nitrogen (N), 2- Phosphorus (P), and 3- Potassium (K). Indeed, they are necessary for the nutrition of plants.

A necessary environmental parameter affecting the performance of the inhibitor via assisting the process of molecular from the bulk to the surface. Despite many researchers have conducted studies regarding the organic compounds' behavior in case of hydrodynamic and static flow, the conditions of hydrodynamic flow can influence the inhibition process such as 1- presence more inhibitor on the surface of metals due to increasing the transfer of mass of inhibitor molecules [7-21], 2- increase the transfer of mass for metal ions, which are produced by dissolution of metals, from the surface of the electrode to the bulk solution and resulting in lower $[Fe-Inh]^{+2}$ complex existing on the electrode. Therefore, the performance of inhibitor is harmfully affected by such transfer of metal ions, and 3- increase shear stress can separate adsorbed complex of $[Fe-Inh]^{+2}$ and layer of inhibitor and leads to extra desorption from the surface of the metals acting as a harmful parameter on the efficiency of the inhibitor [7-13,20-21].

In the present work, the effect of NPK as an inhibitor for carbon steel is discussed employing the method of weight loss. Adsorption entropy and adsorption enthalpy which is thermodynamic parameters were estimated from an empirical data of the process of inhibition at various temperatures and deferent concentration of the inhibitor at 1.2 m/s velocity of the fluid. It is also determined the pre-exponential factor and the apparent activation energy in the presence of various inhibitor concentrations. Also, their influences on the rate of corrosion of carbon steel were deliberated.

2. Experimental Setup

To examine the influence of velocity on the corrosion rate of mild steel, the experimental setup is designed at atmospheric pressure. The experiments can perform at various temperatures (30- 45 °C), 1.2 m/s water velocity, and at running time 3 hours. The layout of the experimental setup is shown in Figure 1. Two coupons (1.4 cm diameter) were placed in the holder of the specimen for the analysis.

2.1 Experimental Method

The method adopted as follows
I.   Three degrees of sandpaper (100, 220, and 400) is used to polish the samples.
II.   Put both samples in Alcohol to remove impurities substance from the samples,

III. Then dry and weight them.
IV. Put the samples in the holder.
V. Add 50 ppm of NPK inhibitor to the water in the tank of the device then heat the water until it reaches 30°C for three hours then record the reading result.
VI. Repeat the same steps using different concentrations (75, 100, and 150 ppm) with various water temperatures of 35, 40 and 45°C.
VII. At the end of each experiment, remove the sample from the holder, dry it, and clean it with rubber.
VIII. Use the Clark solution to remove the corrosion products prepared according to ASTM-G 1-03 guidelines [22].
IX. Record the new weight of the samples.
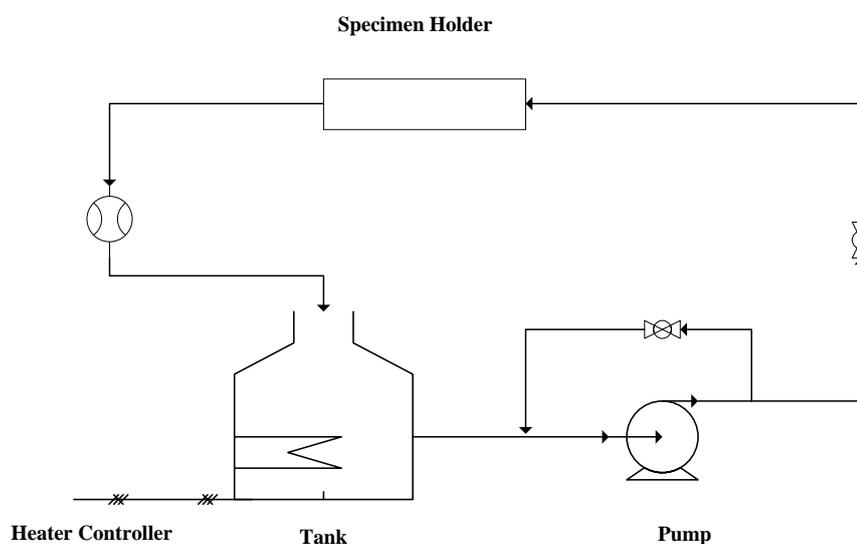
Fig. 1. Flow chart of the experimental setup

3. Results and Discussion

3.1 Effect of Concentration

The following Eq. (1)-(3) are used to calculate the rate of corrosion CR (mpy), an efficiency of inhibitor (%IE), and surface coverage (Ө) by using weight loss method:

$$CR = \frac{87.6 * \Delta W}{7.85 * T \times A} \tag{1}$$

$$\% IE = \frac{CR_o - CR_i}{CR_o} \times 100\% \tag{2}$$

$$\theta = \frac{CR_o - CR_i}{CR_o} \tag{3}$$

where ΔW is the weight loss (g), A is the surface exposed area of the sample (cm^2), T is the time of immersion (hr), CR_o and CR_i are the corrosion rate with and without inhibitor, respectively.

The experimental result showed that the efficiency NPK inhibitors depend on the temperature and the concentration. Besides, when increasing the concentration of inhibitor, the corrosion rate decreases, as shown in Figure 2. The efficiency and coverage ratio increase because of the formation

layer of the inhibitor on the surface of metals; hence, this prevents the reaction of corrosion, as shown in Figure 3 and Figure 4.

For 30 and 35°C temperature, the corrosion rate decreases as increasing the concentration of inhibitor and lead to block the active sites on the metal's surface. In contrast, the corrosion rate decreases at 75 ppm for 40 and 45°C and starts to slightly increase above that concentration. In the case of increasing concentration, this may attribute to exceed critical micelles concentration of the inhibitor and collapse of the corrosion inhibitor's layer in which the inhibition will not exist, and the corrosion is uncontrollable.

In the case of increasing temperature, decreasing the rate of corrosion in each NPK's concentration excluding 75 ppm due to escaping the oxygen from the solution (open system) resulting to decrease the diffusion process, as shown in Figure 2 [2,5,7].

The efficiency and coverage ratio of inhibitor increases with increasing temperature in each concentration from 30 and 35 °C and just below the concentration of 75 ppm for 40 and 45 °C. However, the highest and optimum efficiency is observed at 45°C with a concentration of 75 ppm. When the NPK's concentration is above 75ppm, the efficiency reduces with increasing temperature. This indicates that steel's dissolution dominates adsorption of inhibitor at higher temperatures, as shown in Figure 3 and Figure 4 [15].
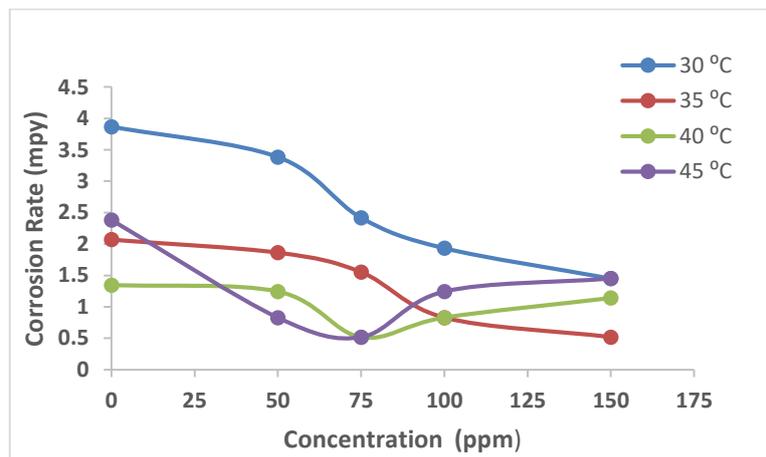
Fig. 2. The Corrosion rate at different concentrations of NPK inhibitor, temperatures at 1.2 m/s
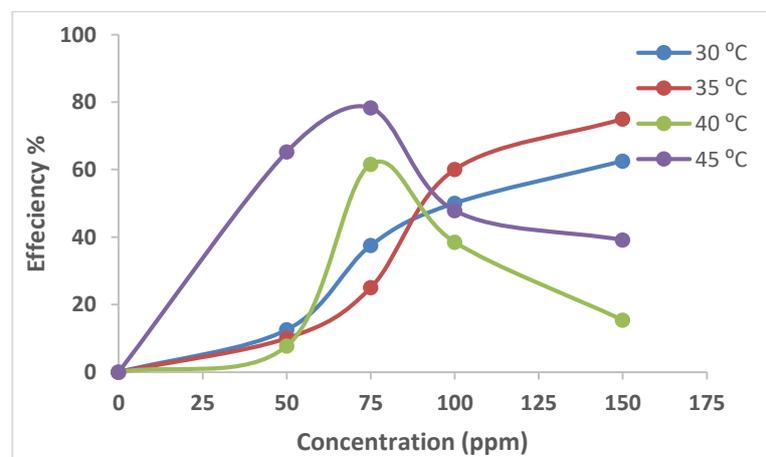
Fig. 3. The efficiency of NPK inhibitors at altered temperatures, concentrations, and at 1.2 m/s
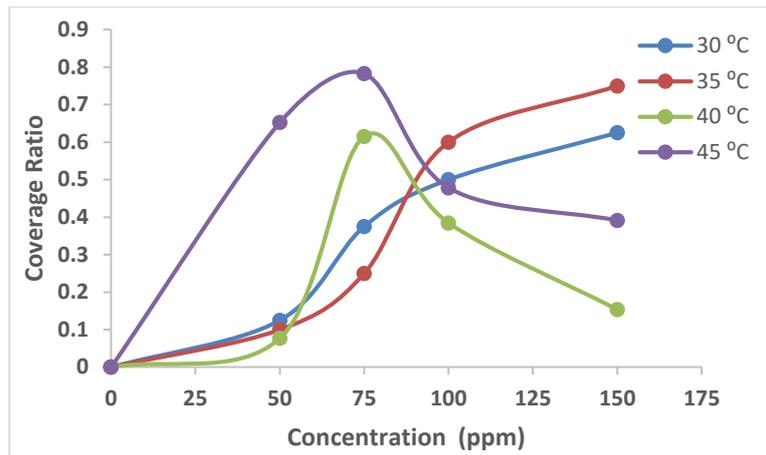
Fig. 4. The Coverage of carbon steel at different concentrations
of NPK, temperatures at 1.2 m/s

3.2 Thermodynamics Parameters

The transition state Eq. (4) and Arrhenius Eq. (5), utilized to evaluate the thermodynamic functions of the disbanding of mild steels without and with of NPK inhibitors. The results are given in Table 1.

$$W = A \exp\left(-\frac{E_a}{RT}\right) \tag{4}$$

$$W = \left(\frac{RT}{Nh}\right) \exp\left(\frac{\Delta S^\circ}{R}\right) \exp\left(\frac{-\Delta H^\circ}{RT}\right) \tag{5}$$

where R denotes to the gas constant, E_a denotes to the appearance of the activation energy, A denotes a pre-exponential factor of the Arrhenius, h denotes constant of Planck, ΔS° denotes the change in entropy of activation, ΔH° denotes the change in enthalpy of activation, and N denotes the number of Avogadro's [23-24].

Table 1
The activation energies of the corrosion of mild steel

Slop (-m)	Ea (kJ/mol)
-0.0682	-0.56606
0.1377	1.14291
0.2856	2.37048
0.0412	0.34196
-0.0503	-0.41749

The activation energy is achieved from plotting LnW versus 1/T for Eq. (4), and the ΔS°, and, ΔH° is got from plotting LnW/T versus 1/T for Eq. (5). At low concentrations of inhibitor, the increase inactivate energy E_a can be understood as physical adsorption. The negative values of ΔH° reveal the exothermic nature of mild steel in the process of disbanding. The negative values ΔS° reveal an increase in disordering. The results are shown in Table 2.

Table 2
Thermodynamic parameters of mild steals at different concentrations of NPK inhibitor

C (ppm)	ΔHº (kJ/mole)	ΔSº (kJ/mole)
0	-33.3724	-84.87
50	-76.7798	-227.621
75	-94.3639	-288.314
100	-3.45031	7.382174
150	15.92131	68.39031

3.3 Adsorption Isotherm
3.3.1 Langmuir isotherm

The model of Langmuir isotherm is effective for adsorption of the monolayer on a covering of surfaces at a limited identical place. This standard simulates unchanging energies of adsorption on the surface and there is no traveling of adsorbate in the surface's plane. Depended on the above facts, such model denoted by Eq. (6).

$$\frac{\theta}{1-\theta} = KC \qquad (6)$$

where θ denotes the coverage's surface, C denotes the concentration of inhibitors, K denotes the equilibrium constant of adsorption-desorption. The Langmuir model represents in Figure 5.
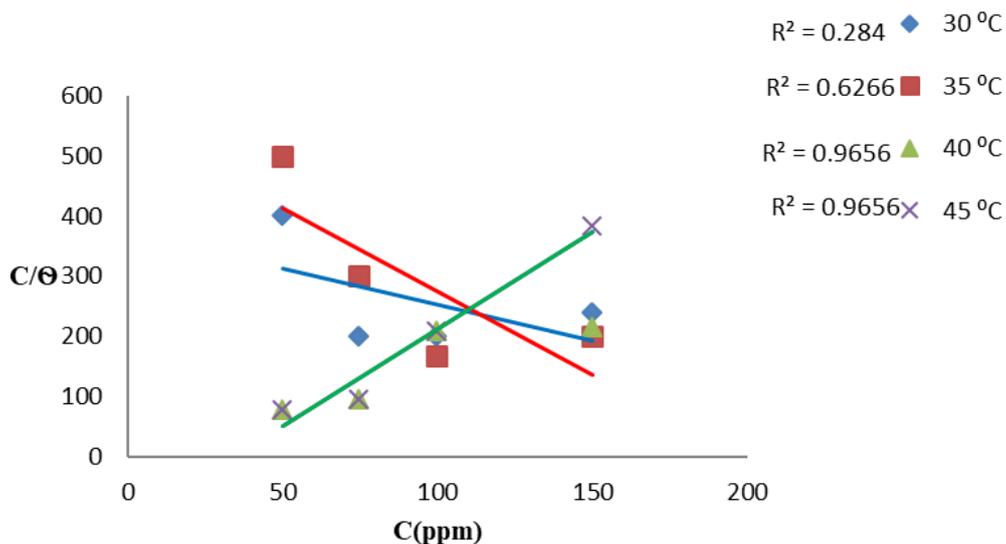
Fig. 5. Langmuir adsorption isotherm for NPK inhibitor

3.3.2 Model of Temkin isotherm

The model of isotherm includes parameters that taking obviously in the account of the interaction of the adsorbate-adsorbent. Disregarding a great and very low value of concentration, Temkin Isotherm supposed that the heat of adsorption (known as an occupation of temperature) of every part of molecules in the scale would reduce linearly instead of logarithmic with the coverage. It denoted by Eq. (7).

$$\log\left(\frac{\theta}{C}\right) = \log K - g\theta \qquad (7)$$

where θ denotes the coverage's surface, C denotes the concentration of inhibitors, K the denotes constant of equilibrium of desorption- adsorption, and g denotes parameter of the interaction of adsorbate. Temkin model represents in Figure 6.
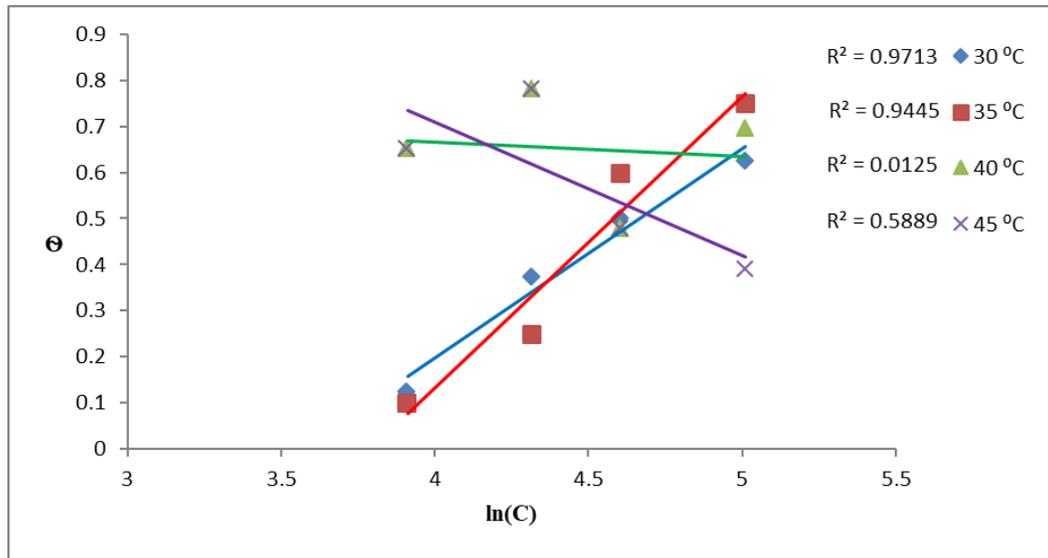
Fig. 6. Timkin adsorption isotherm for NPK inhibitor

3.3.3 Model of Frumkin isotherm

Such a model is generally utilized to define the features of adsorptions for the nonhomogeneous surface. It denoted in Eq. (8).

$$\log\left(\frac{\theta}{(1-\theta)C}\right) = \log K + g\theta \qquad (8)$$

where θ denotes the coverage's surface, C denotes the concentration of inhibitors, K denotes the constant of equilibrium of desorption-adsorption, and g denotes the parameter of interactions of the adsorbate. The Frumkin isotherm model represents in Figure 7. The Frumkin isotherm model is considered as the best to fit the experimental data as compared with other models.
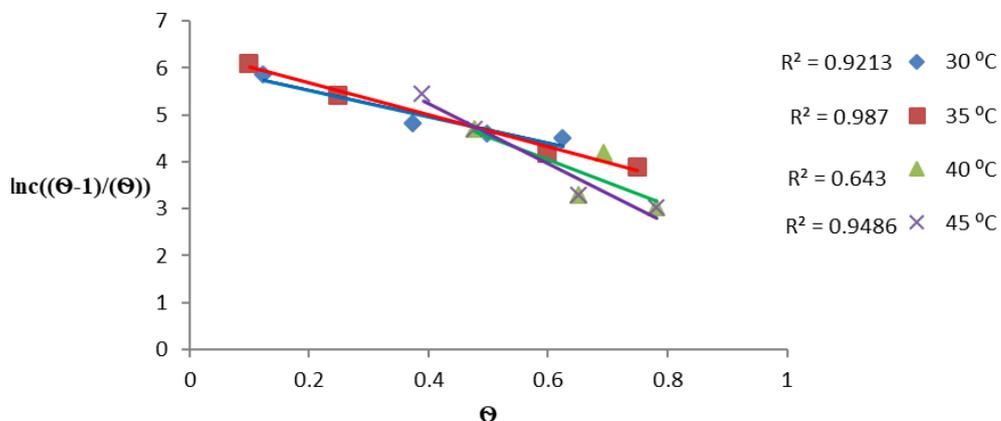
Fig. 7. Frumkin adsorption isotherm for NPK inhibitor

3.3.4 Model of Freundlich isotherm

The model of Frendlich isotherm is considered as nonlinear and can be described by Eq. (9).

$$\log(\theta) = \log K + n \log C \tag{9}$$

This model is presented the data of concentration and adsorption by plotting log C vs log θ, as shown in Figure 8. This plot will lead to a straight line with an intercept of log K and slop of n. It cannot reach maximum adsorption as the linear adsorption isotherm [25].
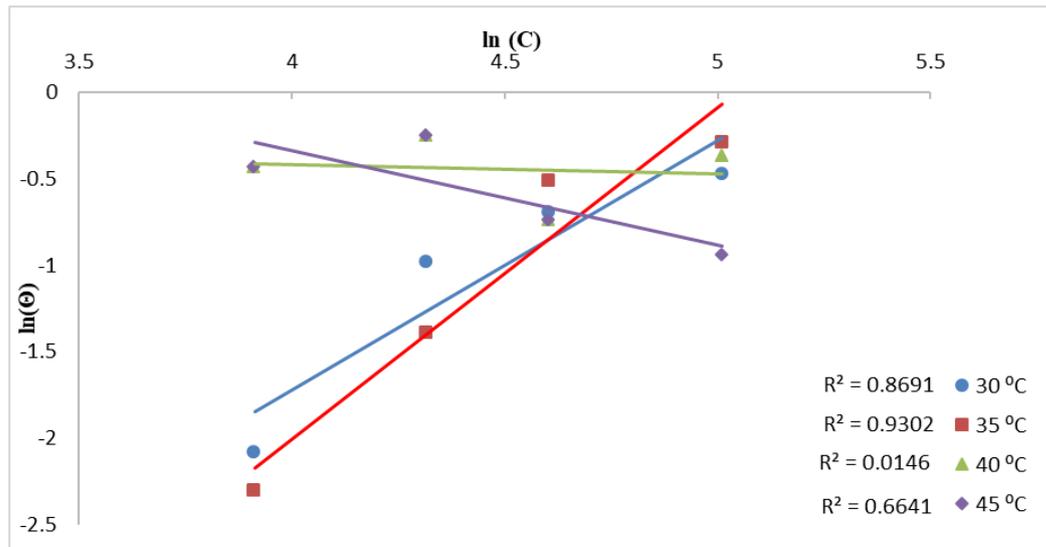
Fig. 8. Freundlich adsorption isotherm for NPK inhibitor

4. Conclusion

NPK performances as an efficient inhibition for the carbon steel at all examined concentrations which is below 75 ppm and its inhibition efficiency exceeds 78% at 45℃ and 75 ppm. The reduction in corrosion rate is observed with increasing temperature excluding above 75 ppm. The efficiency reduces along with increasing temperature above 75ppm. The thermodynamic parameters indicated that NPK inhibitor is caused a physical adsorption and its adsorption obeys to the Frumkin's adsorption isotherm. The negative value of (ΔH°) imitates the exothermic nature of the dissolution of mild steels. Besides, the negative value of (ΔS°) means increasing in disordering.

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