Electrochemical Investigation of Tetrazolium Violet as a Novel Copper Corrosion Inhibitor in an Acid Environment

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ABSTRACT: Tetrazolium violet (TZV) is an important pharmaceutical intermediate for the preparation of various medicines, taking into account microbiological studies and TZV as a new inhibitor of heterocyclic compound. The corrosion inhibiting action of TZV for copper in 0.5 M H₂SO₄ solutions was assessed by potentiodynamic polarization and electrochemical impedance spectroscopy. The corroded copper surfaces were evaluated by scanning electron microscopy. Thereafter, the thermodynamics of TZV adsorption onto copper was computed and evaluated. As a result, the target TZV compound shows great corrosion inhibition performance to protect copper in sulfuric acid. Thermodynamic test results reveal that the Langmuir, Dhar–Flory–Huggins, and Bockris–Swinkels isotherm models provide a better description for the adsorption process of TZV on the metal surface. The calculated values of \( \Delta G_{\text{ads}} \) indicate a spontaneous adsorption process of TZV on the copper surface accompanied by two kinds of interactions, physical adsorption and chemisorption.

1. INTRODUCTION

Copper has excellent mechanical applications and is widely used in a series of industrial processes such as acid washing and industrial purification and helps to interconnect the micropores of 3D packaging.¹⁻¹¹ For electrodeposition, the Cu surfaces must be clean and free from oil, grease, and heavy oxides, and it should be pointed out that copper is susceptible to a more rapid attack in acidic solution.¹²⁻¹⁴ However, the addition of corrosion inhibitors (some organic compounds) can substantially reduce the metal losses during pickling.¹⁵⁻¹⁸ Unfortunately, the majority of the current-inhibiting components were applied to preserve copper from acid solution, which improves the quality of pickling in the industry,¹⁹⁻²² and the disadvantages of BTA and its derivatives are its toxicity and bad water solubility.²³ Therefore, exploiting the high-efficiency and nontoxic inhibitors for copper corrosion in acid solutions is of great importance. Tetrazolium violet (TZV) having an electron-withdrawing chemical group, such as nitroblue tetrazolium, has been shown to bind its electrons using its positive tetrazole ring.²⁴ TZV is an important pharmaceutical intermediate for the preparation of various medicines. High concentrations of TZV can conduce to total inhibition of bacterial growth and TZV have been widely used for microbiological studies.²⁵ The structure of the TZV molecule is shown in Figure 1. No reports have been found about TZV act as an inhibitor for metal in acidic solutions. Therefore, this article is to study the action of the TZV inhibitors to delay the corrosion of copper in acidic solutions. The inhibitory effect of TZV was observed by electrochemical impedance spectroscopy (EIS), scanning electron microscopy (SEM), and potentiodynamic polarization.

2. RESULTS AND DISCUSSION

2.1. Polarization Curves. To reveal the effects of inhibitor concentration and corrosion mechanism, Figure 2 demonstrates the polarization curves of copper in sulfuric acid solution for different TZV concentrations and test temperatures. The anode and cathode current–potential curves are extrapolated and intersected based on the corrosion data of current density \( I_{\text{corr}} \) and potential \( E_{\text{corr}} \). The corrosion parameter of Tafel was observed and calculated from the software of CHI760E, in the study temperature range of some corrosion data such as \( E_{\text{corr}} \), \( I_{\text{corr}} \), cathode, and anode Tafel slopes \( \beta_c, \beta_a \) at different testing temperatures (288–318 K),

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which are listed in Table 1. The efficiency of the inhibitor was obtained by eq 1.

$$I_{\text{eq}} \% = \frac{I_{\text{corr}} - I_{\text{corr(inh)}}}{I_{\text{corr}}} \times 100$$

where $I_{\text{corr}}$ and $I_{\text{corr(inh)}}$ represent the corrosion current density in the absence and presence of various concentrations of TZV in 0.5 M H$_2$SO$_4$ solution, respectively.

According to Figure 2 and Table 1, when the TZV inhibitor was added to the solution, the cathode and anode reactions of the copper corrosion were deferred, and the inhibitor efficiency was increased to a maximum of 95.1% at $3.2 \times 10^{-4}$ M and 298 K, and the inhibition efficiency reveals that the high concentration of TZV had a good inhibitory effect. The slopes of the cathode Tafel line and the anode Tafel line ($\beta_c$ and $\beta_a$) were recognized to shift after adding inhibitors into the solution, indicating the effect of TZV on the cathode and anode reactions, but the anode reaction is more sensitive to TZV. As shown in Figure 2, the cathodic current density decreases after adding TZV into solution, and in anodic domain, the curves drift apparently toward the direction of the current density decreases with the addition of TZV. The results of experiments show that increasing the concentration of the inhibitor can decrease the current density correspondingly because of the adsorption of the inhibitor on the copper surface.

In addition, a major factor that affects the corrosive performance of components in solutions is temperature. In this experiment, the polarization parameters of copper corrosion obtained from polarization curves at different temperatures (288–318 K) are shown in Table 1, and the value of $I_{\text{corr}}$ increases as the temperature of the corrosive medium increases within the temperature range of 288–318 K. However, $I_{\text{corr}}$ has almost no change in the relatively high concentration of TZV within the studied temperature scope (288–318 K). It can also be noticed that the corrosion potential transitions to a further negative value in the presence of TZV confirmed that the oxygen cathode reduction reaction is more sensitive to the presence of inhibitors.

According to Riggs’s theory and others, an anode- or cathode-type inhibitor can be defined as a potential sharp fluctuation exceeding 85 mV between acid solutions containing inhibitor and blank solution. Figure 3 demonstrates the OCP curves of copper metal in 0.5 M sulfuric acid for different TZV concentrations and temperatures. As can be seen from Figure 3, compared with the pure acidic solutions, the displacement of the open-circuit potential of the solution containing TZV is less than 60 mV. Therefore, the TZV compound was demonstrated to be a mixed-type inhibitor.

**2.2. Electrochemical Impedance Spectroscopy.** The EIS spectra of copper in acidic solutions with different concentrations of TZV at a distinct temperature range from 288 to 318 K are shown in Figure 4. The addition of TZV leads to a change in the impedance map of shape and size. It can be seen from the Figure 4 that a single semicircular capacitor ring in the higher-frequency range constitutes some impedance spectrum, and then a Warburg impedance occurs at a low-frequency range as the temperature of the corrosive medium increases within the temperature range of 298–318 K. In general, a high-frequency capacitor loop is similar to a Faraday process, which includes a double-layer capacitive component and a charge-transfer resistor in parallel.
recognized that the hydrogen discharge current density is much lower than the copper reduction current density at the cathode region.33 The existence of Warburg impedance due to corrosive ion motion at the metal/liquid interface and diffusion of oxygen through the sulfuric acid adhere to the copper surface.34,35 In other words, the Warburg impedance appeared in the impedance spectra demonstrates that the corrosive mechanism of copper in sulfuric acid is dominated by both charge-transfer process and diffusion process. It is believed that the concentration polarization does not participate in the anodic dissolution of copper in H2SO4 solution.36 As can be seen from Figure 4, the diameter of capacitive curves increased because the corrosive ion exercises more and more quickly with increases in the temperature of the solution.37,38 Figure 4 shows several raised arcs and each radius of curvature of the capacitor ring decreased with increases in the temperature of the corrosive medium. This indicates a certain decrease in the impedance value and a certain degree of accelerated corrosion because the corrosive ion exercises more and more and quickly on the copper surface.41,42

The EIS diagrams were interpreted by using the equivalent circuits [(R(QR)), Figure 5a; R(Q(RQ(RW))))], Figure 5b] with ZSimpWin software and are given in Table 2. The impedance spectra without Warburg impedance were analyzed using the standard Randles’ circuit model. As can be seen from Figure 5, the impedance spectrum shows the concave semicircle of the capacitor ring, and the experimental arc center can be found beneath the horizontal coordinates. However, other Nyquist diagram shows a depressed capacitor loop in the high frequency, and the Warburg impedance in the low frequency was fitted by the circuit shown in Figure 5b. Taking Figure 6 as an example, the fitting and initial parameter values for copper in 0.5 M H2SO4 solution of 0, 1.0 × 10⁻³, 3.2 × 10⁻³, 1.0 × 10⁻⁴, and 3.2 × 10⁻⁵ M TZV were analyzed. As can be seen from Figure 6a,b, a series of data counted by simulation and experiments can be found a good fit. Based on the above-mentioned equivalent circuit model, the measured charge-transfer resistance Rct, the solution resistances Rs and Rf stand for the resistance of the inhibitor layer on copper metal surface, and Q1 and Q2 ascribe to the constant phase elements (CPE). The CPE and Warburg impedance were recorded in Table 2. The χ² values represented that the equivalent analog circuit (R(Q(R(Q(RW))))) was reasonable. The relationship between inhibition efficiency and charge-transfer resistance was constructed by the following formula44

$$I_{\text{EZ}} \% = \frac{R_\text{ct} - R_\text{ct}^0}{R_\text{ct}} \times 100$$

(2)

where $R_\text{ct}^0$ is the charge-transfer resistance in 0.5 M sulfuric acid and $R_\text{ct}$ is the charge-transfer resistance in 0.5 M sulfuric acid with TZV of different concentrations, respectively.

Analyses of the impedance function of CPE are commonly employed to measure the nonideal capacitive behavior and its frequency dependence. It is usually calculated using the following formula

$$Z_{\text{CPE}} = Y^{-1}(\omega)^{i\pi}$$

(3)

where Y is the CPE amplitude, ω represents the angular frequency (2πf), and deviation exponent n reflects the microscopic fluctuation of the surface, which is a valuable standard for the surface properties of the metal.45 Consider a circuit with CPE in which the double-layer capacitance value (Cdl) can be mathematically expressed as

$$C_{\text{dl}} = \frac{Y \omega^{n-1}}{\sin(n\pi/2)}$$

(4)

Table 1. Corrosion Parameters of Copper in 0.5 M H2SO4 Solution with Different Concentrations of TZV Determined by Tafel Extrapolation Method

| Temperature (K) | Concentration (M) | $E_{corr}$ (mV vs SSE) | $\beta_2$ (mV dec⁻¹) | $\beta_1$ (mV dec⁻¹) | $I_{corr}$ (µA cm⁻²) | $I_{\text{EZ}}$ % |
|----------------|------------------|------------------------|-----------------------|-----------------------|----------------------|------------------|
| 288 blank      | −527             | 193.5                  | 166.6                 | 9.09                  |                      |                  |
| 288 1.0 × 10⁻⁵ | −514             | 221.5                  | 77.5                  | 5.94                  | 34.7                 |                  |
| 288 3.2 × 10⁻⁵ | −550             | 156.3                  | 60.7                  | 2.04                  | 77.6                 |                  |
| 288 1.0 × 10⁻⁴ | −558             | 135.4                  | 130.7                 | 1.91                  | 80.0                 |                  |
| 288 3.2 × 10⁻⁴ | −541             | 139.2                  | 108.7                 | 1.10                  | 87.9                 |                  |
| 298 blank      | −468             | 73.2                   | 48.7                  | 17.23                 |                      |                  |
| 298 1.0 × 10⁻⁵ | −522             | 230.3                  | 124.0                 | 14.19                 | 17.6                 |                  |
| 298 3.2 × 10⁻⁵ | −544             | 165.7                  | 335.0                 | 10.12                 | 41.3                 |                  |
| 298 1.0 × 10⁻⁴ | −545             | 140.2                  | 107.7                 | 2.52                  | 85.4                 |                  |
| 298 3.2 × 10⁻⁴ | −531             | 104.2                  | 76.6                  | 0.84                  | 95.1                 |                  |
| 308 blank      | −463             | 458.5                  | 41.9                  | 29.74                 |                      |                  |
| 308 1.0 × 10⁻⁵ | −509             | 270.2                  | 94.2                  | 22.31                 | 25.0                 |                  |
| 308 3.2 × 10⁻⁵ | −537             | 179.0                  | 290.6                 | 17.72                 | 40.4                 |                  |
| 308 1.0 × 10⁻⁴ | −549             | 124.7                  | 158.4                 | 5.61                  | 81.1                 |                  |
| 308 3.2 × 10⁻⁴ | −543             | 100.2                  | 86.9                  | 1.60                  | 94.6                 |                  |
| 318 blank      | −452             | 319.9                  | 47.6                  | 64.10                 |                      |                  |
| 318 1.0 × 10⁻⁵ | −523             | 256.3                  | 122.0                 | 30.62                 | 52.2                 |                  |
| 318 3.2 × 10⁻⁵ | −483             | 254.9                  | 52.5                  | 18.73                 | 70.8                 |                  |
| 318 1.0 × 10⁻⁴ | −551             | 147.8                  | 228.2                 | 16.32                 | 74.5                 |                  |
| 318 3.2 × 10⁻⁴ | −548             | 108.3                  | 106.8                 | 3.74                  | 94.2                 |                  |
After the addition of organic molecules of TZV, the value of $C_{dl}$ is always reduced, possibly that the water molecules adsorbed at the copper/solution interface were partially replaced by the inhibitor. It can be seen that the deviation parameter $n$ decreases marginally with the increase of the inhibitor concentration. The change in surface roughness caused by the increase of the concentration of the inhibitor caused a change in the value of $n$.46

Figure 3. Open-circuit steady-state potential—time curve for copper in 0.5 M H$_2$SO$_4$ solution with different TZV concentrations at different temperatures: (a) 288, (b) 298, (c) 308, and (d) 318 K.

Figure 4. Nyquist plots for copper in 0.5 M H$_2$SO$_4$ with various concentrations of TZV: (a) 288, (b) 298, (c) 308, and (d) 318 K.
The diffused resistances were determined by the Warburg impedance and expressed as

\[ Z_w = \frac{1}{Y_w^0 \sqrt{j\omega}} \]  

(5)

In general, \( Y_w^0 \) represents a number of \( \Omega \) cm\(^2\) to the electrical admittance. Through analyses and comparisons of different equivalent circuit and fitting impedance curves, parameters which may represent the behaviors of corrosion inhibition were obtained, as shown in Table 2. The test data for \( R_{ct} \gg W \) indicated that the electron-transfer activity of the copper electrode is higher than that of an oxygen diffusion transfer process in acid electrolysis. As shown in Figure 4 and Table 2 that at the same temperature, as the inhibitor concentration increases, the value \( R_{ct} \) increases and the value \( C_{dl} \) decreases. This phenomenon results from the protective films in the metal surface that prevented corrosive medium from attacking the copper surfaces, resulting in an increase in the \( R_{ct} \) value.\(^{47}\)

The related electrochemical equivalent circuit technique was used to determine the 0.5 M H\(_2\)SO\(_4\) solution with various concentrations of TZV: (a) equivalent circuits of \((R(QR))\) and (b) equivalent circuits of \(R(Q(RQW)))\).

![Figure 5. Equivalent circuit model used to fit the EIS experiment data for copper in 0.5 M H\(_2\)SO\(_4\) with various concentrations of TZV: (a) equivalent circuits of \((R(QR))\) and (b) equivalent circuits of \(R(Q(RQW)))\).](image)

![Figure 6. EIS experimental data and fitting results of copper in 0.5 M H\(_2\)SO\(_4\) solution with various concentrations of TZV at 318 K: (a) Nyquist plots and (b) Bode plots.](image)

Table 2. Impedance Parameters and Inhibition Efficiency for the Corrosion of Copper in 0.5 M H\(_2\)SO\(_4\) Solution with Different Concentrations of TZV

| temperature K | concentration (M) | \( R_s \) (\( \Omega \) cm\(^2\)) | \( R_i \) (\( \Omega \) cm\(^2\)) | \( R_d \) (\( \Omega \) cm\(^2\)) | \( Q_1 \) (\( \mu F/cm\)) | \( n_1 \) | \( Q_2 \) (\( \mu F/cm\)) | \( n_2 \) | \( W \) (\( \mu \Omega \) cm\(^2\)) | \( I_{ZE} \% \) | \( \chi^2 \) (\( \times 10^9 \)) |
|---------------|------------------|-----------------|-----------------|-----------------|-----------------|-----------|-----------------|-----------|-----------------|-----------|-----------------|
| 288           | blank            | 1.5             | 2693            | 33.3            | 0.9             | 2.6       |                 |           |                 |           |                 |
|               | 1.0 \( \times 10^{-5} \) | 1.7             | 5391            | 39.6            | 0.8             | 50.0      | 1.9             |           |                 |           |                 |
|               | 3.2 \( \times 10^{-5} \) | 1.5             | 8522            | 18.9            | 0.9             | 68.4      | 3.1             |           |                 |           |                 |
|               | 1.0 \( \times 10^{-4} \) | 2.0             | 12280           | 16.5            | 0.9             | 78.1      | 1.6             |           |                 |           |                 |
|               | 3.2 \( \times 10^{-4} \) | 1.9             | 23610           | 12.5            | 0.9             | 88.6      | 1.8             |           |                 |           |                 |
| 298           | blank            | 1.7             | 333.2           | 121.6           | 0.8             | 306.3     | 0.8             | 261.6     | 0.7             |           |                 |
|               | 1.0 \( \times 10^{-5} \) | 1.7             | 317.4           | 33.6            | 0.9             | 384.3     | 0.8             | 23.2      | 87.8            | 0.9       |                 |
|               | 3.2 \( \times 10^{-5} \) | 1.8             | 5579            | 6.8             | 1.0             | 22.6      | 0.7             | 305.3     | 94.0            | 0.4       |                 |
|               | 1.0 \( \times 10^{-4} \) | 1.8             | 419.1           | 14.7            | 0.9             | 76.8      | 0.8             | 6.5       | 96.6            | 0.8       |                 |
|               | 3.2 \( \times 10^{-4} \) | 1.9             | 72.9            | 4.9             | 1.0             | 13.1      | 0.7             | 261.6     | 98.3            | 0.4       |                 |
| 308           | blank            | 1.9             | 337.8           | 53.3            | 0.9             | 611.0     | 0.4             | 202.7     | 0.4             |           |                 |
|               | 1.0 \( \times 10^{-5} \) | 1.7             | 23.1            | 6.8             | 1.0             | 42.4      | 0.7             | 390.6     | 72.1            | 1.0       |                 |
|               | 3.2 \( \times 10^{-5} \) | 1.9             | 57.3            | 9.0             | 1.0             | 29.5      | 0.7             | 580.8     | 87.9            | 0.3       |                 |
|               | 1.0 \( \times 10^{-4} \) | 1.9             | 65.6            | 4.8             | 1.0             | 16.8      | 0.7             | 2687      | 94.9            | 0.3       |                 |
|               | 3.2 \( \times 10^{-4} \) | 1.9             | 48.9            | 4.0             | 1.0             | 16.3      | 0.7             | 1653      | 97.3            | 0.5       |                 |
| 318           | blank            | 1.6             | 84.7            | 2.7             | 0.8             | 314.0     | 0.7             | 1676      | 4.4             |           |                 |
|               | 1.0 \( \times 10^{-5} \) | 1.2             | 15.8            | 9.0             | 1.0             | 102.8     | 0.6             | 4134      | 84.8            | 0.5       |                 |
|               | 3.2 \( \times 10^{-5} \) | 1.9             | 15.9            | 6.1             | 1.0             | 39.7      | 0.6             | 5289      | 92.7            | 0.6       |                 |
|               | 1.0 \( \times 10^{-4} \) | 1.8             | 38.0            | 5.0             | 1.0             | 20.5      | 0.7             | 9590      | 97.0            | 0.5       |                 |
|               | 3.2 \( \times 10^{-4} \) | 1.6             | 90.7            | 3.8             | 1.0             | 14.0      | 0.7             | 9480      | 98.7            | 0.8       |                 |

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M TZV at 288, 298, 308, and 318 K calculated as 23 610, 19 560, 12 420, and 6657 Ω cm². The test data of ƞEZ % through eq 2 can reach 88.6, 98.3, 97.3, and 98.7 in the different temperatures, respectively. In fact, the inhibition efficiency data were obtained with EIS test and Tafel polarization of experiment, whose trend is very similar, but the corresponding values are quite different.

2.3. Adsorption Isotherms. The inhibition and adsorption mechanism of the TZV inhibitors in metal surfaces could be specified by the adsorption model, and the adsorption and thermodynamics were analyzed by the Tafel and EIS experiment parameter; in other words, the surface coverage (θ) values have been evaluated from the inhibitive efficiency based on the average number of Tafel and EIS, and the different concentrations of TZV were measured using appropriate adsorption isotherms to explain the inhibition mechanism within the temperature range of 288–318 K. The adsorption of inhibitor molecules was replaced by water molecules at the copper/solution interface for substitution adsorption process. Refer to the following formula

\[ \text{Org}_{\text{sol}} + X\cdot\text{H}_2\text{O}_{\text{ads}} \leftrightarrow \text{Org}_{\text{ads}} + X\cdot\text{H}_2\text{O}_{\text{sol}} \]  

Org_{sol} symbol stands for the organic inhibitor molecules in the solution and Org_{ads} for adsorbed molecules on the copper surface. The symbol of X stands for that the numbers of water molecules are replaced by an organic inhibitor molecule. To get the most fitting isotherms for θ, the following formula is usually used.

The adsorption isotherm equations of Langmuir

\[ K_{\text{ads}} C = \frac{\theta}{1 - \theta} \]  

(7)

The equation of Flory–Huggins

\[ K C = \frac{\theta}{X(1 - \theta)^X} \]  

(8)

The equation of Dhar–Flory–Huggins

\[ K C = \frac{\theta}{\exp(X - 1)(1 - \theta)^X} \]  

(9)

The equation of Frumkin isotherm

\[ K C = \frac{\theta}{X(1 - \theta)^X \exp(-2a\theta)} \]  

(10)

The equation of Bockris–Swinkels

\[ K C = \frac{\theta \left[\theta + X(1 - \theta)\right]^{X-1}}{X^X} \]  

(11)

The equation of Temkin isotherm

\[ K C = \exp(-2a\theta) \]  

(12)

In the above equation, C represents the concentration of inhibitor, \( \alpha \) represents the parameter of the molecular interaction adsorbed on the copper surface, and \( K \) represents the inhibitor adsorption equilibrium constant. According to the correlation coefficient (R²), the most suitable fitting isotherm equation was determined within the studied temperature range. According to the correlation coefficient (R²), the most suitable fitting isotherm equation is determined. From 288 to 318 K, Dhar–Flory–Huggins (eq 9) and Bockris–Swinkels model isotherms (eq 11) supply a more intuitive overview of the adsorption of TZV on the copper surfaces. We fitted the adsorption curve of TZV on the metal surface in H₂SO₄ solutions, as shown in Figure 7, which represents the relationship between concentration solution and surface coverage. The fitting parameters of \( R^2 \), K, X, and so forth are

![Figure 7. Adsorption isotherm for copper in 0.5 M H₂SO₄ solution containing various concentrations of TZV under the different temperatures: (a) Langmuir isotherm model, (b) Dhar–Flory–Huggins model, and (c) Bockris–Swinkels model.](https://dx.doi.org/10.1021/acsomega.9b03475)
listed in Figure 7. At the same temperature, the two isotherms of the Bockris–Swinkels and Dhar–Flory–Huggins models produce approximate results. The K values could be calculated from the relation among the concentration of inhibitor and the surface coverage using linear and nonlinear regression methods. The free energy of inhibitor adsorption of $\Delta G_{ads}$ can be obtained from the following formula:

$$K = \frac{1}{55.5} \exp(-\Delta G_{ads}/RT)$$

(13)

The number 55.5 represents the molal concentration of a water solute. The symbol $T$ stands for the test temperature and $R$ for the general gas constant. For the physical and chemistry combined action of adsorption, the $\Delta G_{ads}$ value is usually in the range of $-40$ to $-20$ kJ mol$^{-1}$. The $\Delta G_{ads}$ value less than $-40$ kJ mol$^{-1}$ may involve the process of chemisorption. $^{53,54}$

As can be seen from Figure 7, the $\Delta G_{ads}$ in this study ranged from $-36.2$ to $-41.6$ kJ mol$^{-1}$, indicating that the TZV adsorption on the surface of copper was processed spontaneously, and the adsorption of those adsorbents were the result of physical and chemical adsorption withing the temperature range studied (288–318 K). It can be seen from Figure 7 that the $\Delta G_{ads}$ will be more negative with the increase of temperature, which indicates that higher temperature is helpful for the absorption. $^{44}$ $X = 2.0$ for Dhar–Flory–Huggins isotherms model means that a TZV molecule can replace about two water molecules on the copper metal surface at 298 K. In accordance with Figure 7, the $X$ value decreases as the temperature of the corrosive solution increases. In theory, the physical adsorption of molecule is only stable at low temperatures owing to the low adsorption heat, while the chemical adsorption energy is relatively high and more stable at high temperatures. $^{35}$ This result may be due to small changes in the properties of the adsorption model: physical adsorption plays a leading role at the low-temperature range for the result of physical adsorption and chemical adsorption, as the temperature increases, the chemical adsorption gradually takes over the main position and coexisted with physical adsorption in the high-temperature experiment for TZV on the copper surface adsorptive behavior.

2.4. SEM Analyses. Figure 8 shows an SEM image of copper exposed to a 0.5 M H$_2$SO$_4$ solution after immersing with and without 3.2 × 10$^{-4}$ M TZV for 8 h at 308 K. The SEM morphology of copper before immersion in corrosive solution showed a freshly polished metal surface (Figure 8a). As shown in Figure 8b, the surface of copper without TZV was severely corroded and some corrosion pitting appears. The SEM images of copper specimens after immersing in acid with 3.2 × 10$^{-4}$ M TZV are shown in Figure 8c, the rate of corrosion was suppressed, and the corrosion pitting was significantly reduced. Despite these superficial resemblances for cracks and holes appears whether the freshly polished copper surface or the morphology of copper immersed in 0.5 M H$_2$SO$_4$ solution. Comparing the two illustrations in Figure 8b,c, it can be concluded that Figure 8c shows smoother surface with the TZV-inhibited Cu corrosion.

3. CONCLUSIONS

TZV has been proven as an efficient inhibitor for the corrosion of Cu in 0.5 M H$_2$SO$_4$ solution. Under the same temperature conditions, the inhibition efficiency increases with the concentration of TZV. The charge transfer resistance decreases as the temperature increases. At the maximum inhibitor concentration of 3.2 × 10$^{-4}$ M, the results of EIS measurements show that the inhibition efficiencies were 88.6, 98.3, 97.3, and 98.7% at 288, 298, 308, and 318 K, respectively. It is known from the OCP curve that TZV is a mixed inhibitor. All measurements showed that the inhibitor of TZV had excellent inhibition effect for copper within the studied temperature scope. The TZV adsorption on the copper surface follows the Langmuir isotherm, the isotherm adsorption curves of Bockris–Swinkels and Dhar–Flory–Huggins. The fitting results of Bockris–Swinkels and Dhar–Flory–Huggins models indicate that at 288 K, TZV molecules can replace about two water molecules. The inhibition adsorption process of TZV was spontaneous and includes two types of adsorptions, physisorption and chemisorption.

4. MATERIALS AND METHODS

4.1. Materials. The 0.5 M H$_2$SO$_4$ solutions were prepared by diluting the analytical grade sulfuric acid with doubly distilled water. The concentration of the TZV inhibitor ranged from 1 × 10$^{-5}$ to 3.2 × 10$^{-4}$ M in the solutions of 0.5 M H$_2$SO$_4$. In addition, the solution containing no TZV inhibitor was used as a blank for comparison. TZV was purchased from Shanghai Yuanye Bio-Technology Co., Ltd.

4.2. Electrochemical Measurements. Measurements were performed through the CHI 760E electrochemical workstation with a standard three-electrode glass cell, and a pure copper wire (99.999%) was cut into 1 cm in diameter as the working electrode. The reference electrode with the saturated state of mercuric sulfate (SSE) and corrosive solution can be easily connected by Luggin capillary. A 1.0 cm × 2.0 cm of platinum sheet was placed pointed right at the working electrode to ensure that a sufficient isoelectric point was generated. The cell was placed in an atmospheric environment and measurements were taken under various temperatures (288–318 K) with a water bath. All the tests were conducted at desired temperatures with an aqueous thermostat. According to SSE, we obtained all the potentials reported. Before electrochemical measurements, the working electrode was grounded with a sandpaper of 1000–2000 grit and then ultrasonically treated in ethyl alcohol, and the organic.
residue was removed in distilled water finally. The treated working electrode was bathed in an electrolyte solution. Before EIS measurement, steady-state open-circuit potential was recorded in acid solutions installed with a thermostat water bath to control temperature accurately. The EIS experiment was carried out by setting the frequency range from 0.01 Hz to 100 kHz at the open-circuit potential. The amplitude of the sinusoidal potential disturbance was 5 mV. More accurate corrosion curves of the anode and cathode current—potential were obtained for some concreted potential range between 250 and 250 mV (SSE) relative to OCP with 1 mV/s potential scan rate by using a Tafel polarization method.

4.3. SEM Analyses. The pure copper sample used for SEM experiments was cut into a rectangular parallelepiped with a size of 2.0 cm × 1.0 cm × 1.0 cm. The samples were placed in stable solutions of 0.5 M H2SO4 with and without 3.2 × 10−4 M TZV. The copper samples were taken out after marinating 8 h and dried after being washed by deionized water and absolute alcohol successively. SEM pictures were obtained using a Hitachi SU3500 SEM instrument under high vacuum at 15 keV.

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Notes
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■ REFERENCES

(1) Wang, X.; Yang, Z.; Wang, Z.; Shi, Q.; Xu, B.; Zhou, C.; Zhang, L.; Zhang, L. The influence of copper on the stress corrosion cracking of 304 stainless steel. Appl. Surf. Sci. 2019, 478, 492–498.
(2) Qiang, Y.; Zhang, S.; Guo, L.; Zheng, X.; Xiang, B.; Chen, S. Experimental and theoretical studies of four allyl imidazolium-based ionic liquids as green inhibitors for copper corrosion in sulfuric acid. Corros. Sci. 2017, 119, 68–78.
(3) Qiang, Y.; Zhang, S.; Tan, B.; Chen, S. Evaluation of Ginkgo leaf extract as an eco-friendly corrosion inhibitor of X70 steel in HCl solution. Corros. Sci. 2018, 133, 6–16.
(4) Wang, Y.; Yu, Y.; Zhang, J.; Gao, L.; Feng, L.; Zhang, D. Click-assembling triazole membrane on copper surface via one-step or two-steps and their corrosion inhibition performance. Appl. Surf. Sci. 2018, 427, 1120–1128.
(5) Li, Z.-y.; Cai, Z.-b.; Yang, W.-j.; Chen, X.-y.; Xue, G.-h.; Zhu, M.-h. Characterization and corrosion behavior of Fe6NM stainless steel treated in high temperature water. Appl. Surf. Sci. 2018, 435, 312–319.
(6) Li, F.; Bai, M.; Wei, S. A.; Jin, S.; Shen, W. Multidimension Insight Involving Experimental and in Silico Investigation into the Corrosion Inhibition of N,N-Dibenzyli Dithiocarbamate Acid on Copper in Sulfuric Acid Solution. ACS Appl. Mater. Interfaces 2019, 58, 7166–7178.
(7) Han, Y.; Wang, J. H.; Li, J.; Chen, Z. L.; Li, W. W.; Jiang, B. B.; Yao, J. Copper Corrosion Products Catalyzed Reduction of 1,42-Nitrosodimethylamine with Iron. ACS Appl. Mater. Interfaces 2018, 52, 11735–11742.
(8) Huang, H.; Fu, Y.; Wang, X.; Gao, Y.; Wang, Z.; Zhang, S.; Li, H.; Gao, F.; Chen, L. Nano-to Micro-Self-Assemblies of New Bisimidazole-Based Copoly(ionic liquid)s for Protecting Copper in Aqueous Sulfuric Acid Solution. ACS Appl. Mater. Interfaces 2019, 11, 10135–10145.
(9) Gerengi, H.; Mielenz, M.; Gece, G.; Solomon, M. M. Experimental and Quantum Chemical Evaluation of 8-Hydroxyquinoline as a Corrosion Inhibitor for Copper in 0.1 M HCl. Ind. Eng. Chem. Res. 2016, 55, 9614–9624.
(10) Daubert, J. S.; Hill, G. T.; Gotsch, H. N.; Gremaud, A. P.; Ovental, J. S.; Williams, P. S.; Oldham, C. J.; Parsons, G. N. Corrosion Protection of Copper Using Al2O3, TiO2, ZnO, HFO2, and ZrO2 Atomic Layer Deposition. ACS Appl. Mater. Interfaces 2017, 9, 4192–4201.
(11) Björkbacka, Å.; Johnson, C. M.; Leygraf, C.; Jonsson, M. Role of the Oxide Layer in Radiation-Induced Corrosion of Copper in Anoxic Water. ACS Appl. Mater. Interfaces 2016, 2016, 11450–11455.
(12) Xu, Y.; Zhang, S.; Li, W.; Guo, L.; Xu, S.; Feng, L.; Madkour, L. H. Experimental and theoretical investigations of some pyrazolopyrimidine derivatives as corrosion inhibitors on copper in sulfuric acid solution. Appl. Surf. Sci. 2018, 459, 612–620.
(13) Tian, H.; Cheng, Y. F.; Li, W.; Hou, B. Triazolyl-acetylene derivatives as novel inhibitors for copper corrosion in chloride solutions. Corros. Sci. 2015, 100, 341–352.
(14) Chen, Y.-H.; Erbe, A. The multiple roles of an organic corrosion inhibitor on copper investigated by a combination of electrochemistry-coupled optical in situ spectroscopies. Corros. Sci. 2018, 145, 232–238.
(15) Shi, C.; Wang, Y.; Yu, Y.; Li, J.; Zhang, D.; Gao, L. The role of cuprous ions on the click-assembled triazole films against copper corrosion. Corros. Sci. 2018, 145, 100–108.
(16) Qin, T. T.; Li, J.; Luo, H. Q.; Li, M.; Li, N. B. Corrosion inhibition of copper by 2,5-dimercapto-1, 3,4-thiadiazole monolayer in acidic solution. Corros. Sci. 2011, 53, 1072–1078.
(17) Sherif, E. S. M. Effects of 2-amino-5-(ethylthio)-1, 3,4-thiadiazole on copper corrosion as a corrosion inhibitor in 3% NaCl solutions. Appl. Surf. Sci. 2006, 252, 8615–8623.
(18) Solmaz, R.; Altmunbaş Şahin, E.; Dönner, A.; Kardaş, G. The investigation of synergistic inhibition effect of rhodanine and iodide ion on the corrosion of copper in sulphuric acid solution. Corros. Sci. 2011, 53, 3231–3240.
(19) Khaled, K. F. Guanidine derivative as a new corrosion inhibitor for copper in 3% NaCl solution. *Mater. Chem. Phys.* 2008, 112, 104–111.

(20) Finisgär, M. 2-Mercaptobenzimidazole as a copper corrosion inhibitor: Part II. Surface analysis using X-ray photoelectron spectroscopy. *Corros. Sci.* 2013, 72, 90–98.

(21) Ravichandran, R.; Nanjundan, S.; Rajendran, N. Effect of benzotriazole derivatives on the corrosion of brass in NaCl solutions. *Appl. Surf. Sci.* 2004, 236, 241–250.

(22) Pan, Y.-C.; Wen, Y.; Guo, X.-Y.; Song, P.; Shen, S.; Du, Y.-P.; Yang, H.-F. 2-Amino-5-(4-pyridyl)-1,3,4-thiadiazole monolayers on copper surface: Observation of the relationship between its corrosion inhibition and adsorption structure. *Corros. Sci.* 2013, 73, 274–280.

(23) Stupnišek-Lisac, E.; Gavazoda, A.; Madzarac, M. Evaluation of non-toxic corrosion inhibitors for copper in acidic acid. *Electrochim. Acta* 2002, 47, 4189–4194.

(24) Paredes, A. J.; Tattiana, N.; Hilda, M.; Alfaro, V.; Andrés, B.; Jorge, B.; Christian, A. M. New visible and selective DNA staining method in gels with tetrazolium salts. *Anal. Biochem.* 2017, 517, 31–35.

(25) Junillon, T.; Lucie, M.; Jean, P. Enhanced tetrazolium violet reduction of Salmonella spp. by magnesium addition to the culture media. *Food Microbiol.* 2014, 42, 132–135.

(26) Tao, Z.; He, W.; Wang, S.; Zhou, G. Electrochemical Study of Cyproconazole as a Novel Corrosion Inhibitor for Copper in Acidic Solution. *Ind. Eng. Chem. Res.* 2013, 52, 17891–17899.

(27) Hosseini, M. G.; Tahavoli, H.; Shahraei, T. Synergism in copper corrosion inhibition by sodium dodecylbenzenesulphonate and 2-mercaptopbenzimidazole. *J. Appl. Electrochem.* 2008, 38, 1629–1636.

(28) Lowmunkhong, P.; Ungthararak, D.; Sutthivayakit, P. Tryptamine as a corrosion inhibitor of mild steel in hydrochloric acid solution. *Corros. Sci.* 2010, 52, 30–36.

(29) Quartrone, G.; Battilana, M.; Bonaldo, L.; Tortato, T. Investigation of the inhibition effect of indole-3-carboxylic acid on the copper corrosion in 0.5 M H₂SO₄. *Corros. Sci.* 2008, 50, 3467–3474.

(30) Vaidyanathan, H.; Hackerman, N. Effect of furan derivatives on the anodic dissolution of Fe. *Corros. Sci.* 1971, 11, 737–750.

(31) Ferreira, E. S.; Giacomelli, C.; Giacomelli, F. C.; Spinelli, A. Evaluation of the inhibition effect of L-ascorbic acid on the corrosion of mild steel. *Mater. Chem. Phys.* 2004, 83, 129–134.

(32) Barcia, O. E.; Mattos, O. R. Reaction model simulating the role of sulphate and chloride in anodic dissolution of iron. *Electrochim. Acta* 1990, 35, 1601–1608.

(33) Smyrl, W. H. In *Electrochemistry and Corrosion on Homogeneous and Heterogeneous Metal Surface*; Bockris, J. O. M., Conway, B., Yager, E., White, R. E., Eds.; Comprehensive Treatise of Electrochemistry; Plenum Press: New York, London, 1981; Vol. 4, p 97.

(34) Ma, H.; Chen, S.; Yin, B.; Zhao, S.; Liu, X. Impedance spectroscopic study of corrosion inhibition of copper by surfactants in the acidic solutions. *Corros. Sci.* 2003, 45, 867–882.

(35) Zhang, D.-Q.; He, X.-M.; Gao, Q.-R.; Guo, L.-X.; Kim, G. S. Arginine self-assembled monolayers against copper corrosion and synergistic effect of iodide ion. *J. Appl. Electrochem.* 2009, 39, 1193–1198.

(36) Ma, H.; Chen, S.; Niu, L.; Zhao, S.; Li, S.; Li, D. Inhibition of corrosion by several Schiff bases in aerated halide solutions. *J. Appl. Electrochem.* 2002, 32, 65–72.

(37) Shukla, S. K.; Quraishi, M. A. The effects of pharmaceutically active compound doxycycline on the corrosion of mild steel in hydrochloric acid solution. *Corros. Sci.* 2010, 52, 314–321.

(38) Ashassi-Sorkhabi, H.; Ghalebsaz-Jeddi, N.; Hashemzadeh, F.; Jahani, F. Corrosion inhibition of carbon steel in hydrochloric acid by some polyethylene glycols. *Electrochim. Acta* 2006, 51, 3848–3854.

(39) Li, P.; Lin, J. Y.; Tan, K. L.; Lee, J. Y. Electrochemical impedance and X-ray photoelectron spectroscopic studies of the inhibition of mild steel corrosion in acids by cyclohexylamine. *Electrochim. Acta* 1997, 42, 605–615.

(40) López, D. A.; Simison, S. N.; de Sánchez, S. R. The influence of steel microstructure on CO₂ corrosion EIS studies on the inhibition efficiency of benzimidazole. *Electrochim. Acta* 2003, 48, 845–854.

(41) da Silva, A. B.; D’Elia, E.; da Cunha Ponciano Gomes, J. A. Carbon steel corrosion inhibition in hydrochloric acid solution using a reduced Schiff base of ethylenediamine. *Corros. Sci.* 2010, 52, 788–793.

(42) Asemi, D.; Arami, M.; Mahmoody, N. M. Electrochemical effect of cationic gemini surfactant and halide salts on corrosion inhibition of low carbon steel in acid medium. *Corros. Sci.* 2010, 52, 794–800.

(43) Tao, Z.; He, W.; Wang, S.; Zhang, S.; Zhou, G. A study of differential polarization curves and thermodynamic properties for mild steel in acidic solution with nitrophenyltriazole derivative. *Corros. Sci.* 2012, 60, 205–213.

(44) Tao, Z.; Zhang, S.; Li, W.; Hou, B. Corrosion inhibition of mild steel in acidic solution by some oxo-triazole derivatives. *Corros. Sci.* 2009, 51, 2588–2595.

(45) Mertens, S. F.; Khofer, C.; De Cooman, B. C.; Temmerman, E. Short-Term Deterioration of Polymer-Coated 55% Al-Zn - Part 1: Behavior of Thin Polymer Films. *Corros. 1997, 53, 381–388.

(46) Tao, Z.; Zhang, S.; Li, W.; Hou, B. Adsorption and corrosion inhibition behavior of mild steel by one derivative of benzoic-triazole in acidic solution. *Ind. Eng. Chem. Res.* 2010, 49, 2593–2599.

(47) Murlidharan, S.; Phani, K. L. N.; Pitchumani, S.; Ravichandran, S. V. K.; Iyer, S. V. K. Polyamino-Benzquinone Polymers: A New Class of Corrosion Inhibitors for Mild Steel. *J. Electrochem. Soc.* 1995, 142, 1478–1483.

(48) Bhar, H. P.; Conway, B. E.; Joshi, K. M. On the form of adsorption isotherms for substitutional adsorption of molecules of different sizes. *Electrochim. Acta* 1973, 18, 789–798.

(49) Do, D. Adsorption Analysis: Equilibria and Kinetics; Imperial College Press: London, 1980; pp10–60.

(50) Bockris, J. O. M.; Swinkels, D. A. J. Adsorption of Decylamine on Solid Metal Electrodes. *J. Electrochem. Soc.* 1964, 111, 736–743.

(51) Eriksson, M.; Bockris, J. O. M.; Ekedahl, L.-G. A model of the Temkin isotherm behavior for hydrogen adsorption at Pd–SiO₂ interfaces. *J. Appl. Phys.* 1997, 82, 3143–3146.

(52) Fils, J.; Zakroczemski, T. Impedance Study of Reinforcing Steel in Simulated Pore Solution with Tannin. *J. Electrochem. Soc.* 1996, 143, 2458–2464.

(53) Szkłarska-Smialowska, Z.; Mankowski, J. Crevice corrosion of stainless steels in sodium chloride solution. *Corros. Sci.* 1978, 18, 953–960.

(54) Doner, A.; Yüce, A. O.; Kardağ, G. Inhibition Effect of Rhodamine-N-Acetic Acid on Copper Corrosion in Acidic Media. *Ind. Eng. Chem. Res.* 2013, 52, 9709–9718.

(55) Singh, A. K.; Quraishi, M. A. Effect of Cefazolin on the corrosion of mild steel in HCl solution. *Corros. Sci.* 2010, 52, 152–160.