Anticorrosion Study for Brass Alloys in Heat Exchangers during Acid Cleaning Using Novel Gemini Surfactants Based on Benzalkonium Tetrafluoroborate

Ashraf M. Ashmawy,* Ragab Said, Ibrahim A. Naguib, Bo Yao, and Mahmoud A. Bedair*

ABSTRACT: For a variety of applications, the brass alloy has been utilized to replace titanium tubes in heat exchangers. Copper alloys’ high corrosion rate during the acid cleaning procedure remains a significant concern. To inhibit the corrosion of brass alloys, we prepared two novel gemini surfactants (GSs), \(N_1N_3\)-dibenzyl-\(N_1N_3N_1N_3\)-tetramethylpropane-1,3-diaminium tetrafluoroborate (I H) and \(N_1N_3N_1N_3\)-tetramethyl-N_1N_3-bis (4-methyl benzyl) propane-1,3-diaminium tetrafluoroborate (I Me), and they were characterized using Fourier transform infrared spectroscopy and \(^1\)H nuclear magnetic resonance spectroscopy. Their inhibition performance against corrosion of brass alloys in 1 M HCl was studied using electrochemical techniques including potentiodynamic polarization (PP), electrochemical impedance spectroscopy, and electrochemical frequency modulation. The inhibition effect of the synthesized compounds was high, and it increased as the inhibitor’s concentration was increased. The maximum level of inhibition efficiency was achieved at an inhibitor concentration of 100 ppm, reaching 96.42% according to PP measurements. From Langmuir data, the mechanisms of adsorption of the two GSs on the surface of copper was found to be physisorption and chemisorption adsorption. X-ray photoelectron spectroscopy and scanning electron microscopy show that the addition of the two compounds lowers the dissolution of brass ions in the corrosive solution and forms a protective layer on the surface of the brass.

1. INTRODUCTION

Surfactants are molecules with a nonpolar hydrophobic tail and a polar hydrophilic head. Upon dissolving surfactants in nonpolar or polar liquids, their unique molecular architecture produces a wide range of complicated self-assembling phenomena.\(^1\)\(^-\)\(^5\) Gemini surfactants (GSs) provide unique performance in terms of their critical micelle concentrations (CMCs), solubility in water, and interface properties.\(^6\)\(^-\)\(^11\) GSs provide high efficiency compared to their corresponding monomer counterparts either in reducing solution surface tension or in micelle formation. GSs are made up of two surfactant monomers that are covalently bonded together by either a hard or a flexible spacer group.\(^12\)\(^-\)\(^16\)

GSs have recently been used as anticorrosion materials due to their various advanced properties. Ma and Chen et al.\(^17\) used electrochemical impedance spectroscopy (EIS) to evaluate the effects of four surfactants, sodium dodecyl sulfate, cetyltrimethylammonium bromide, polyoxyethylene sorbitan monooleate, and sodium oleate, on the corrosion behavior of copper in aerated 0.5 mol dm\(^{-3}\) H\(_2\)SO\(_4\) solutions. These surfactants were found to be mixed-type inhibitors that slowed down the corrosion by blocking the copper surface via electrostatic adsorption or chemisorption. El Achouri et al.\(^18\) synthesized three novel GSs as the series of alkane diyl bis (dimethyl alkyl ammonium) bromide with varying spacer lengths and tested them as CIs in 1 M HCl solution. The three surfactants used in this study performed as effective cathodic inhibitors; the inhibitory efficiency increased to a peak near the CMC value. Additionally, as the gemini molecule’s spacer length is reduced, surfactant surface characteristics is improved dramatically. Heakal and Elkholy\(^19\) studied GSs for their corrosion inhibition properties for carbon steel. They discovered that GSs have low surface energy and low CMC. Cationic GSs behaved as a corrosion inhibitor and showed more than 90% inhibition efficiency.

Brass tubes are commonly used in cooling water applications such as heat exchangers and coolers. Brass heat exchanger

Received: February 24, 2022
Accepted: May 12, 2022
Published: May 20, 2022

© 2022 The Authors. Published by American Chemical Society
nuclear magnetic resonance (1H NMR) spectra (DMSO-6, 400 MHz for 1H NMR). Chemical shifts are expressed in ppm.

2. MATERIALS AND EXPERIMENTAL METHODS

2.1. Materials and Tools. Benzyl chloride 99%, 4-methylbenzyl chloride, and N,N,N,N-tetramethyl-1,3-propanediamine were obtained from Sigma-Aldrich. Ethyl alcohol and 37% HCl were obtained from Merck chemicals. Using Fourier transform infrared (FT-IR) spectroscopy (plus 460 or Pye Unicam SP-1000 spectrophotometer, Pye Unicam, Cambridge, UK), IR spectra (KBr discs) were measured. A Bruker spectrophotometer was used to acquire 1H nuclear magnetic resonance (1H NMR) spectra (DMSO-d6) (400 MHz for 1H NMR). Chemical shifts are expressed in parts per million using deuterated dimethyl sulfoxide (DMSO-d6) as a solvent and tetramethyl silane (TMS) as an internal standard. Brass alloy electrodes have the following composition (wt %): Sn, 0.41%; P, 0.01%; Mn, 0.0025%; Fe, 0.0041%; Al, 0.032%; Pb, 2.09%; Zn, 38.01%; and Cu, balance.

2.2. Preparation of the Corrosive Solution. HCl solution (1.0 M) was prepared with distilled water from 37% HCl. The concentration range of the GS was from 20 to 100 ppm.

2.3. Synthesis of the Inhibitors. N,N,N,N,N,N,N-tetramethyl-1,2-diamine (0.01 mol) was dissolved in acetonitrile in the presence of ammonium tetrafluoroborate; after that, benzyl chloride or 4-methylbenzyl chloride (0.02 mol) was added, and the mixture was refluxed at 80 °C for 2 h. The products were crystallized from ethanol three times (Scheme 1 summarizes the process of preparation).

2.4. Electrochemical Investigations. Brass alloy, a saturated calomel electrode (SCE), and a platinum wire were used as working, reference, and counter electrodes, respectively, in a three-electrode electrochemical cell. The corrosion inhibition behavior was investigated using electrochemical techniques such as potentiodynamic polarization (PP), EIS, and electrochemical frequency modulation (EFM). PP measurement was performed at a 5 mV/s scan rate. The corrosion current was calculated using the Stern–Geary method. The inhibition efficiency (IE) was estimated using the following equation:

IE = 100 × \left(1 - \frac{i_{corr\text{(inh)}}}{i_{corr\text{(free)}}}\right)

EIS spectra were recorded at an open-circuit voltage with a modest alternating voltage (10 mV) spanning the frequency range of 100 kHz to 20 mHz after immersing the electrode in the test solution for 1 h at 25 °C. The inhibition efficiency (IE), and θ were calculated from the following equation:

IE = 100 × \left(1 - \frac{R_{ct\text{(inh)}}}{R_{ct\text{(unk)}}}\right)

where \(i_{corr\text{(inh)}}\) and \(i_{corr\text{(free)}}\) are the corrosion current densities for the inhibitor and blank, respectively.

2.5. Surface Examination Using Scanning Electron Microscopy, Energy-Dispersive X-ray Spectroscopy, and X-ray Photoelectron Spectroscopy. The surface morphology of the examined sample was evaluated after...
immersion in 1 M HCl solution for 24 h in the absence and presence of the inhibitor at a maximum concentration of 100 ppm. After the investigated specimen was withdrawn from the solution and dried, scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) examinations were performed (JOEL, JSM-T20, Japan). X-ray photoelectron spectroscopy (XPS) measurements carried out using an XPS system (Thermo Fisher Scientific, USA) with Al Kα radiation with an energy of 1350 eV. The emission voltage and power of this source are set to be 11 kV and 220 W, respectively. The pressure was fixed in the analyzing chamber at 10⁻⁹ mbar throughout the analysis.

3. RESULTS AND DISCUSSION

3.1. Structural Confirmation of the Prepared NIS Compound. 3.1.1. Fourier Transform Infrared Spectroscopy
**The infrared spectra of the purified GSs prepared in this study are presented in Figure 1.**

**Table 1. Electrochemical Parameters for Brass Alloys in 1 M HCl Solution Containing Different Concentrations of the GS Obtained from Polarization Measurements at 25 °C**

| inhibitor name | conc (ppm) | $E_{corr}$ vs SCE (mV) | $I_{corr}$ ($\mu$A cm$^{-2}$) ± SD | $\beta_a$ (mV dec$^{-1}$) ± SD | $\beta_c$ (mV dec$^{-1}$) ± SD | $k$ (mpy) | $\theta$ | IEPP % |
|----------------|------------|------------------------|-----------------------------------|--------------------------------|--------------------------------|----------|---------|--------|
| blank          |            | -256                   | 259 ± 4.1                         |                                |                                |          |         |        |
| 1 H            | 20         | -222                   | 171 ± 4.4                         | 53.0 ± 3.1                     | 302.00 ± 9.53                   | 157.2    | 0.3398  | 33.98  |
|                | 40         | -228                   | 122 ± 3.9                         | 67.1 ± 3.2                     | 319.66 ± 10.06                  | 111.7    | 0.5290  | 52.90  |
|                | 60         | -236                   | 92.5 ± 4.2                        | 54.2 ± 3.3                     | 257.33 ± 9.02                   | 85.1     | 0.6429  | 64.29  |
|                | 80         | -250                   | 24.5 ± 3.7                        | 51.4 ± 5.7                     | 225.66 ± 8.02                   | 22.4     | 0.9054  | 90.54  |
|                | 100        | -264                   | 9.84 ± 1.9                        | 52.1 ± 3.4                     | 164.00 ± 9.54                   | 9.8      | 0.9620  | 96.20  |
| 1 Me           | 20         | -219                   | 170 ± 2.4                         | 67.4 ± 2.4                     | 323.33 ± 8.73                   | 156.2    | 0.3436  | 34.36  |
|                | 40         | -229                   | 100 ± 2.9                         | 87.9 ± 5.1                     | 491.66 ± 10.07                  | 92.3     | 0.6139  | 61.39  |
|                | 60         | -224                   | 34 ± 3.1                          | 57.2 ± 5.4                     | 274.66 ± 7.51                   | 31.3     | 0.8687  | 86.87  |
|                | 80         | -263                   | 13.8 ± 1.7                        | 46.3 ± 2.9                     | 208.66 ± 9.50                   | 12.6     | 0.9467  | 94.67  |
|                | 100        | -254                   | 9.27 ± 1.2                        | 46.6 ± 3.4                     | 180.33 ± 8.50                   | 8.5      | 0.9642  | 96.42  |

**Figure 3.** Polarization for brass alloys with and without GS (left) I H and (right) I Me in 1 M HCl.

**Figure 4.** Impedance curves for brass alloys with and without GS (I H) and (I Me) in 1 M HCl, (a) Nyquist plots, and (b) Bode plots.

The infrared spectra of the purified GSs prepared in this study are presented in Figure 1.

For the two surfactants $[N_1,N_3$-dibenzyl-$N_1,N_3$-tetramethylpropane-1,3-diaminium tetrafluoroborate (I H)
Table 2. Collection of the EIS Parameters for Corrosion of Brass Alloys in 1.0 M HCl in the Absence and Presence of Different Concentrations of the GS at 25 °C

| Inhibitor | Conc. (M) | $R_\text{ct}$ (Ω cm²) | $R_\theta$ (Ω cm²) | $Y_\text{a}$ (µΩ⁻¹ s cm⁻²) | n | $C_\text{dl}$ (µF cm⁻²) | $\chi$ squared | S | $\alpha°$ | $\theta$ | IEIEIS % |
|-----------|----------|------------------------|------------------|---------------------------|---|-------------------------|----------------|---|------------|-------|----------|
| Blank     |          | 2.957                  | 60.26            | 12410                     | 0.5377 | 9666.499 | 3.94×10⁻³ | -0.165 | -31.54        |       |          |
| 1 H       | 20       | 10.480                 | 115.90           | 2370                      | 0.5586 | 853.727 | 1.23×10⁻³ | -0.258 | -30.07        | 0.4801 | 48.01 |
| 40        |          | 5.541                  | 134.00           | 1098                      | 0.5863 | 284.006 | 3.36×10⁻³ | -0.398 | -36.87        | 0.5503 | 55.03 |
| 60        |          | 6.037                  | 403.80           | 2096                      | 0.5651 | 1843.485 | 2.53×10⁻³ | -0.385 | -41.32        | 0.8508 | 85.08 |
| 80        |          | 6.769                  | 655.00           | 1098                      | 0.5966 | 878.628 | 1.23×10⁻³ | -0.437 | -45.51        | 0.9080 | 90.80 |
| 100       |          | 11.640                 | 323.90           | 1009                      | 0.5560 | 413.078 | 1.25×10⁻³ | -0.353 | -36.54        | 0.8140 | 81.40 |
| 1 M       | 20       | 5.050                  | 128.80           | 2091                      | 0.5792 | 806.184 | 2.99×10⁻³ | -0.367 | -37.74        | 0.5321 | 53.21 |
| 40        |          | 7.255                  | 151.70           | 1891                      | 0.5653 | 723.870 | 1.88×10⁻³ | -0.340 | -35.09        | 0.6028 | 60.28 |
| 60        |          | 6.773                  | 347.20           | 1612                      | 0.5969 | 1089.297 | 3.02×10⁻³ | -0.394 | -42.60        | 0.8264 | 82.64 |
| 80        |          | 5.115                  | 693.70           | 710                       | 0.6294 | 468.113 | 8.69×10⁻³ | -0.473 | -46.46        | 0.9131 | 91.31 |
| 100       |          | 5.464                  | 808.20           | 1074                      | 0.5928 | 974.485 | 3.13×10⁻³ | -0.536 | -49.22        | 0.9254 | 92.54 |

and N$_1$N$_2$N$_3$N$_4$N$_5$-tetramethyl-N$_1$N$_7$-bis (4-methyl benzyl) propane-1,3-diaminium tetrafluoroborate (I Me), the peaks at 2972 and 2970 cm⁻¹ could be due to aliphatic (-CH₂-) groups. The peak appearing at about 1420–1383 cm⁻¹ represents the C–N (stretching vibration) band. The presence of hydrogen-bonded H₂O molecules is explained with the 3411 and 3415 cm⁻¹ broad stretch bands. The asymmetric B–F bond was connected to the vibrational bands at 1059 cm⁻¹, whereas the symmetric vibrational peaks appeared at 521 cm⁻¹ for the two surfactants.

3.1.2. ¹H NMR Spectroscopy. The chemical structures of the two surfactants were confirmed using ¹H NMR spectroscopy using DMSO as a solvent and TMS as an internal reference.

The spectrum illustrated in Figure 2 for I H demonstrated peaks at a chemical shift of 7.5 ppm, indicating the benzene ring, while peaks at a chemical shift of 4.75 ppm indicate methylene groups in the center of the benzene ring. Peaks at chemical shifts of 3.1–3.4 ppm indicate bonding of aliphatic CH₃ to the N atom.

3.2. Electrochemical Studies. 3.2.1. PP Measurements. Figure 3 shows the PP curves of the brass alloy in 1 M HCl solution in the absence and presence of variable amounts of the GS. Table 1 lists kinetic parameters such as corrosion potential ($E_{\text{corr}}$), corrosion current density ($i_{\text{corr}}$), and anodic and cathodic Tafel slopes ($b_\alpha$ and $b_\beta$). Figure 3 shows that both cathodic and anodic current densities have decreased significantly; indicating that corrosion has been effectively suppressed. When compared to those of the system without the inhibitor, the potential curves move toward higher negative potentials, showing that the cathodic reaction is largely slowed. The cathodic reaction is predominantly slowed in the system without the inhibitor. The corrosion inhibitor compounds can be labeled as the anodic or cathodic type when the shift in $E_{\text{corr}}$ is at higher than 85 mV with respect to the blank solution. The $E_{\text{corr}}$ differs by less than 85 mV between the inhibited and uninhibited systems, implying that the GS is a mixed-type inhibitor.

These results revealed that the investigated GS compounds significantly lowered both the anodic dissolution reaction and the cathodic reaction to some extent. The values of the cathodic slopes $b_\beta$ and the anodic slopes $b_\alpha$ vary delicately with the addition of the GS compounds, which indicates that the GS compounds act as mixed inhibitors. The changes for both $b_\alpha$ and $b_\beta$ upon the addition of the GS reflect the reduction of both the anodic dissolution and hydrogen evolution reaction rather than only the surface blocking. The IEIEIS % values increase upon increasing the concentration of the GS at an optimum concentration. The efficiencies obtained are around 96.20 and 96.42% for I H and I Me, respectively.

3.2.2. Electrochemical Impedance Spectroscopy. EIS tests for brass alloys in 1 M HCl solution without and with varying concentrations of the GS were performed to obtain data about the surface properties of the brass alloys as well as the kinetics of the electrode processes.

The best fit equivalent circuit applied for fitting of the impedance data is presented in Figure 4. This circuit consists of the following components, that is, charge transfer resistance ($R_\text{ct}$), solution resistance ($R_\theta$), and a constant phase element. Some electrochemical parameters including $R_\theta$ (solution resistance), $R_\text{ct}$, and $C_\text{dl}$ were extracted from impedance data and are presented in Table 2. The capacitance loop and the low-frequency impedance modulus increase gradually with the increasing concentration of I H or I Me, indicating the improved corrosion inhibition. In contrast to that of the blank solution, the $R_\theta$ and IEIEIS % in the inhibited solutions increase remarkably with the increased inhibitor concentration. A higher $R_\theta$ value indicates a higher surface coverage of the protective film that has been formed on the substrate surfaces. As the substrate dissolution was controlled by the charge transfer process, an increase of charge transfer resistance indicates a reduction of substrate dissolution (reduced corrosion attack).

The values of $n$ are in the range of 0.53–0.62, suggesting the inhomogeneity of the brass surface after corrosion in the solution with or without inhibitors, and the corrosion of brass in the solution is primarily controlled by the charge transfer process. In the presence of inhibitors, a decline in $C_\text{dl}$ indicates a decrease (according to Table 2) in the local dielectric constant and/or an increase in the thickness of the double layer. This can be attributed to the adsorbed inhibitors on the metal surface replacing the water molecules. Regarding Bode plots, the curves exhibit a single time constant, and an increase of the module impedance and phase angle is observed in the presence of I H or I Me inhibitors.

Additionally, adsorption of the GS creates a barrier between the metal and the acid media, enhancing the resistance to polarization. From Table 2, all concentrations of the GS have a very favorable effect on corrosion inhibition. In the presence of 100 ppm of the GS, the IEIEIS % is around 91% for the two surfactants.

3.2.3. Electrochemical Frequency Modulation. EFM intermodulation spectra of brass alloys in 1 M HCl solutions in the absence and presence of varying concentrations of the GS are indicated in Figure 5. The electrochemical parameters...
obtained from the EFM spectrum analysis are summarized in Table 3. The value of the $I_{\text{corr}}$ decreases as the inhibitor concentration increases, meaning that $\text{IEEFM}$ increases, implying that the GS inhibits corrosion via adsorption on the brass alloy surface, resulting in the creation of a protective barrier layer over the surface.43 The values of $\beta_c$ and $\beta_a$ are changed significantly with the presence of GS compounds, confirming that the cathodic hydrogen evolution and anodic copper and zinc dissolution were considerably diminished in the presence of these compounds. Therefore, the GS compounds effectively influence both the cathodic and anodic processes on the brass surface.44 Theoretically, the values of CF-2 and CF-3 are equal to 2 and 3, respectively.45 The experimental values of causality factors (CF-2 and CF-3) are quite close to the

| inhibitor name | conc (M) | $I_{\text{corr}}$ ($\mu$A cm$^{-2}$) $\pm$ SD | $\beta_c$ (mV dec$^{-1}$) $\pm$ SD | $\beta_a$ (mV dec$^{-1}$) $\pm$ SD | CF-2 | CF-3 | $\kappa$ (mpy) | $\theta$ | IE$\text{EFM}$ % |
|----------------|----------|-------------------------------------------|---------------------------------|---------------------------------|------|------|----------------|------|---------------|
| blank          |          | 424.26 $\pm$ 11.45                        | 31.78 $\pm$ 4.82                | 83.93 $\pm$ 4.61                | 1.96 | 3.80 | 389.5          |      |               |
| I H            | 20       | 133.16 $\pm$ 6.95                         | 25.82 $\pm$ 3.12                | 108.56 $\pm$ 6.74               | 1.79 | 2.83 | 122.3          | 0.686| 68.61         |
|                | 40       | 99.68 $\pm$ 9.98                          | 25.89 $\pm$ 2.85                | 65.89 $\pm$ 5.20                | 1.79 | 3.53 | 91.5           | 0.765| 76.50         |
|                | 60       | 75.80 $\pm$ 6.45                          | 25.38 $\pm$ 4.60                | 64.31 $\pm$ 4.30                | 1.88 | 2.89 | 69.7           | 0.821| 82.13         |
|                | 80       | 42.97 $\pm$ 8.40                          | 27.76 $\pm$ 4.92                | 83.12 $\pm$ 4.80                | 1.84 | 2.60 | 39.3           | 0.899| 89.87         |
|                | 100      | 30.76 $\pm$ 7.20                          | 28.93 $\pm$ 4.70                | 63.98 $\pm$ 5.10                | 1.69 | 2.77 | 28.4           | 0.927| 92.75         |
| I Me           | 20       | 119.80 $\pm$ 9.75                         | 28.77 $\pm$ 3.55                | 57.79 $\pm$ 7.20                | 1.72 | 3.11 | 109.8          | 0.718| 71.76         |
|                | 40       | 81.40 $\pm$ 8.60                          | 31.67 $\pm$ 4.55                | 87.82 $\pm$ 7.15                | 1.96 | 2.82 | 74.8           | 0.808| 80.81         |
|                | 60       | 54.33 $\pm$ 9.08                          | 26.36 $\pm$ 5.05                | 60.90 $\pm$ 5.60                | 1.84 | 3.24 | 49.9           | 0.872| 87.19         |
|                | 80       | 29.26 $\pm$ 8.11                          | 30.41 $\pm$ 3.25                | 80.06 $\pm$ 6.30                | 1.77 | 2.52 | 26.9           | 0.931| 93.10         |
|                | 100      | 22.94 $\pm$ 4.06                          | 31.33 $\pm$ 4.76                | 69.22 $\pm$ 6.30                | 1.63 | 2.47 | 21.0           | 0.946| 94.59         |

Figure 5. Electrochemical frequency for brass alloys with and without GS (top) I H and (bottom) I Me in 1 M HCl.

Table 3. EFM Parameters for Corrosion of Brass Alloys in 1 M HCl in the Absence and Presence of Different Concentrations of the GS at 25 °C
theoretical values, meaning that Tafel slopes and corrosion current densities are correct, according to the EFM analysis.\textsuperscript{46}

Comparing PP, EIS, and EFM data to the data without the inhibitor, it is found that the two GSs were successful in inhibiting the corrosion. This is due to the presence of Zn at a concentration of 38% in alloys, which decreases the stability in chloride solution when the two compounds are combined, and adsorption films are formed via heteroatoms and electrons, resulting in the production of a protective layer.

3.3. Adsorption Considerations. Mechanism of adsorption of the GS onto the surface of alloys can be determined via the adsorption isotherm.

The Langmuir adsorption isotherm was employed to deal with the experimental data of I H and I Me study obtained using EIS. The values of the adsorption binding constant ($K_{ads}$)), obtained from adsorption isotherms, are related to Gibbs energy ($\Delta G_{ads}$) as follows:\textsuperscript{47–49}

$$\frac{C_{ads}}{\theta} = \frac{1}{K_{ads}} + C_{inh}$$

(4)

$$\Delta G_{ads} = -RT \ln(1 \times 10^{-6} K_{ads})$$

(5)

where $C_{GS}$ is the concentration of the GS, $K$ is the adsorption constant (L mg$^{-1}$), and $\theta$ is the surface coverage.\textsuperscript{50} A linear relationship is obtained between ($C_{gs}/\theta$) and $C_{GS}$ if the adsorption process follows the Langmuir adsorption isotherm Figure 6.

![Figure 6. Langmuir adsorption isotherms of the two GSs in the brass alloys.](image)

The linear regression coefficient values are around 1 for the two compounds, revealing that Langmuir single-layer adsorption of the GS molecules occurs on the selected metal surface.\textsuperscript{51} Based on the Langmuir isotherm, it can be concluded that the cationic GS (I H and I Me) is adsorbed on the alloys in the form of a monolayer with a lateral interlink between the GS molecules. The negative value obtained for $\Delta G_{ads}$ replicates the spontaneity and great adsorption aptitude of GS molecules on the brass surface and reveals the stability of the formed layer on the brass surface,\textsuperscript{52} according to the $\Delta G_{ads}$ values of $-27.76$ and $-27.45$ kJ/mol for I H and I Me,\textsuperscript{53–55} respectively. $\Delta G_{ads}$ values of $-20$ kJ mol$^{-1}$ or lower are related to electrostatic attraction between charged molecules and the charged metal (physical adsorption); $\Delta G_{ads}$ values of $-40$ kJ mol$^{-1}$ or higher involve charge sharing or transfer from organic molecules to the metal surface to form a coordinate type of bond (chemisorption).\textsuperscript{56} The absolute values of $\Delta G_{ads}$ are in the range of 20–40 kJ mol$^{-1}$, indicating that the adsorption of the GS on the brass surface is a mixed adsorption containing physisorption as well as chemisorption.\textsuperscript{57}

3.4. Surface Examination. 3.4.1. Scanning Electron Microscopy. SEM is a reliable tool to analyze the surface and morphologies of a wide range of materials. SEM can monitor the surface change during corrosion inhibition.\textsuperscript{58,59} SEM micrographs of the examined specimens following immersion in 1 M HCl solution for 24 h in the absence and presence of the inhibitor at the highest concentration of 100 ppm are shown in Figure 7. In the absence of the inhibitor, the surface of the brass specimen corroded in 1 M HCl revealed deep black grooves with gray zones, which match the dandruff of the generated corrosion products. Meanwhile, in the presence of this inhibitor, which was uniformly distributed across the alloy surface, no grooves were visible in SEM pictures of the alloy specimens. This effect could be due to the GS compounds forming a protective thin film on the metal surface, which effectively blocked the formation of salt and oxide deposits on the metal surface. Consequently, the adsorption of HCl molecules was importantly diminished, and the corrosion destruction of the metal surface was maximally reduced.\textsuperscript{60} As validated by EDX analysis, the adsorbed inhibitor appeared as white spots covering the whole surface of the tested brass specimen.

3.4.2. Energy-Dispersive X-ray Spectroscopy. Table 4 and Figure 8 show the EDX spectra for the blank solution and the inhibited solution containing I H or I Me. It is noted that the Zn peak intensity is more decrease than the Cu peak intensity, indicating the selective dissolution for zinc rather than copper. For the blank solution, it is noticed that the ratio of Zn is the

![Figure 7. SEM micrographs of the brass alloy after a 24 h immersion period: (a) fresh, (b) 1.0 M HCl, (c) I H, and (d) I Me.](image)

| Table 4. Weight Percentages of Elements on the Brass Alloys in the Presence and Absence of 100 ppm of GSs, Determined Using EDX Analysis |
|-----------------|-----------------|-----------------|-----------------|-----------------|
| element         | brass alloy in | brass alloy in | brass alloy in |
|                 | (1 M HCl)       | (1 M HCl + I Me)| (1 M HCl + I H) |
| mass %          | atom %          | mass %          | atom %          |
| Cl              | 15.91           | 25.31           | 10.63           | 15.23           | 13.94           | 22.19 |
| C               | 0.62            | 2.62            | 0.48            | 2.07            |
| N               | 0.16            | 0.59            | 0.12            | 0.49            |
| F               | 0.15            | 0.39            | 0.14            | 0.41            |
| Cu              | 54.35           | 49.13           | 47.92           | 44.55           | 46.84           | 40.45 |
| Zn              | 29.74           | 25.56           | 40.52           | 36.62           | 38.48           | 34.19 |
| total           | 100             | 100             | 100             | 100             | 100             | 100   |
Figure 8. EDX patterns of the film formed on the brass alloy surface after immersion in HCl in the absence and presence of investigated inhibitors.

Figure 9. XPS survey, Cu 2p, C 1s, and N 1s spectra of the film formed on the brass alloy surface after immersion in HCl in the presence of the I Me inhibitor.

lowest in comparison to the other inhibited solutions, which causes a mechanical failure resulting from inner stresses formed by the process of dezincification. The presence or absence of the inhibitor GS in the solution causes a considerable change.
in the components of the film generated on the surface of the alloy. In the absence of the GS corrosion inhibitors, peaks of Cl, Zn, and Cu were observed. In the presence of the GS corrosion inhibitor, the height of the Cl peak decreased, and the peaks of N, C, and F (which certainly correspond to the GS inhibitors) were also detected, indicating a coating of inhibitor molecules on the surface of the alloy.

3.4.3. X-ray Photoelectron Spectroscopy. XPS has been broadly used in the corrosion protection field in recent years to determine the composition of molecular protective films and the bonding of heteroatoms and metals in corrosion inhibitors. The XPS studies were conducted on the inhibited brass samples pre-exposed to electrolytic conditions for 24 h to examine the interaction of the studied Imo inhibitor molecules with the brass surface. The analyses were carried out in the binding energy (BE) range of Cu 2p3/2, C 1s, and N 1s peaks. The acquired XPS spectra are presented together with the proposed peak deconvolution in Figure 9. The XPS survey spectra reveal the presence of Cu and Zn as the major components of the brass alloy beside other elements related to the organic inhibitor (C, N, and F), which confirms their presence on the brass surface. The Cu 2p3/2 spectra reveal several peaks. The first one at 932.63 eV is characteristic of metallic Cu, with a good agreement with the literature data. The second peak is related to Cu oxides with a BE of 934.9 eV. The presence of Cu oxides may be further confirmed through the strong satellite feature observed at a higher energy range of approx. 940–945 eV.

The measured peaks for the C 1s spectrum showed that the BEs of (C−C, C=O, and C−H aromatic); C−N; and (C−O and C==O) bonds are 284.95, 286.8, and 288.45 eV, respectively, and provide advantageous authentication for the adsorption of the Imo inhibitor onto the brass interface. The BEs of the relevant N 1s bonds (N+−C and N+−M) are 399.72, 400.68, and 402.37 eV, respectively. This further supports our conclusion that Imo forms coordination bonds on the brass surface. The F 1s spectrum shows a characteristic peak of 684.82 eV, attributed to the metal fluorides as good evidence of Imo adsorption.

3.5. Mode and Mechanism of Protection. According to the previous discussed results, we can conclude that the inhibition activity of the two GSs studied at the brass/solution interface could be attributed to the adsorption process. The adsorption process may be considered to be due to electrostatic attraction between charged inhibitors (the positive and negative charges of the GS) and the charged metal surface,
the molecule’s unshared electron pair donation to the metal surface, the π and conjugated electron interaction with the metal surface, or a combination of all the mentioned processes. The two aromatic moieties present in I H and I Me highly participate in the adsorption and protection process. As a consequence, unshared electron pairs of π-bonds of the two aromatic moieties are potential reaction centers (donation reaction centers) to the vacant d orbital of the copper metal (chemisorption mechanism). In addition, the presence of the ammonium cation (N+) and BF4– ions in I H and I Me induces electrostatic attraction between them and the charged brass surface (physisorption mechanism). As shown in Figure 10, the multiple active sites for adsorption via physical electrostatic attraction and chemisorption enhance the protecting ability of the surfactants toward the brass surface. A comparison between our investigated GSs and other published inhibitors for copper and its alloys in HCl is listed in Table 5. It is clear from the comparison table that our investigated compounds have higher efficiency and better protection ability.

4. CONCLUSIONS

Two GSs, I H and I Me, were synthesized and investigated using electrochemical techniques as a corrosion inhibitor for brass alloys in heat exchanger application. The results demonstrate that the two GSs investigated in this study had a significant inhibition efficiency for brass alloys in 1 M HCl and that the inhibition efficiency increases as the inhibitor concentration increases. According to PP statistics, the high efficiency is around 96%. The findings of the experiments revealed that the investigated GSs adsorb spontaneously on the brass alloy surfaces and follow the Langmuir adsorption isotherm through the physisorption and chemisorption mechanism. We hope that this study may assist in extending the life of desalination plants, reducing corrosion costs, and reducing environmental issues.

■ AUTHOR INFORMATION

Corresponding Authors

Ashraf M. Ashmawy — Department of Chemistry, Faculty of Science (Men’s Campus), Al-Azhar University, Nasr City 11884 Cairo, Egypt; orcid.org/0000-0002-8006-7605; Email: ashraf Ashmawy2002@azhar.edu.eg, ashraf_Ashmawy2002@yahoo.com

Mahmoud A. Bedair — College of Science and Arts, University of Bisha, Al-Namas 61977, Saudi Arabia; Department of Chemistry, Faculty of Science (Men’s Campus), Al-Azhar University, Nasr City 11884 Cairo, Egypt; orcid.org/0000-0002-2236-7837; Email: mbedair@ub.edu.su, m_bedier@azhar.edu.eg, m_bedier@yahoo.com

Authors

Ragab Said — Department of Pharmaceutical Analytical Chemistry, Faculty of Pharmacy, Al-Azhar University, Nasr City 11751 Cairo, Egypt; Pharmaceutical Chemistry Department, Faculty of Pharmacy, Helwan University for Sustainable Development, Helwan 11785 Cairo, Egypt

Abdulrahman A. Naguib — Department of Pharmaceutical Chemistry, College of Pharmacy, Taif University, Taif 21944, Saudi Arabia

Bo Yao — Chemical and Materials Engineering Department, Faculty of Engineering, University of Alberta, Edmonton T6G 2R3, Canada; orcid.org/0000-0001-8029-2514

Complete contact information is available at: https://pubs.acs.org/10.1021/acsomega.2c01119

Author Contributions

A.M.A. and M.A.B.: conceptualization, experimental execution, validation, formal analysis, data curation, writing—original draft and review. R.S. and I.A.N.: investigation, experimental execution, and resources. B.Y.: resources, conceptualization, methodology, validation, and writing—review.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

“Authors would like to thank Taif University Researchers Supporting project number (TURSP-2020/56), Taif University, Taif, Saudi Arabia.”

■ REFERENCES

(1) Malik, M. A.; Hashim, M. A.; Nabi, F.; Al Thabaiti, S. A.; Khan, Z.; Lumpur, K.; Arabia, S. Anti-Corrosion Ability of Surfactants: A Review. Int. J. Electrochem. Sci. 2011, 6, 1972.

(2) Encyclopedia of Colloid and Interface Science; Tadros, T., Ed.; Springer Berlin Heidelberg: Berlin, Heidelberg, 2013.

(3) Guo, J.; Zhang, L.; Liu, S.; Li, B. Effects of Hydrophobic Groups of Nonionic Surfactants on the Wettability of Lignite Surface: Molecular Dynamics Simulation and Experimental Study. Fuel 2018, 231, 449–457.

(4) Badr, E. A.; Bedair, M. A.; Shaban, S. M. Adsorption and Performance Assessment of Some Imine Derivatives as Mild Steel Corrosion Inhibitors in 1.0 M HCl Solution by Chemical, Electrochemical and Computational Methods. Mater. Chem. Phys. 2018, 219, 444–460.

(5) Cai, L.; Fu, Q.; Shi, R.; Tang, Y.; Long, Y.-T.; He, X.-P.; Jin, Y.; Liu, G.; Chen, G.-R.; Chen, K. ‘Pungent’ Copper Surface Resists Acid Corrosion in Strong HCl Solutions. Ind. Eng. Chem. Res. 2014, 53, 64–69.

(6) Pal, N.; Saxena, N.; Mandal, A. Studies on the Physicochemical Properties of Synthesized Tailor-Made Gemini Surfactants for Application in Enhanced Oil Recovery. J. Mol. Liq. 2018, 258, 211–224.

(7) Shakil Hussain, S. M.; Kamal, M. S.; Murtaza, M. Effect of Aromatic Spacer Groups and Counterions on Aqueous Micellar and Thermal Properties of the Synthesized Quaternary Ammonium Gemini Surfactants. J. Mol. Liq. 2019, 296, 111837.

(8) Ansari, F. A.; Quraishi, M. A. Inhibitive Effect of Some Gemini Surfactants as Corrosion Inhibitors for Mild Steel in Acetic Acid Media. Arabian J. Sci. Eng. 2011, 36, 11–20.

(9) Pakiet, M.; Kowalczyk, I. H.; Leiva Garcia, R.; Akid, R.; Brycki, B. E. Influence of Different Counterions on Gemini Surfactants with Polyamine Platform as Corrosion Inhibitors for Stainless Steel AISI 304 in 3 M HCl. J. Mol. Liq. 2018, 268, 832–831.

(10) Wang, X. The Inhibitive Effects of Gemini Imidazoline Surfactants on Copper in Hydrochloric Acid Solution. Int. J. Electrochem. Sci. 2020, 15, 4338–4351.

(11) Sudheer, S.; Quraishi, M. A. The Corrosion Inhibition Effect of Aryl Pyrazole Pyridines on Copper in Hydrochloric Acid System: Computational and Electrochemical Studies. RSC Adv. 2015, 5, 41923–41933.

(12) Singh Rajan, D.; Shiv, D.; Malik, D. Surfactants as Corrosion Inhibitors for Stainless Steel in HCl Solution. J. Pure Appl. Sci. Technol. 2011, 1, 23–35. NLSS 2011

(13) Bhadani, A.; Kataria, H.; Singh, S. Synthesis, Characterization and Comparative Evaluation of Phenoxyl Ring Containing Long Chain Gemini Imidazolium and Pyridinium Amphiphiles. J. Colloid Interface Sci. 2011, 361, 33–41.
Khamis, E. The Effect of Temperature on the Acidic Dissolution of Steel in the Presence of Inhibitors. *Corrosion* 1990, 46, 476-484.

Vasudha, V. G.; Priya, S. K. Polyalthia Longifolia as a Corrosion Inhibitor for Mild Steel in HCl Solution. *Res. J. Chem. Sci.* 2013, 3, 21-26.

Mostafa, M. A.; Ashmawy, A. M.; Reheim, M. A. M. A.; Bedair, M. A.; Abuelela, A. M. Molecular Structure Aspects and Molecular Reactivity of Some Triazole Derivatives for Corrosion Inhibition of Aluminium in 1 M HCl Solution. *J. Mol. Struct.* 2021, 1236, 130292.

Alarfaji, S. S.; Ali, I. H.; Bani-Fwaz, M. Z.; Bedair, M. A. Synthesis and Assessment of Two Malonyl Dihydrazide Derivatives as Corrosion Inhibitors for Carbon Steel in Acidic Media: Experimental and Theoretical Studies. *Molecules* 2021, 26, 3183.

Ashmawy, A. M.; Mostfa, M. Study of Eco-Friendly Corrosion Inhibition for Mild Steel in Acidic Environment. *Egypt. J. Chem.* 2021, 64, 1285.

Abdallah, M.; Sobhi, M.; Altass, H. M. Corrosion Inhibition of Aluminum in Hydrochloric Acid by Pyrazinamide Derivatives. *J. Mol. Liq.* 2016, 223, 1143-1150.

Chugh, B.; Singh, A. K.; Chaouiuki, A.; Salghi, R.; Thakur, S.; Pani, B. A Comprehensive Study about Anti-Corrosion Behaviour of Pyrazine Carboxyhydrazide: Gravimetric, Electrochemical, Surface and Theoretical Study. *J. Mol. Liq.* 2020, 299, 112160.

Zakaria, K.; Abbas, M. A.; Bedair, M. A. Herbal Expired Drug Bearing Glycosides and Polysaccharides Moieties as Green and Cost-Effective Oilfield Corrosion Inhibitor: Electrochemical and Computational Studies. *J. Mol. Liq.* 2022, 352, 118689.

Zhang, F.; Li, X.; Deng, S.; Tang, M.; Du, G. Amphoteric Surfactant of Octadecyl Dimethyl Betaine as an Efficient Corrosion Inhibitor for Cold Rolled Steel in Phosphoric Acid Solution. *J. Mater. Res. Technol.* 2021, 15, 7050-7069.

El-Sabbah, M. M. B.; Bedair, M. A.; Abbas, M. A.; Fahmy, A.; Hassaballa, S.; Mostafa, A. A. Synergistic Effect between Natural Honey and 0.1 M KI as Green Corrosion Inhibitor for Steel in Acid Medium. *Z. Phys. Chem.* 2019, 233, 627-649.

Mabille, I.; Bertrand, A.; Sutter, E. M. M.; Fiaud, C. Mechanism of Dissolution of a Cu–13Sn Alloy in Low Aggressive Conditions. *Corros. Sci.* 2003, 45, 855-866.

Bedair, M. A.; Abuelela, A. M.; Zoghaib, W. M.; Mohamed, T. A. Molecular Structure, Tautomer’s, Reactivity and Inhibition Studies on 6-Methyl-2-Thioxouracil for Mild Steel Corrosion in Aqueous HCl (1.00 M): Experimental and Theoretical Studies. *J. Mol. Struct.* 2021, 1244, 130927.

Bedair, M. A.; Alosaimi, E. H.; Melhi, S. A. Study of the Inhibitive Effect for Corrosion of Steel in 1.0 M HCl Using a New Nonionic Surfactant Based on Coumarin Moiety: Chemical, Electrochemical and Quantum Mechanics Calculations. *J. Adhes. Sci. Technol.* 2021, 1–31.

Biesinger, M. C.; Lau, L. W. M.; Gerson, A. R.; Smart, R. S. C. Resolving Surface Chemical States in XPS Analysis of First Row Transition Metals, Oxides and Hydroxides: Sc, Ti, V, Cu and Zn. *Appl. Surf. Sci.* 2010, 257, 887-898.

Akçül, F. A.; Akçül, G.; Yıldırım, N.; Uналın, H. E.; Turan, R. Influence of Thermal Annealing on Microstructural, Morphological, Optical Properties and Surface Electronic Structure of Copper Oxide Thin Films. *Mater. Chem. Phys.* 2014, 147, 987-995.

Dehghani, A.; Mostafatabar, A. H.; Bahlakeh, G.; Ramezanzadeh, B.; Ramezanzadeh, M. Detailed-Level Computer Modeling Explorations Complemented with Comprehensive Experimental Studies of Quercetin as a Highly Effective Inhibitor for Acid-Induced Steel Corrosion. *J. Mol. Liq.* 2020, 309, 113035.