Corrosion Control of Carbon Steel in Water-Based Mud by Nanosized Metallo-Cationic Surfactant Complexes During Drilling Operations

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ABSTRACT: In this work, three nanometal complexes named cetyltrimethyammonium dibromodichloro zincate (CT-Zn), cetyltrimethyammonium dibromodichloro cuprate (CT-Cu), and cetyltrimethyammonium dibromodichloro manganesate (CT-Mn) were prepared, characterized, and evaluated as corrosion inhibitors for carbon steel in water-based mud (WBM). The chemical structure of the prepared complexes was confirmed by the use of Fourier transform infrared spectroscopy, Raman spectroscopy, elemental analysis, atomic absorption spectroscopy, dynamic light scattering, and thermogravimetric analysis techniques. The surface tension of the complexes was measured. The critical micelle concentrations and some of the surface properties were also determined. The compounds were evaluated as corrosion inhibitors for carbon steel in the prepared WBM using potentiodynamic polarization and weight loss methods during the static and dynamic conditions of the drilling operations. The results indicated that the prepared metal complexes showed high anticorrosion action as the inhibition efficiency increased gradually with the increase in the concentrations of the prepared complexes until it reached the maximum value (93.1%) at 300 ppm for CT-Cu. The order of inhibition efficiency of these inhibitors was as follows: CT-Cu > CT-Zn > CT-Mn. The polarization curves showed that these complexes acted as mixed-type inhibitors. According to the results, the adsorption of these compounds obeyed Langmuir adsorption isotherm. Surface analysis of the carbon steel samples was investigated using scanning electron microscopy, energy dispersive X-ray, and X-ray diffraction techniques. Rheological properties, gel strength, thixotropy, and filtration properties were also measured according to American Petroleum Institute specifications.

1. INTRODUCTION
Drilling fluid is one of the most critical components of the oil-well drilling operation. In some cases, the drilling fluid may represent the highest fraction of the overall cost of the drilling operation as it serves many purposes during the drilling operation. The functions of the drilling fluids include the removal of cuttings from the well, lubrication and cooling of drill bits, support of the stability of the hole, prevention of the influx of formation fluid into the well, and suspension of the cuttings when the circulation is interrupted. The selection of appropriate drilling fluid is essential for the successful drilling operation. It is classified into three main groups as water-based mud (WBM), oil-based mud (OBM), and gas-based mud (GBM). WBM contains freshwater, saltwater, or seawater as a continuous medium. GBM is the mud in which air or other gases is the continuous phase, while OBM is the mud in which the base fluid is diesel or synthetic oil with a mixture of solids and other chemicals as additives. WBM is the most suitable of all types and is widely used in the industry because it is significant and environmentally friendly. However, WBM is considered corrosive during the drilling process because it may be contaminated with corrosion accelerators such as oxygen, carbon dioxide, hydrogen sulfide, salts, and organic acids as shown in Figure 1. The corrosion of the drill bits, protective casing, drill string, and other related equipment is a serious problem that needs to be controlled. In order to reduce the corrosion caused by the WBM, the pH value of the mud should be kept above 7. Also, corrosion inhibitors can be used to control the corrosion of carbon steel in the oil industry so
that the WBM can be treated with corrosion inhibitors to mitigate the corrosion.9,10

Organic compounds containing heteroatoms such as nitrogen, sulfur, and oxygen are effective corrosion inhibitors because they can be adsorbed and block the active sites on the metal surface and therefore reduce the occurrence of corrosion.11 These organic inhibitors are mostly surface-active compounds as they contain two parts, one being hydrophobic (nonpolar) part and the other part being hydrophilic (polar). Typically, the hydrophilic head group is ionizable and has a strong affinity to water (polar solvent). The hydrophobic tail group, on the other hand, is usually a hydrocarbon (branched or linear). The head group can be adsorbed on the metal surface. As a result, protective layers are formed on the metal surface to protect the surface from corrosion in the acidic or corrosive medium.12

One of the most popular categories of surfactants is the cationic surfactant. Cationic surfactants have many uses; they can be used as fabric softeners and solid particle dispersants, as well as antiseptic agents in cosmetics. Cationic surfactant has various advantages, such as high inhibition efficiency, low cost, low toxicity, and ease of production. Most cationic surfactants are biologically active in that they can kill or inhibit the growth of many microorganisms. They can be used as corrosion inhibitors because they are positively charged and can be adsorbed on negatively charged surfaces.13,16

Cetyl trimethyl ammonium bromide (CTAB) used in this study is a cationic surfactant that is widely used because of its useful physical and chemical properties.17 CTAB is an effective corrosion inhibitor that can hinder the corrosion of metals because of the presence of long alkyl chain (16-carbon), positively charged quaternary ammonium head group (N+) with three methyl groups attached, and (Br−) ion in its structure. Such characteristics facilitate the adsorption process of CTAB molecules on the metal surface and thus protect the surface from corrosion.18 Fouda et al. investigated the corrosion inhibition behavior of CTAB and dodecyl trimethyl ammonium chloride (DTAC) for the metal in 0.5 M HCl acidic medium. The results showed the high inhibition efficiency of CTAB compared to DTAC, as CTAB gave 87.1 % inhibition efficiency at 8 × 10^{-4} and DTAC gave 86.5 % inhibition efficiency.19 Khamis et al. studied the inhibition performance of four cationic surfactants [CTAB, tetradecyl trimethyl ammonium bromide (TDTAB), dimethyl dioctadecyl trimethyl ammonium bromide (DDTAB), and dodecyl trimethyl ammonium bromide (DTAB)] in 0.1 H_{2}SO_{4} and found the high protection efficiency of CTAB relative to other cationic surfactants. CTAB achieved 94.8% inhibition efficiency at 5 × 10^{-4} M, TDTAB achieved 94.2% at 5 × 10^{-4} M, DDTAB achieved 90.7 % at 10 × 10^{-4} M, and DTAB achieved 85.3% at 5 × 10^{-4} M.20 Besides, it was reported in many research studies that CTAB has high corrosion inhibition properties as it was used to protect different metals such as Fe, Al, and Cu in various corrosive media.21−23

Nanoparticles are tiny particles that range between 1 and 100 nm in size and have unique physical and chemical properties.24 The use of corrosion inhibitor in nanosized gains importance because it possesses many advantages. These advantages include the high corrosion inhibition efficiency owing to the increased surface-to-volume ratio compared to microsized, and thus the number of active centers increases. These features lead to efficient chemical and physical adsorption of nanosized inhibitors on the metal surface and blocking of active sites. These nanoparticles possess other advantages such as low cost, low toxicity, and ease of production.25−27

Herein, three nanosized tetrahalometallate surfactant complexes based on CTAB have been prepared by the reaction of

Figure 1. Cross-section of the WBM during drilling operations.
different transition metal halides with CTAB. The metal halides used in the synthesis are ZnCl₂, CuCl₂, and MnCl₂, which are available at low cost. It is expected that the transition-metal complexes give high inhibition efficiency because of their larger size and compactness and the synergistic action of metal–organic blends. The prepared complexes have been investigated as corrosion inhibitors for the carbon steel in the prepared WBM through potentiodynamic polarization and weight loss methods. Our study includes the corrosion of carbon steel during the static and dynamic conditions of the drilling operation and the explanation of the corrosion protection mechanism. The surface properties of the prepared complexes have been studied. Besides, the research is extended to study the effect of these corrosion inhibitors as additives for the WBM.

2. RESULT AND DISCUSSION

2.1. Structure Characterization. The structures of the prepared complexes were characterized via Fourier transform infrared (FTIR) spectra, Raman spectra, microelemental analysis, and atomic absorption spectroscopy.

2.1.1. FTIR Spectra. FTIR spectrum of CT-Cu as a representative sample of the other complexes presented in Figure 2 exhibited an absorption band at 3014 cm⁻¹ that corresponds to the asymmetric stretching mode of C–H in the N⁺(CH₃)₃ group, while absorption bands at 2919 and 2850 cm⁻¹ correspond to the asymmetric and symmetric stretching modes of the CH₂ groups. The absorption band at 1468 cm⁻¹ corresponds to CH₂ bending (scissoring), while the band at 965 cm⁻¹ represents out-of-plane –CH vibration of –CH₃. The peak at 909 cm⁻¹ represents the stretching vibration mode of N’=CH₂, and the peak at 722 cm⁻¹ corresponds to the rocking mode of –CH₂ chain.

Figure 2. FTIR spectrum of the prepared nanosized metallo-cationic surfactant complexes (CT-Cu).

Figure 3. Raman spectrum of the prepared nanosized metallo-cationic surfactant complexes (CT-Cu).

Table 1. Microelemental Analysis and Atomic Absorption Data for the Nanosized Metallo-Cationic Surfactant Complexes

| compound | structure | M. Wt (g/mol) | carbon % | hydrogen % | nitrogen % | chloride % | bromide % | metal % |
|----------|-----------|---------------|----------|------------|------------|------------|-----------|---------|
|          |           | calc.        | found    | calc.       | found      | calc.       | found    | calc.    | found   |
| CT-Zn    | C₃₆H₃₈N₂Cl₂Br₂Zn | 865.18      | 52.75    | 52.63  | 9.79        | 9.74       | 3.23       | 3.19     | 8.20    | 8.14    | 18.47    | 18.34    | 7.56     | 7.48    |
| CT-Cu    | C₃₆H₃₈N₂Cl₂Br₂Cu | 863.35      | 52.86    | 52.74  | 9.81        | 9.76       | 3.24       | 3.21     | 8.22    | 8.13    | 18.51    | 18.39    | 7.36     | 7.27    |
| CT-Mn    | C₃₆H₃₈N₂Cl₂Br₂Mn | 854.74      | 53.40    | 53.28  | 9.91        | 9.83       | 3.27       | 3.20     | 8.30    | 8.21    | 18.70    | 18.57    | 6.42     | 6.32    |
2.1.2. Raman Spectra. Raman spectrum of CT-Cu as an illustrative specimen of the other complexes presented in Figure 3 displayed the subsequent stretching bands at 73.95, 124.09, and 224.3 cm$^{-1}$ for the CT$^{-}$Cu complex, which represent M$^{-}$X (M: metal and X: halogen) stretching frequencies for the [MX$_4$]$^{-2}$ anion. These findings are in good agreement with the characteristic bands of tetrahalometallate ion in the complex as previously reported. These bands indicate the formation of the complexes.

2.1.3. Microelemental Analysis and Atomic Absorption Spectroscopy. Table 1 illustrates the data of elemental analysis and atomic absorption spectroscopy for the prepared complexes. The values of the calculated and obtained data are in close agreement. Accordingly, the results indicate the formation of complexes in the stoichiometric ratio and their purity.

2.1.4. Thermogravimetric Analysis. The thermogravimetric analysis (TGA) diagram in Figure 4 indicates that the three prepared metal complexes have high thermal stability. CT-Zn is thermally more stable than other complexes. The decomposition of CT-Zn starts at 250 °C, while for CT-Mn, it starts at 220 °C, and for CT-Cu, it starts at 205 °C. The overall weight changes in CT-Zn, CT-Cu, and CT-Mn are 90.21, 88.41, and 85.69%, respectively.

2.1.5. Dynamic Light Scattering. Dynamic light scattering (DLS) is a technique performed to understand the particle size distribution of the prepared metal complexes. DLS measurement of CT-Cu as a representative sample of the complexes is presented in Figure 5. Other DLS curves of CT-Zn and CT-Mn are included in the Supporting Information (Figures S5 and S6). DLS results reveal the successful formation of the metal complexes in the nanosized. For each complex, the distribution of the particles has a main peak at a specific particle size diameter with area intensity (%) for the prepared complexes: CT-Cu = 13.54 nm (100% area intensity), CT-Mn = 58.77 nm (100% area intensity), and CT-Zn = 77.79 nm (100% area intensity). Size is a characteristic parameter for the prepared complexes. Figure 5 reveals the size distribution of complexes. The particle sizes are in the range of 11.7–15.69 nm for CT-Cu, 50.75–68.06 nm for CT-Mn, and 58.77–91.28 nm for CT-Zn. Similar observations have been reported for other metal complexes in the literature.

The DLS technique is used to calculate the polydispersity index (PDI) of prepared complexes. PDI determines the nanoparticle uniformity and describes the particle size.
The surface tension values vary linearly with the concentration of the parent surfactant. The surface tension of the complex at a concentration lower than the critical micelle concentration (cmc) is followed by a gradual reduction of the surface tension until the surface of the solution becomes fully occupied with surfactant molecules. After a certain concentration, the surfactant molecules tend to aggregate in the bulk solution and form micelles. This concentration is known as the critical micelle concentration (cmc). The surface tension at the cmc expresses the number of surfactant molecules located in unit area at the air–water interface. It has been reported that the cmc values increased by complexation because the cmc value at cmc is used to determine the value of effectiveness (πcmc) from the following equation:

\[
π_{cmc} = γ_o - γ_{cmc}
\]  

(1)

where γ_o is the surface tension of water without additives at 25 °C. The results of the effectiveness in Table 2 show that the effectiveness values increased by complexation. The most effective complex, which gives the greatest lowering in surface tension at the cmc region, is CT-Cu. Besides, the efficiency parameter (PC20) represents the concentration required to decrease the surface tension of water by 20 mN m⁻¹ and the ability of surfactants to adsorb at the air–water interface. PC20 was calculated by extrapolating from γ = 52 to the linear part before cmc. The results in Table 2 show that the efficiency increases with complexation because the efficiency of adsorption at interfaces increases with the increase in hydrophobicity.

Additional significant parameters, such as the maximum surface excess (Γ_max) and the minimum area per molecule (A_min) are measured. Γ_max expresses the number of surfactant molecules located in unit area at the air–water interface at cmc at 25 °C. A_min is the average area occupied by a single surfactant molecule at the air–water interface. It has been reported that Γ_max and A_min were calculated via the following Gibbs adsorption isotherm eqs 2 and 3:

\[
Γ_{max} = \frac{1}{2.303 \times RT} \left( \frac{dγ}{d\log C} \right)_T
\]  

(2)

\[
A_{min} = \frac{1}{N_AΓ_{max}} \times 10^{14}
\]  

(3)

where R is the universal gas constant, T is the absolute temperature, dγ/dlog C is the slope of γ versus log C profile in the steeper region, A_min is in nm², and N_A is the Avogadro’s number. The results in Table 2 reveal that CT-Cu has a high cmc value γcmc at cmc is used to determine the value of effectiveness (πcmc) from the following equation:

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π_{cmc} = γ_o - γ_{cmc}
\]  

(1)
The maximum value compared to CT-Zn and CT-Mn as CT-Cu molecules tend to adsorb on the surface and then form micelles directly at low concentration. Moreover, when $\Gamma_{\text{max}}$ increases, crowding occurs between complex molecules at the interface. This crowding causes a decrease in $A_{\text{min}}$ value because of the compactness of the complex molecules at the interface. Similar results of the surface properties for other metal complexes have been reported in the literature.34,37

2.3. Corrosion Inhibition Evaluation. 2.3.1. Open-Circuit Potential. It is essential to ensure that there is a

Figure 7. OCP measurements of the carbon steel in the prepared WBM without and with various doses of CT-Cu at 25 °C.

Figure 8. Anodic and cathodic Tafel curves for the carbon steel in the prepared WBM without and with various doses of CT-Cu at 25 °C.

Table 3. Electrochemical Polarization Parameters for Corrosion of the Carbon Steel Immersed in the Synthesized WBM without and with Various Doses of the Prepared Nanosized Metallo-Cationic Surfactant Complexes at 25 °C

| Inhibitors | Conc. (ppm) | $E_{\text{corr}}$ (mV vs SCE) | $i_{\text{corr}}$ ($\mu$A cm$^{-2}$) | $\beta_a$ (mV dec$^{-1}$) | $\beta_c$ (mV dec$^{-1}$) | $R_p$ (Ω cm$^2$) | $\eta_p$ % |
|------------|-------------|-----------------------------|--------------------------------|-----------------------------|-----------------------------|-----------------|-----------|
| Blank      | 0           | $-677.7 \pm 6.2$            | $123.4 \pm 1.3$               | $135.2 \pm 1.9$            | $118.7 \pm 1.9$            | 307.9           |           |
| CT-Mn      | 25          | $-606.8 \pm 5.3$            | $72.5 \pm 1.1$               | $123.4 \pm 2.1$            | $139.4 \pm 2.4$            | 500.6           | 0.412     |
|            | 50          | $-627.8 \pm 4.1$            | $60.9 \pm 0.8$               | $95.5 \pm 1.3$             | $160.1 \pm 1.6$            | 637.7           | 0.506     |
|            | 100         | $-613.9 \pm 3.6$            | $40.9 \pm 1.4$               | $111.7 \pm 1.6$            | $107.3 \pm 3.1$            | 784.95          | 0.668     |
|            | 200         | $-645.4 \pm 4.4$            | $26 \pm 0.9$                 | $106.9 \pm 2.4$            | $110.2 \pm 1.8$            | 1183.4          | 0.789     |
|            | 300         | $-691.2 \pm 4.1$            | $14.1 \pm 1.1$               | $168.1 \pm 1.7$            | $153.8 \pm 1.2$            | 2999.3          | 0.885     |
| CT-Zn      | 25          | $-645.3 \pm 3.3$            | $71 \pm 0.9$                 | $98.2 \pm 1.3$             | $174.4 \pm 2.6$            | 567.3           | 0.424     |
|            | 50          | $-607.1 \pm 5.7$            | $52.9 \pm 1.5$               | $102.1 \pm 0.9$            | $168.6 \pm 3.4$            | 754.4           | 0.571     |
|            | 100         | $-671.5 \pm 6.1$            | $35.1 \pm 1.9$               | $135.4 \pm 1.2$            | $110.5 \pm 1.9$            | 930.2           | 0.715     |
|            | 200         | $-732.6 \pm 6.6$            | $20.2 \pm 1.4$               | $169.7 \pm 1.7$            | $93.9 \pm 1.4$             | 1609            | 0.836     |
|            | 300         | $-713.5 \pm 5.1$            | $11.3 \pm 1.3$               | $1093.2 \pm 2.8$           | $142.7 \pm 0.9$            | 3909            | 0.908     |
| CT-Cu      | 25          | $-621.4 \pm 6.3$            | $68.7 \pm 1.1$               | $90.2 \pm 2.6$             | $196.8 \pm 2.7$            | 610.1           | 0.443     |
|            | 50          | $-675.3 \pm 4.3$            | $51 \pm 0.9$                 | $83.7 \pm 2.1$             | $160.5 \pm 2.2$            | 836             | 0.586     |
|            | 100         | $-636.8 \pm 4.4$            | $29.3 \pm 1.4$               | $101.4 \pm 2.4$            | $212.1 \pm 1.5$            | 1117.2          | 0.762     |
|            | 200         | $-701.3 \pm 3.7$            | $17.1 \pm 1.6$               | $145.3 \pm 1.7$            | $168.3 \pm 1.1$            | 2530.6          | 0.861     |
|            | 300         | $-657.7 \pm 5.9$            | $8.4 \pm 1.3$                | $134.8 \pm 1.5$            | $150.2 \pm 0.9$            | 4731.3          | 0.931     |

$^a$Tafel parameters as mean values ± standard deviation as the error values.
steady-state potential on the working electrode surface before carrying out the potentiodynamic polarization test. The open-circuit potential (OCP) of the carbon steel electrode is a parameter that depends on the immersion time in the test solution.\textsuperscript{38} Measurements were performed until the steady-state potentials were achieved, at which the equilibrium state occurs between the oxidation current ($i_{\text{oxd}}$) and reduction current ($i_{\text{red}}$). Figure 7 exhibits the variation of OCP ($E_{\text{OCP}}$) as a function of the immersion time in the absence and presence of CT-Cu inhibitor at different doses in the WBM at 25 °C. Other plots of CT-Zn and CT-Mn are included in the Supporting Information (Figures S7 and S8). It was observed that the OCP for all tests inclines toward more negative values. This behavior occurred owing to the dissolution of the preimmersion air-formed oxide film on the electrode surface.\textsuperscript{39} After adding different doses of CT-Cu inhibitor to the prepared WBM, slight positive and negative shifts in the $E_{\text{OCP}}$ values occurred, which could be attributed to the formation of a protective film on the electrode surface.\textsuperscript{40} This will be discussed in more detail later. The immersion time in the corrodéd solution was 60 min to reach stable OCP values, and then the potentiodynamic polarization test was performed.

2.3.2. Potentiodynamic Polarization Measurements.

Figure 8 represents the anodic and cathodic Tafel plots of carbon steel in the prepared WBM without and with various concentrations of CT-Cu nanoparticles at 25 °C. Other Tafel plots of CT-Zn and CT-Mn are included in the Supporting Information (Figures S9 and S10). Polarization parameters including corrosion current density ($i_{\text{corr}}$), corrosion potential ($E_{\text{corr}}$), and anodic and cathodic Tafel slopes ($\beta_a$, $\beta_c$) were determined by extrapolating the anodic and cathodic plots and are listed in Table 3. From corrosion current density values, the surface coverage value ($\theta$) and corrosion inhibition efficiency ($\eta_i$) of prepared complexes were calculated via the following equation\textsuperscript{41,42}

$$\eta_i = \theta = \frac{i_{\text{corr}} - i_{\text{corr}}^0}{i_{\text{corr}}^0} \times 100$$

(4)

where $i_{\text{corr}}$ and $i_{\text{corr}}^0$ represent corrosion current densities without and with nanometallo-cationic surfactant complexes, respectively. Tafel polarization curves show that the presence of these complexes in the WBM decreases the corrosion reaction of carbon steel compared to the uninhibited mud (blank). It is clearly observed that the increase in the concentration of these complexes from 25 to 300 ppm is followed by a gradual decrease in the corrosion current density. Consequently, the degree of surface coverage and the corrosion inhibition efficiency increase with the increase in the concentration of the prepared complexes. These findings may be attributed to the adsorption of these complex molecules on the carbon steel electrode surface immersed in WBM and the formation of a protective layer on the electrode surface.\textsuperscript{43} It has been reported in other studies that the presence of corrosion inhibitors in corrosive media hindered anodic and cathodic reactions on the metal surface, and as a result, the corrosion current density decreased.\textsuperscript{44,45}

The data in Table 3 show that the addition of various concentrations of the different complexes slightly changed the anodic and cathodic Tafel slopes ($\beta_a$, $\beta_c$). This indicates that the inhibitors decrease the corrosion process without changing the reaction mechanism. It is noted that the maximum shift in corrosion potential ($E_{\text{corr}}$) after the addition of inhibitors is ±70.8 mV (within ±85 mV range). Moreover, the presence of these inhibitors in the test solution shifts the corrosion current values corresponding to cathodic and anodic Tafel lines to lower values concerning the blank curve. Accordingly, the prepared complexes act as mixed-type inhibitors. This means that the inhibitors can decrease the anodic dissolution of carbon steel and inhibit the cathodic reactions.\textsuperscript{39,46–48}

The prepared WBM was slightly acidic medium (pH = 6), so the possible cathodic reactions are oxygen reduction ($\text{H}_2\text{O} + \text{O}_2 + 4\text{e}^- \rightarrow 4\text{OH}^-$) in addition to hydrogen evolution ($2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$).\textsuperscript{49}

The data in Table 3 reveal that the corrosion inhibition efficiency of the prepared inhibitors increased in the following order: CT-Cu $>$ CT-Zn $>$ CT-Mn. The variation in inhibition effectiveness between these inhibitors is due to the difference in the electronegativity of the transition-metal ions. These ions have the following electronegativity, Cu$^{2+} = 1.90$, Zn$^{2+} = 1.65$, and Mn$^{2+} = 1.55$, according to Allen scale.\textsuperscript{50} Hence, the prepared complexes of these ions with the cationic surfactant (CTAB) are polar in kind. The polarity increases with the increase in the electronegativity of metal ions, so the adsorption of the prepared inhibitors on the metal surface increases. As a result, the inhibition efficiency increases with the increase in the electronegativity of these ions. The effect of the electronegativity of metal ions on the corrosion inhibition efficiency was reported in other previous studies.\textsuperscript{51,52}

Table 4 illustrates the comparison between the inhibition efficiency of the prepared complex CT-Cu and some other reported inhibitors for corrosion in drilling fluids and other media.\textsuperscript{5,53–57}

### 2.3.3. Weight Loss Method under Static Conditions.

In the static condition of the prepared WBM at 25 °C, the corrosion rate ($C_{\text{corr}}$) of the carbon steel specimens is calculated from the equation:\textsuperscript{59}

$$C_{\text{corr}} = \frac{m}{A \times t}$$

where $m$ is the mass loss, $A$ is the area of the specimen, and $t$ is the time of exposure.
The corrosion inhibition efficiency of the investigated complexes is in the following order, CT-Cu > CT-Zn > CT-Mn, which follows the same order as in potentiodynamic polarization measurements. Therefore, the rate of corrosion of carbon steel specimens declines from 0.0759 (mg cm\(^{-2}\) h\(^{-1}\)) to 0.0099, 0.0083, and 0.0065 for CT-Mn, CT-Zn, and CT-Cu, respectively at 300 ppm.

2.3.4. Weight Loss Method under Dynamic Conditions. In the dynamic test, the roller oven was used to simulate the flow of prepared WBM and investigate the effects of temperature, pressure, and rotational conditions on the corrosion of carbon steel and the corrosion inhibition efficiency of complexes. The results in Table 6 show that the corrosion rate in the case of dynamic conditions is more severe than that in the static conditions because of the effects of temperature, pressure, and rotational speed.\(^{60}\) The inhibition efficiency of the prepared complexes at their successful concentrations (300 ppm) in WBM is listed in Table 6. The results indicate that the corrosion rate of the specimens decreases in the presence of inhibitors, and the inhibition efficiencies are 77.3, 74.4, and 72.7% for CT-Cu, CT-Zn, and CT-Mn, respectively.

2.4. Adsorption Isotherm. The adsorption isotherms are performed to determine the mechanism of corrosion inhibition and provide an explanation of the interaction between the inhibitor molecules themselves and the carbon steel surface in WBM. Inhibitors reduce the corrosion of carbon steel by the adsorption of inhibitor molecules at the active sites of the metal surface.\(^{61}\) Two forms of adsorption can occur on the carbon steel surface: physical adsorption and chemical adsorption. The physical adsorption results from electrostatic interaction between the charged inhibitors and the charged carbon steel surface. On the other hand, the chemical adsorption process results from a coordination bond formed between the inhibitor molecules and the carbon steel surface through charge transfer.\(^{61,62}\) The degree of surface coverage values (\(\theta\)) obtained from the weight loss measurements under static conditions are used to be fitted with different models of adsorption isotherms such as Langmuir, Frumkin, Freundlich, Temkin, and Flory–Huggins. The results reveal that the adsorption process of inhibitors is in agreement with the Langmuir adsorption isotherm that is given by the equation\(^{63}\)

\[
\frac{C_{\text{inh}}}{\theta} = \frac{1}{K_{\text{ads}}} + C_{\text{inh}}
\]

where \(C_{\text{inh}}\) represents the molar concentration of the investigated inhibitors and \(K_{\text{ads}}\) is the standard equilibrium constant of the adsorption process and calculated from the reciprocal of the intercept. Figure 9 shows the linear relationship via plotting \(C_{\text{inh}}/\theta\) versus \(C_{\text{inh}}\). The slopes of these straight lines are around 1. The regression coefficients are close to unity (\(r^2 > 0.9949\)). These results show that the adsorption process of inhibitors on the carbon steel surface is in agreement with Langmuir adsorption isotherm.\(^{64}\) The

Calculation of the average weight loss for the carbon steel under static conditions are included in the Supporting Information (Table S2). Results in Table 5 reveal that the presence of inhibitors in the prepared WBM reduces the corrosion rate of carbon steel. It is clear that the degree of surface coverage and the inhibition efficiency gradually increase with the increase in the concentration of inhibitors until it reaches 91.3% at 300 ppm of CT-Cu. The anticorrosion efficiency is attributed to the adsorption of inhibitor molecules on the carbon steel surface, which contributes to the formation of a protective layer on the steel surface. As a result, this protective layer reduces the contact between the metal surface and the corrosive species in the prepared WBM.\(^{59}\)

### Table 5. Weight Loss Results under Static Conditions for Corrosion of the Carbon Steel Immersed in the Prepared WBM without and with Various Doses of the Prepared Nanosized Metallo-Cationic Surfactant Complexes at 25 °C"\(^4\)

| inhibitors | conc. (ppm) | weight loss (mg) | corrosion rate \((C_{\text{th}})\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\theta\) | \(\eta_{\%}\) |
|------------|-------------|-----------------|---------------------------------|------|---------|
| blank      | 0.0         | 472.5 ± 5.29    | 0.0759                          |      |         |
| CT-Mn      | 25          | 292.4 ± 4.35    | 0.0469                          | 0.381| 38.1    |
|            | 50          | 243.5 ± 5.56    | 0.0339                          | 0.485| 48.5    |
|            | 100         | 166.4 ± 4.35    | 0.0267                          | 0.648| 64.8    |
|            | 200         | 112.4 ± 4.58    | 0.0181                          | 0.762| 76.2    |
|            | 300         | 62.3 ± 3.60     | 0.0099                          | 0.868| 86.8    |
| CT-Zn      | 25          | 281.8 ± 4.33    | 0.0452                          | 0.404| 40.4    |
|            | 50          | 223.5 ± 5.29    | 0.0355                          | 0.527| 52.7    |
|            | 100         | 143.8 ± 4.4     | 0.0233                          | 0.697| 69.7    |
|            | 200         | 87.8 ± 3.60     | 0.0139                          | 0.815| 81.5    |
|            | 300         | 52.4 ± 4.35     | 0.0083                          | 0.889| 88.9    |
| CT-Cu      | 25          | 274.9 ± 4.58    | 0.0444                          | 0.419| 41.9    |
|            | 50          | 214.6 ± 3.60    | 0.0334                          | 0.546| 54.6    |
|            | 100         | 128.8 ± 3.60    | 0.0202                          | 0.728| 72.8    |
|            | 200         | 80.8 ± 4.35     | 0.0112                          | 0.83  | 83      |
|            | 300         | 41.8 ± 4.58     | 0.0065                          | 0.913| 91.3    |

"Reported results weight loss as mean ± standard deviation as error values.

### Table 6. Weight Loss Results under Dynamic Conditions for Carbon Steel Specimens Immersed in the Prepared WBM without and with Successful Concentrations of the Prepared Nanosized Metallo-Cationic Surfactant Complexes

| corrosion conditions | inhibitors | conc. (ppm) | weight loss (mg) | corrosion rate \((C_{\text{th}})\) (mg cm\(^{-2}\) h\(^{-1}\)) | \(\theta\) | \(\eta_{\%}\) |
|----------------------|------------|-------------|-----------------|---------------------------------|------|---------|
| 95 °C, 100 psi, 200 rpm | Blank      | 0.0         | 1112            | 0.178                           |      |         |
|                      | CT-Mn      | 300         | 303.5           | 0.0488                          | 0.727| 72.7    |
|                      | CT-Zn      | 300         | 284.6           | 0.0457                          | 0.744| 74.4    |
|                      | CT-Cu      | 300         | 252.4           | 0.0406                          | 0.773| 77.3    |
parameters obtained from different models of adsorption isotherms are recorded in the Supporting Information (Figures S11–S14) (Tables S3–S6). The standard free energy of adsorption ($\Delta G_{ads}$) is obtained from the equilibrium constant of adsorption ($K_{ads}$) by the following equation:

$$\Delta G_{ads} = -RT \ln (55.5K_{ads})$$  \hspace{1cm} (8)$$

where $R$ represents the universal gas constant, $T$ is the absolute temperature, and 55.5 is the concentration of water expressed in the molar concentration. The values of $K_{ads}$ and $\Delta G_{ads}$ were calculated and are tabulated in Table 7. The results reveal that the high $K_{ads}$ values signify strong adsorption of the inhibitors on the carbon steel surface and hence better inhibition efficiency. $K_{ads}$ values of the prepared complexes increase in the sequence $\text{CT-Cu} > \text{CT-Zn} > \text{CT-Mn}$. Also, the negative values of $\Delta G_{ads}$ indicate that the adsorption of the inhibitor molecules is a spontaneous process, and the layer formed on the surface is stable.\(^6\) Generally, the $\Delta G_{ads}$ values around $-20$ kJ mol\(^{-1}\) or higher indicate physical adsorption. However, those around $-40$ kJ mol\(^{-1}\) or lower are associated with chemical adsorption, as previously reported in the literature.\(^7\)\(^8\)

Table 7. Fitting Parameters Obtained from the Adsorption Isotherms of the Prepared Nanometal Complex Inhibitors on the Carbon Steel Surface in the Prepared WBM at 25 °C

| Inhibitor | Regression Coefficient ($R^2$) | Slope | Intercept | $K_{ads}$ (L mol\(^{-1}\)) | $-\Delta G_{ads}$ (kJ mol\(^{-1}\)) |
|----------|-------------------------------|-------|-----------|-----------------------------|-------------------------------|
| CT-Mn    | 0.9949                        | 1.0136| 0.0572    | 17482.52                    | 34.15                         |
| CT-Zn    | 0.9987                        | 0.9951| 0.0489    | 20449.90                    | 34.54                         |
| CT-Cu    | 0.9984                        | 0.9755| 0.0467    | 21413.28                    | 34.67                         |

Figure 9. Langmuir adsorption isotherm model of the prepared nanometal complex inhibitors on the carbon steel in the synthesized WBM without and with various doses at 25 °C.

The formation of the protective layer owing to the adsorption of inhibitor molecules is confirmed by energy dispersive X-ray (EDX) analysis. In Figure 10a, the EDX spectrum of the polished specimen shows the prominent Fe peak. In Figure 10b, the EDX result of the specimen in the uninhibited solution shows the appearance of O and Fe peaks, which indicates the presence of iron oxides in solution. These results indicate that the oxide film covered the carbon steel surface in the absence of the inhibitor. In the presence of the inhibitor, EDX in Figure 10c displays a decrease in the O peak and the appearance of N, Cu, and C peaks, indicating the adsorption of CT-Cu molecules on the carbon steel surface and the formation of a protective film. These surface analysis results are consistent with the reported literature.\(^5\)\(^4\)\(^6\)\(^4\)\(^6\)\(^7\)

X-ray diffraction (XRD) analysis was performed to determine the nature of the protective film and corrosion products formed over the carbon steel surface in the absence and presence of CT-Cu at 300 ppm in the test solution. Figure 11a reveals the XRD patterns of the metal surface immersed in the uninhibited WBM (blank). The peaks indicate the formation of Fe-oxides ($\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$) and Fe-carbonates ($\text{FeCO}_3$), which are present in the solution as corrosion products.\(^7\)\(^2\) Furthermore, Figure 11b shows the XRD patterns for the metal surface immersed in WBM in the presence of CT-Cu at 300 ppm. It is observed that the peaks of corrosion products reveal a noticeable decrease in the intensity compared to those that appeared for the uninhibited surface. Meanwhile, the increase in the intensity of the Fe peaks is noted. These data indicated that the inhibitor molecules had adsorbed on the steel surface. As a result, the adsorbed molecules isolate the surface from the corrosive medium and thereby resist the formation of corrosion products. These observations are in agreement with the previously reported literature.\(^7\)\(^3\)\(^4\)\(^7\)

SEM, EDX, and XRD analyses indicate the anticorrosion behavior of the prepared CT-Cu, consistent with the potentidynamic polarization and weight loss results. As previously mentioned, the main protection mechanism is due to the formation of a protective layer made up of the adsorbed CT-Cu molecules on the steel surface. This protective layer is smooth and compact and can isolate the carbon steel surface from corrosive attacks, while in the absence of the inhibitor,
the oxide layer formed on the untreated carbon steel is a corrosion product that is porous and rough and provides inferior protection. These observations make it clear that the corrosion rate of carbon steel decreased in the presence of the inhibitor. The corrosion rate in the absence of the inhibitor was 0.0759 (mg cm$^{-2}$ h$^{-1}$). With the addition of different concentrations of CT-Cu from 25–300 ppm, the corrosion rate gradually decreased until it reached 0.0065 (mg cm$^{-2}$ h$^{-1}$) at 300 ppm.

2.6. Inhibition Mechanism. The results reveal that the addition of CT-Cu, CT-Zn, or CT-Mn to the prepared WBM decreases the corrosion rate of carbon steel. The corrosion inhibition of carbon steel results from the adsorption of inhibitor molecules on the metal surface. The adsorption process may be physical or chemical. The physical adsorption occurs by electrostatic interaction between the charged inhibitor and the charged metal surface, while the chemical adsorption occurs by a coordination bond between the vacant d-orbitals of Fe and a lone pair of electrons in heteroatoms (N).

The chemical structure of the prepared complex molecule has two alkyl chains and two quaternary nitrogen atoms –N$^\text{+}$. The role of the counter anions (MBr$_2$Cl$_2$)$^{-2}$ in the adsorption of the prepared complex is an important factor, as shown in Scheme 1. The positively charged carbon steel surface becomes negatively charged through the adsorption of counter anions (MBr$_2$Cl$_2$)$^{-2}$. Consequently, electrostatic attraction occurs between the positive charge on the two quaternary nitrogen atoms (N$^\text{+}$) and the negative carbon steel surface to form a protective layer on the metal surface where the anions are sandwiched between the positively charged part on the complex and the metal surface. In addition, it may be considered that the cationic part of the prepared complex could be directly adsorbed on the cathodic sites of the mild

Figure 10. SEM and EDX analyses of the carbon steel surface. (a) Polished sample, (b) after immersion in the prepared WBM for 168 h, and (c) after immersion in the prepared WBM containing 300 ppm of CT-Cu for 168 h.
steel surface, and as a result, the cathodic reactions are inhibited. A coordination bond could be formed between the free electron pairs of nitrogen and the vacant d-orbital of Fe, so the reactions of anodic metal dissolution are inhibited. Besides, the presence of two long alkyl chains in the complex molecule can increase the corrosion inhibition by increasing the adsorption of inhibitors on the carbon steel and keeping the surface away from the corrosive medium. It could be emphasized that the large size of the prepared complex, its complexity, and its high molecular weight can also lead to greater corrosion inhibition.

2.7. Evaluation of the Successful Concentration of the Prepared Nanosized Metallo-Cationic Surfactant Complex Inhibitors as Additives for the Synthesized WBM. 2.7.1. Rheological Properties. The addition of the prepared complexes to the synthesized WBM was primarily intended to inhibit corrosion. However, the rheological properties of this mud must be investigated. Figure 12 shows the rheological properties of the synthesized WBM [plastic viscosity (PV), yield point (YP), and apparent viscosity (AV)] before and after adding the inhibitors at the concentration (300 ppm) that gave a high corrosion inhibition efficiency. The results show that the addition of these complexes to the mud does not negatively affect the rheological properties. The properties of the mud without and with the inhibitors are compatible with American Petroleum Institute (API) specifications.

2.7.2. Gel Strength and Thixotropy. Figure 13 shows the gel strength and thixotropy properties of the prepared WBM before and after the addition of the successful concentration (300 ppm) of the inhibitors that gave a high corrosion inhibition efficiency. It is observed from Figure 13 that the addition of these complexes to the prepared WBM has a slight effect on the gel strength ($G_{10s}$), gel strength ($G_{10min}$), and thixotropy.

2.7.3. Filtration Properties. The filter loss results of the prepared WBM before and after adding the successful concentration (300 ppm) of the inhibitors are illustrated in Figure 14. A slight improvement in the results of the filter loss was observed after the addition of the corrosion.

3. CONCLUSIONS

The main outputs of the present study can be summarized in the following points:

1. Nanosized dibromodichlorometallate cetyltrimethylammonium complexes (CT-Zn, CT-Cu, and CT-Mn) were successfully prepared and then characterized by microelemental analysis, atomic absorption, TGA, DLS, and FTIR and Raman spectroscopies.
2. The corrosion inhibition of the carbon steel in the prepared WBM was evaluated under static and dynamic conditions during operation processes. The obtained results revealed that the corrosion rate of carbon steel in the presence of the prepared complexes inhibitors decreased because of the formation of a protective layer on the carbon steel by adsorption.

3. The obtained results revealed that the order of corrosion inhibition efficiency of these complexes was CT-Cu > CT-Zn > CT-Mn because the electronegativity of this transition metal was increased in the following order: Cu$^{2+}$ > Zn$^{2+}$ > Mn$^{2+}$.

4. Polarization measurements indicate that the corrosion current density is reduced by the addition of the prepared complexes, and these compounds acted as mixed-type inhibitors. The obtained results indicate that the prepared inhibitors inhibit both anodic and cathodic reactions without affecting the corrosion mechanism.

5. The adsorption of these compounds on the carbon steel surface obeyed Langmuir adsorption isotherm. The
negative sign of $\Delta G_{ads}$ indicated the spontaneity of the adsorption process.

6. SEM, EDX, and XRD analyses declared that the inhibitor molecules adsorb on the CR surface and form a protective layer, which isolates the surface from the corrosive species.

7. The rheological properties, gel strength, thixotropy, and filter loss of the prepared WBM before and after the addition of the successful concentration of the complexes are compatible with the API standard.

4. MATERIALS AND EXPERIMENTAL PROCEDURES

4.1. Chemicals and Instruments. CTAB was purchased from Alfa Aesar, Germany. Zinc chloride anhydrous, copper chloride anhydrous, manganese chloride anhydrous, and sodium carbonate were obtained from Aldrich, USA. Bentonite and barite were purchased from Baroid Co. Egypt. Ethanol, hydrochloric acid, diethyl ether, and acetone were obtained from ADWIC, Egypt. All chemicals were utilized without any purification.

Instruments used in this study included a Nicolet iS10 FT-IR spectrometer at wavenumbers of 4000−500 cm$^{-1}$. The Raman spectra were recorded using a dispersive Raman microscope with a laser source 322 nm and scanned in a range of 5000−0 cm$^{-1}$. Elemental analyses were performed using a Vario Elementar Instrument, USA. Atomic absorption spectroscopy was carried out using a PerkinElmer AS 90Plus Autosampler Analyst 100/300 AA. The TGA was performed in the air using the thermogravimetric analyzer (Q500, Germany). DLS measurements were carried out using a Malvern Zetasizer, NANO ZS (Malvern Instruments Limited, UK) equipped with a He−Ne laser operating at a wavelength of 633 nm.

4.2. Chemical Composition of Carbon Steel Specimens. The carbon steel samples used in this work have the following elemental composition (wt %): C, 0.027; Si, 0.1; Al, 0.35; Cu, 0.28; Ni, 0.16; Ti, 0.11; Mn, 1.51; V, 0.02; Nb, 0.93; Cr, 0.27; and remainder Fe.

4.3. Preparation of Nanosized Tetrahalometallate Cetyltrimethylammonium Complexes. Dibromodichlorometallate cetyltrimethylammonium complex was prepared by refluxing 0.02 mol (7.28 g) of CTAB with 0.01 mol (1.36, 1.34, or 1.23 g) of anhydrous ZnCl$_2$, CuCl$_2$, or MnCl$_2$ respectively, in 100 ml of ethanol as a solvent at 75 °C for 2 h. Afterward, ethanol was evaporated. The remaining dibromodichlorometallate cetrimonium complex was obtained and washed with diethyl ether. The reaction product was white crystals for CT-Zn, dark red crystals for CT-Cu, or pink crystals for CT-Mn. The synthesis process is illustrated in Scheme 2.

The nanosized dibromodichlorometallate cetyltrimethylammonium complex was prepared by grinding it in the ball mill [PM400-ball mill-RETSCH Planetar] at 350 rpm for 8 h. The chemical structure of these nanometallo-surfactant complexes was investigated by using spectrum analysis and analytical methods.

4.4. Surface Tension Tests. Surface tension ($\gamma$) measurements were determined using a De-Nouy Tensiometer (Kruss-K6 type) calibrated by bidistilled water to get the standard surface tension value of the bidistilled water (72.3 mN/m) at 25 °C. The prepared aqueous solutions of the nanosized dibromodichlorometallate cetrimonium complexes were
freshly prepared at doses ranging from (0.05–0.0000244 mol·L⁻¹ at 25 °C) and poured into a clean Teflon cup. The measurements were taken three times to get the average value.⁶₄,⁶₅

4.5. Preparation of WBM. WBM was prepared by mixing bentonite and other chemicals such as soda ash and barite with the formation water using a Hamilton Beach mixer for 20 min and was covered overnight. The testing mud in this study is WBM in which the deep oil well formation water is the continuous phase. This formation water presents in the reservoir rocks during the drilling process and contains a variety of dissolved organic and inorganic compounds, which can cause corrosion problems.⁶⁹ The components of the prepared WBM are that every 100 mL of the formation water contains 6.42 g of bentonite, 1.49 gm of barite, and 0.059–0.149 g of sodium carbonate.⁶⁷ The pH value of the prepared mud is about 6. CT-Zn, CT-Cu, or CT-Mn nanoparticles were added at various concentrations to be studied as corrosion inhibitors in the WBM.

4.6. Corrosion Inhibition Tests. During the drilling operation, the drilling mud cycle is always unstable and changes between dynamic and static states. The corrosion of carbon steel and inhibition was studied in the prepared WBM under static conditions at room temperature (25 °C). In the dynamic conditions, a roller oven and high-temperature high-pressure aging cells were used to simulate the flow and rotational conditions of the WBM at 200 rpm under high temperature (95 °C) and high pressure (100 psi). Nanosized dibromodichlorometallate cetrimonium complexes were evaluated as corrosion inhibitors for the carbon steel in the synthesized WBM under static conditions of the drilling operation by potentiodynamic polarization and weight loss methods and under dynamic conditions by the weight loss method.⁶⁰

4.6.1. Weight Loss Test under Static Conditions. Carbon steel specimens with dimensions of 7 × 2.0 × 0.5 cm were polished using a series of emery papers (400, 600, 800, 1000, and 1200) and then cleaned with distilled water and acetone. The carbon steel specimens were precisely weighed and were recorded (Wᵢ). The samples were immersed in 250 mL of the prepared WBM in the absence and presence of different concentrations of CT-Zn, CT-Cu, or CT-Mn nanoparticles for 168 h. After 168 h, the specimens were washed, dried, and accurately weighed. The weight loss was measured using the same equation as in the static technique.

4.6.3. Potentiodynamic Polarization Technique. Polarization tests were conducted at room temperature by using Voltalab 80 (Tacussel-Radiometer PGZ-402) equipment. A conventional 250 mL Pyrex glass cell contains three different electrodes. The reference electrode was a saturated calomel electrode, the working electrode was made of a carbon steel sample, and the counter electrode was of platinum. Before each experiment, the surface of the working electrode was polished with a series of fine grade emery papers up to 1200 grit and cleaned with distilled water and acetone and then immersed in the corroded solution for 60 min to reach the OCP. Electrochemical polarization curves were obtained by changing the electrode potential to ±300 mV relative to the steady-state potential with a scan rate of 1 mV/s. The experiments were repeated three times, and the corrosion parameter values were recorded as mean values ± standard deviation. The test solution was WBM without and with different concentrations of CT-Zn, CT-Cu, or CT-Mn at room temperature (25 °C).

4.6.4. Surface Characterization (SEM–EDX and XRD). The surface morphology of carbon steel specimens before and after the immersion of these specimens in the prepared WBM in the absence and presence of 300 ppm of CT-Cu for 168 h was examined using SEM. Also, the chemical configuration of the adsorbed film formed on these specimens was examined using a Zeiss Evo 10 instrument supplied with the EDX spectroscopy system. The beam accelerating voltage was 25 kV. The micrographs of the carbon steel specimens were taken at a magnification power of X 1700. Besides, XRD analysis was performed to detect the nature of a protective film formed on the carbon steel surface in the absence and presence of 300 ppm of CT-Cu in the test solution. XRD analysis was performed using an X-ray Diffractometer (X’Pert PRO PANalytical) 2θ from 5 to 70 with conditions at 40 kV, 40 mA, and Cu (Kα) radiation at a wavelength of 1.5406 Å.

4.7. Effects of the Successful Concentration of the Corrosion Inhibitors as Additives for the Prepared WBM. 4.7.1. Rheological Properties. Rheological properties of the WBM were measured before and after adding the successful concentration of the corrosion inhibitors (300 ppm). The PV, AV, and YP were measured according to API specification. The prepared WBM was poured into a cup and subjected to shear using a viscometer (Chan 35 model 3500). Dial readings at 600 and 300 rpm were recorded.⁶⁰ The rheological properties can be calculated through the following equations

\[
P V \text{ (cPa) } = \theta_{600} - \theta_{300} \tag{10}
\]

\[
AV \text{ (cPa) } = \frac{\theta_{600}}{2} \tag{11}
\]

\[
YP(1b/100ft^2) = \theta_{300} - PV \tag{12}
\]

where \(\theta_{600}\) and \(\theta_{300}\) are dial readings at 600 and 300 rpm, respectively.
4.7.2. **Gel Strength and Thixotropy.** The gel strength is the capability of the drilling mud to suspend the drilling cuttings when the circulation of mud stops. Using a rotating viscometer, the gel strength of the mud was determined. After that, the mud samples were stopped for 10 s and 10 min. The maximum deflection value at 3 rpm was recorded to be 10 s gel and 10 min gel. 81

4.7.3. **Filtration Properties.** The filtration properties of drilling mud should be controlled to reduce the fluid loss to permeable formations. When the pressure of the drilling mud is higher than the formation pressure, it enters the formations until a layer of solid particles forms on the walls of the well. The layer is known as a filter cake. The filtration properties of the WBM were determined using a standard filter press fann model 300 multichamber by filtration at 100 psi for 30 min. 81

### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.0c03653.

FTIR and Raman spectra of the prepared nanosized metallo-cationic surfactant complex (CT-Mn, CT-Zn); particle size distribution measurements by area and by number of the prepared nanosized metallo-cationic surfactant complex (CT-Mn, CT-Zn); OCP measurements of the carbon steel in the prepared WBM without and with various doses of CT-Mn and CT-Zn at 25 °C; anodic and cathodic Tafel curves for carbon steel in the prepared WBM without and with various doses of CT-Mn and CT-Zn at 25 °C; Flory–Huggin, Freundlich, Temkin, and Frumkin adsorption isotherm models of the prepared non-metal complex inhibitors on the carbon steel in the synthesized WBM without and with various doses at 25 °C; measurements of the average surface tension of the prepared nanosized metallo-cationic surfactant complexes at 25 °C based on three attempts; calculation of the average weight loss for the carbon steel under static conditions of the prepared WBM without and with successful concentrations of the prepared nanosized metallo-cationic surfactant complexes at 25 °C based on three attempts; and parameters obtained from Flory–Huggin, Freundlich, Temkin, and Frumkin adsorption isotherms of the prepared nanometal complex inhibitors on the carbon steel surface in the prepared WBM at 25 °C (PDF)

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#### Notes

The authors declare no competing financial interest.

#### ACKNOWLEDGMENTS

This work has been financially supported by the Egyptian Petroleum Research Institute (EPRI) fund. The authors are greatly thankful to EPRI fund and support.

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