

Inhibition of copper corrosion in acidic chloride solution by methionine combined with cetrimonium bromide/cetylpyridinium bromide

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Abstract Methionine (MET) is non-toxic and easily biodegradable so that it is an alternative corrosion inhibitor in the water treatment and industrial pickling process. In this article, the inhibition behavior of MET combined with cetrimonium bromide (CTAB) and cetylpyridinium bromide (CPB) for copper corrosion in 0.5 M HCl solution has been investigated by using the electrochemical impedance spectroscopy (EIS), cyclic voltammetry, and polarization curve methods. It shows that combination of MET with CTAB or CPB improves the inhibition performance effectively, and produces strong synergistic inhibition effect. The combined inhibitors suppress cathodic reaction and shift the corrosion potential toward more negative values. The mixed CTAB/MET has a better synergistic effect compared with the mixed CPB/MET. The quantum chemical parameters were calculated by PM3 semi-empirical quantum method. The better synergistic inhibition between MET and CTAB is attributed to their stronger electrostatic interaction.

Keywords Copper · Corrosion · Amino acids · Methionine · Synergistic effect

1 Introduction

Copper and its alloys are widely used in heating and cooling systems due to their good thermal conductivity and mechanical properties. Copper is a relatively noble metal, but it can suffer severe corrosion in aerated acidic media. Thus, its corrosion inhibition study has attracted much attention. The use of inhibitors is one of the most practical methods to protect copper from corrosion [1]. Benzotriazole (BTA) is well known as an effective inhibitor of copper corrosion in neutral/alkaline solutions [2–4]. However, in acidic solutions, BTA exists predominantly as a protonated species, BTAH^+ , which is less strongly chemisorbed on the copper surface as the metal is thought to be positively charged in an acidic solution [5]. This in turn leads to decrease the inhibition efficiency of BTA in an acidic solution. On the other hand, a very important disadvantage of BTA is its non-biodegradable property [6]. The lack of biodegradability causes the emission of industrial waste water carrying a large amount of hazardous material to public waterways [7]. Thus, it is necessary to find alternative inhibitors against copper corrosion in acidic media.

Amino acids are nontoxic, biodegradable, and relatively cheap. They are of particular importance as green corrosion inhibitors. The publications about the corrosion inhibition of some amino acids increase. El-Shafei et al. studied the effect of six α -amino acids for pitting corrosion of aluminum in chloride media [8]. They reported that all the six compounds shift the pitting potential (E_p) and the protection potential (E_{pp}) toward more positive values, and arginine was the more effective inhibitor. Morad examined the effect of amino acids containing sulfur on the corrosion of mild steel in phosphoric acid solutions containing Cl^- , F^- and Fe^{3+} ions [9]. He found that the binary mixtures of Cl^- or F^- with cysteine or methionine (MET) have the best

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inhibition efficiency exceeding 90%. However, Ramakrishnaiah measured the corrosion of steel in a number of amino acids in sodium chloride solutions at pH 8 [10]. He showed that while some amino acids have corrosion inhibition property, other such as aspartic acid actually seemed to accelerate corrosion. In no case was the corrosion rate reduced enough so that any of the amino acids could act as a practical corrosion inhibitor.

Inhibition of amino acids for copper corrosion in acidic media has also attracted many interests. Ismail reported that the maximum inhibition efficiency of cysteine can achieve at about 84%, and the presence of Cu^{2+} ion increases the inhibition efficiency to 89.52% for copper in neutral and acidic chloride solution [11]. Matos examined the effect of cysteine on the anodic dissolution of copper in sulfuric acid media [12]. They found that cysteine is an inhibitor for copper dissolution in sulfuric acid media at low anodic polarization, and its inhibitory effect is based on the formation of the cysteine-Cu (I) intermediate. Despite cysteine is a very interesting corrosion inhibitor for copper, there remains relatively few works directed toward the corrosion inhibition effect of other amino acids for copper in acidic chloride media [13].

Methionine (MET) is an amino acid containing both the ($-\text{NH}_2$) and ($-\text{S}-\text{CH}_3$) groups in its molecule. Some researchers studied its inhibiting effect for mild steel corrosion in sulfuric acid [14, 15]. We studied the inhibitory action of methionine on copper corrosion in 0.5 M HCl solution. The combination of MET and Zn^{2+} ions increases the inhibition efficiency to 91.96% [16]. Synergism is one of the most important effects in inhibition processes, and it serves as a basis for all modern corrosion inhibitor formulations. However, there is little information on the synergistic effect of MET with other organic compounds.

In this article, the synergistic effect between MET and two kinds of quaternary ammonium salt against copper corrosion were investigated in 0.5 M HCl solution. The two quaternary ammonium salts are cetrimonium bromide (CTAB) and cetylpyridinium bromide (CPB). Their molecular structure is shown in Fig. 1. Electrochemical impedance spectroscopy

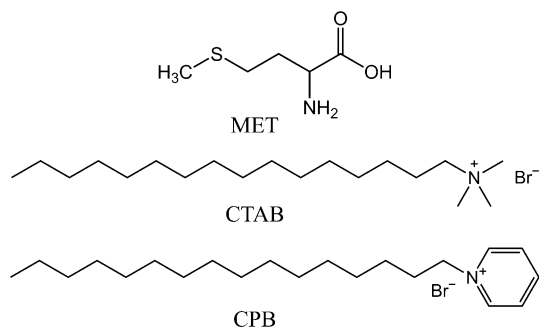


Fig. 1 Molecular structures of methionine (MET), cetrimonium bromide (CTAB), and cetylpyridinium bromide (CPB)

(EIS) and electrochemical polarization techniques were used to measure the protection effect of the mixed inhibitors for copper in acidic chloride media. In addition, the synergistic mechanism of the combined MET/CTAB or MET/CPB on copper corrosion was discussed by PM3 semi-empirical quantum chemical calculation.

2 Experimental methods

2.1 Materials and apparatus

The material used for test was pure copper (99.99%) supplied in the form of a drawn copper rod. The working electrode (WE) for electrochemical measurements was sealed with epoxy resin so that only the circular cross section (0.4 cm^2) of the rod was exposed. The chemicals were analytical grade reagent (AR) and used as received. The aggressive environment was 0.5 M HCl solution prepared from AR chemicals and deionized water. Electrochemical measurements were performed in a three-electrode cell using a Solartron 1287 Electrochemical Interface coupled with a 1260 Impedance/Gain-Phase Analyzer, and Zplot and CorrWare software packages.

2.2 Electrochemical measurements

A three-electrode cell, employing a copper rod-working electrode (WE), platinum foil counter electrode, and saturated calomel electrode reference electrode (SCE), was used for electrochemical measurements. During the measurements, the solution was not stirred or deaerated. The cell was open to air and the measurement was carried out at room temperature. All potential values reported were against SCE. The WEs were mechanically abraded by emery paper (400, 800, 1200 grit), rinsed with deionized water, degreased with ethanol, and dried at room temperature. The degreased WEs were inserted into the solution. After the corrosion potential (E_{corr}) was stable, it was then polarized from -250 to $+250$ mV (vs. E_{corr}) at 1 mV/s. The EIS experiments were performed at open circuit potential over a frequency range 100 kHz–0.02 Hz. The sinusoidal potential perturbation was 5 mV in amplitude. Cyclic voltammetry was carried out with the WEs scanning from -0.6 to 0.6 V at a scan rate of 20 mV/s [17].

2.3 Calculation method

Most semi-empirical molecular orbital (MO) programs are based on the linear combination of atomic orbital by self-consistent field (LCAO-SCF) type of procedure. The PM3 quantum chemical method is based on one of the levels of integral approximation known as the neglect of diatomic

differential overlap (NDDO) [18]. All the calculations were carried out at the basis of complete geometry optimization. Initial estimates of the geometry data were obtained from the Pmodel 6.0 packet program, and subsequent PM3 calculations were performed with MOPAC 7.0 packet program on a PC implemented with a 1.5 GHz Intel Pentium Processor.

3 Results and discussion

3.1 Electrochemical impedance spectroscopy (EIS)

Figure 2 shows Nyquist plots for copper in 0.5 M HCl solution with and without various concentrations of MET.

An obvious capacitive loop in high frequency (HF) was observed by a line portion (Warburg impedance) in the low frequency (LF) region. Similar results have been reported in the literature for copper corrosion in HCl solution in the presence of Schiff bases [19]. The Warburg impedance is attributed to the diffusion of soluble reactant or product species [20]. From Fig. 2, one will find that the corrosion of copper is obviously inhibited in the presence of MET. The Nyquist plots of the copper electrode in HCl containing the mixed MET/CTAB and MET/CAB are shown in Figs. 3 and 4, respectively.

It clearly shows that the shape of the impedance plots for inhibited electrodes is not substantially different from those of uninhibited electrodes. These results show that the inhibitor does not change the corrosion mechanism of copper in HCl solutions [21]. It inhibits corrosion primarily through its adsorption on the metal surface. The impedance plots are analyzed in terms of the equivalent circuits shown in Fig. 5. In general, these circuits fall in with the classical

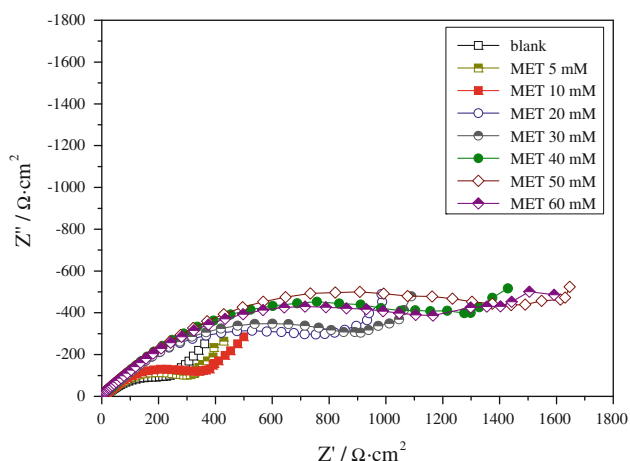


Fig. 2 Nyquist plots for copper in 0.5 M HCl containing different concentrations of MET after 1 h immersion

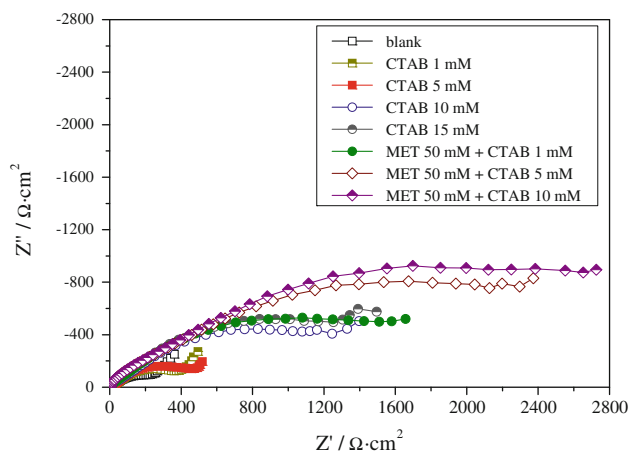


Fig. 3 Nyquist plots for copper in 0.5 M HCl containing CTAB and its mixture with MET after 1 h immersion

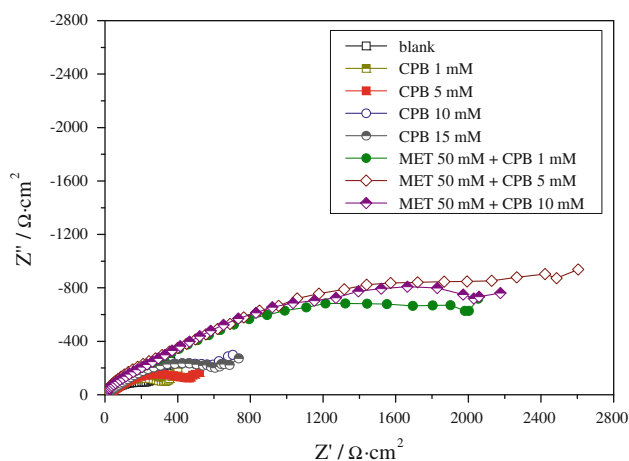


Fig. 4 Nyquist plots for copper in 0.5 M HCl containing CPB and its mixture with MET after 1 h immersion

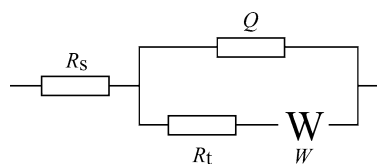


Fig. 5 Equivalent circuits of the impedance spectra with Warburg impedance

parallel capacitor and resistor combination with the solution resistance.

In the circuits, W stands for the Warburg impedance, R represents a resistor (R_s represents solution resistance; R_t , charge-transfer resistance), Q a constant phase element (CPE) which admittance is described as:

$$Q = Y_0(j\omega)^n \tag{1}$$

where j is the imaginary root, w is the angular frequency, Y_0 is the magnitude, and n is the exponential term [18].

The inhibition efficiency ($\eta\%$) is calculated using charge transfer resistance as follows:

$$\eta\% = \frac{R_t - R_{t0}}{R_t} \times 100 \quad (2)$$

R_{t0} and R_t are the electron transfer resistance in uninhibited and inhibited solution, respectively. The ZSimpWin software is used for impedance data analysis and the fit parameters are listed in Table 1.

Increased inhibition was shown with increasing MET concentration reaching 78.0% at 50 mM level. MET shows increased inhibition with increasing concentration reaching 78.0% at 50 mM level. A slight decrease in the inhibition efficiencies was found above the 50 mM. This phenomenon is consistent with results obtained for our previous research and is due to the dissolution of the adsorbed film [22]. The CTAB and CPB have some inhibition effect on copper corrosion in 0.5 M HCl solution. η is up to its maximum values at 10 mM level, which is 78.8 and 61.2% for CTAB and CPB, respectively. Above this concentration, it has no evident increasing. Table 1 shows that using the mixed of MET/CTAB in 0.5 M HCl solution increases the η value more than either MET or CTAB alone. This indicates that there is a synergistic effect between MET and CTAB. The same result is also obtained for MET and CPB.

The mixed MET/CTAB is more efficient as an inhibitor for copper corrosion compared with the mixed MET/CPB.

3.2 Cyclic voltammetric study

Figure 6 shows the cyclic voltammograms of the copper electrodes in HCl solution with and without MET, CTAB, and CPB, respectively.

There are two anodic current peaks and one cathodic peak in blank solution. The first anodic peak is attributed to the oxidation of copper to cuprous Cu (I). Consequently, the second oxidation peak represents the process of Cu (I) to soluble Cu^{2+} [23]. In the reverse sweep, the corrosion product of Cu can be partially reduced to copper. Meanwhile, the corrosion process would be restrained on a certain extent by the increase in salt layer in this step. Owing to the competition of dissolution and precipitation of the film on copper, an anodic current hump appears in CV plot on the reverse sweep at about +0.05 V [24].

It shows that the presence of MET in different concentration causes the significant decrease in the current density of the first anodic and the cathodic peaks. This indicates MET can effectively inhibit the Cu (I) oxidation to soluble Cu^{2+} . The results suggest that the additives have inhibition effect for copper corrosion. As for the MET/CTAB and

Table 1 Electrochemical impedance parameters for copper in 0.5 M HCl with and without inhibitors after 1 h immersion

Inhibitors (mM)	CPE		R_t ($\text{k}\Omega \text{ cm}^2$)	$W \times 10^3$ ($\text{S s}^{0.5} \text{ cm}^{-2}$)	η (%)
	Y_0 ($\text{S s}^n \text{ cm}^{-2}$)	n			
Blank	1425	0.58	0.33	0.75	–
5 MET	901.2	0.61	0.39	0.76	15.4
10 MET	764.0	0.64	0.43	0.70	23.3
20 MET	516.3	0.65	1.02	0.76	67.6
30 MET	450.0	0.65	1.12	0.76	70.5
40 MET	425.4	0.66	1.48	0.73	77.7
50 MET	326.0	0.67	1.50	0.39	78.0
60 MET	386.3	0.67	1.45	0.43	77.2
1CTAB	929.0	0.59	0.47	0.74	29.8
5 CTAB	1216	0.59	0.62	0.89	46.8
10 CTAB	632.1	0.59	1.56	0.68	78.8
15 CTAB	618.7	0.59	1.59	0.72	79.2
50 MET + 1 CTAB	592.4	0.62	1.73	0.32	80.9
50 MET + 5 CTAB	381.0	0.62	2.74	0.46	88.0
50 MET + 10CTAB	347.5	0.62	3.01	0.73	89.0
1CPB	1193	0.58	0.44	0.86	25.0
5 CPB	1060	0.56	0.59	0.84	44.1
10 CPB	1072	0.59	0.85	0.83	61.2
15 CPB	1066	0.59	0.82	0.81	59.8
50 MET + 1 CPB	401.0	0.63	2.11	0.62	84.4
50 MET + 5 CPB	327.2	0.64	2.45	0.63	86.5
50 MET + 10 CPB	439.6	0.63	2.27	0.58	85.5

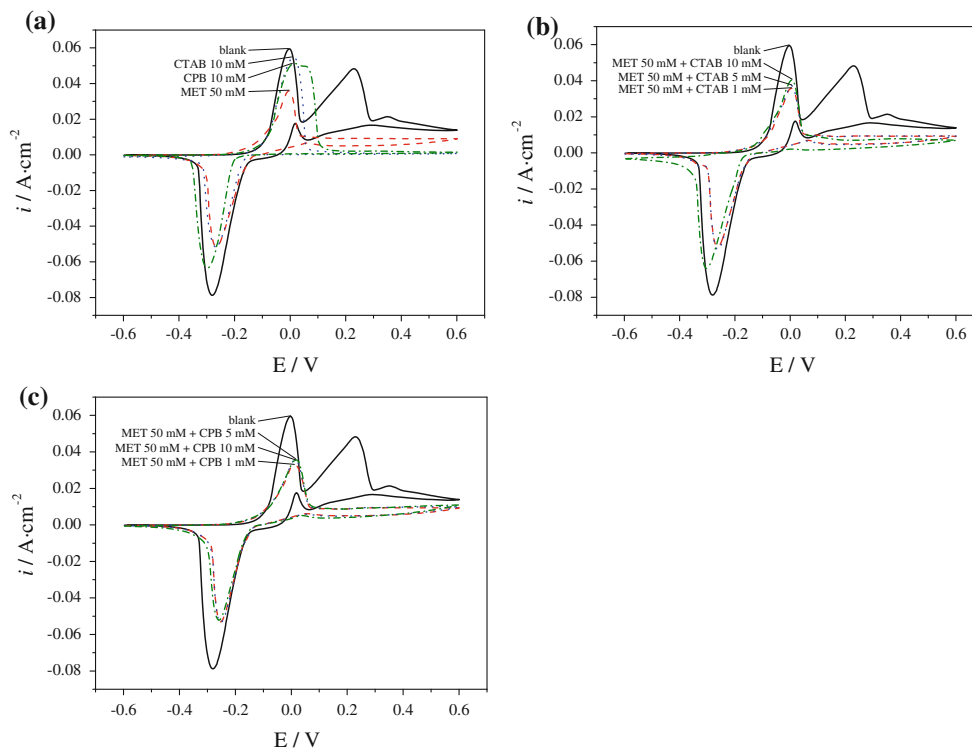


Fig. 6 Cyclic voltammograms for copper in 0.5 M HCl with and without inhibitors: **a** the single component inhibitors; **b** the mixed MET/CTAB; and **c** the mixed MET/CPB

MET/CPB systems, the first anodic and the cathodic peaks are further depressed. This certifies the synergistic effect among them.

3.3 Polarization curve measurements

Figure 7 shows the anodic and cathodic polarization curves recorded on the copper electrode in 0.5 M HCl with and without different inhibitors.

It is well known that the anodic reaction of copper is the dissolution of copper due to oxidation of Cu to Cu⁺ and then Cu⁺ to Cu²⁺ [25]:



So the reaction mechanism of copper has two steps in 0.5 M HCl solution [24, 25]:



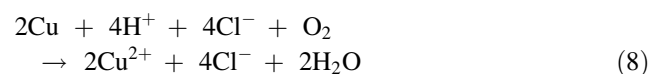
The anodic curve for the copper electrode in 0.5 M HCl blank solution exhibits three distinct regions, which are the active dissolution (apparent Tafel region), the transition region, and the limiting current region. The limiting current plateau indicates a role of a diffusion-limiting rate,

probably both the transport of chloride (Cl⁻) to the surface and the diffusion of (CuCl₂⁻) in the solution [23]. An anodic current peak appeared at a potential of about -25 mV (SCE) is related to the CuCl film formation.

The cathodic corrosion reaction is as follows:



The total corrosion reaction of copper in acidic chloride solutions is as follows [26]:



It is clear from the potentiodynamic polarization experiments that the presence of inhibitors decreases the corrosion rate, i.e., the value of *i*_{corr} decreases. Furthermore, *E*_{corr} shifts more negative values. Particularly, the cathodic process is inhibited to a larger extent than the anodic reaction. It can be inferred that the adsorbed layer behaves as a cathodic inhibitor to copper corrosion by retarding the transfer of O₂ to the cathodic sites of the copper surface. The transfer of oxygen from the bulk solution to the copper/solution interface will strongly affect the cathodic reaction rate of oxygen reduction. The corresponding corrosion potentials (*E*_{corr}), corrosion currents (*i*_{corr}), anodic Tafel slopes (Ba), and cathodic Tafel slopes (Bc) are calculated by

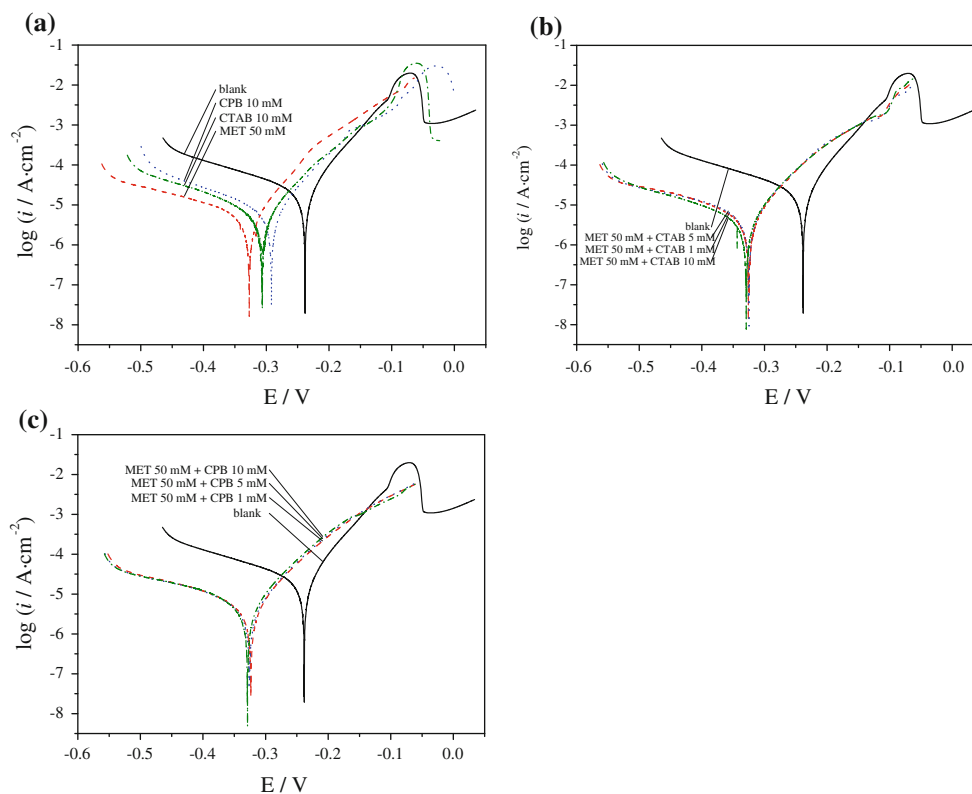


Fig. 7 Electrochemical polarization curves for copper in 0.5 M HCl with and without inhibitors after 1 h immersion: **a** the single component inhibitors; **b** the mixed MET/CTAB; and **c** the mixed MET/CPB

CorrWare software and listed in Table 2. The corrosion inhibition efficiency ($\eta\%$) was calculated from the corrosion current density according to:

$$\eta\% = \frac{i_{\text{corr}} - i_{\text{corr(inh)}}}{i_{\text{corr}}} \times 100 \quad (9)$$

where i_{corr} is the corrosion current density for the metal in the blank solution and $i_{\text{corr(inh)}}$ is its value in the presence of the inhibitor.

The η values in Table 2 show that all the additives have inhibition effect for copper corrosion in 0.5 M HCl solution. The constancy of this anodic slope indicates that the mechanism of the anodic reaction is not changed by the addition of inhibitors. The cathodic portion of the polarization curve is a composite and represents copper ion and oxygen reduction. The cathodic current densities were greatly decreased near E_{corr} region. The inhibitors behave as a barrier to retard the transfer of O_2 to the cathodic sites of the copper surface [23]. This can decrease the rate of oxygen reduction of the cathodic reaction. This suggests that the binary mixtures of MET/CTAB have a better synergistic effect compared with that of MET/CPB in inhibiting the copper corrosion in the hydrochloride acid solution. The data obtained from polarization curves are in agreement with that from EIS.

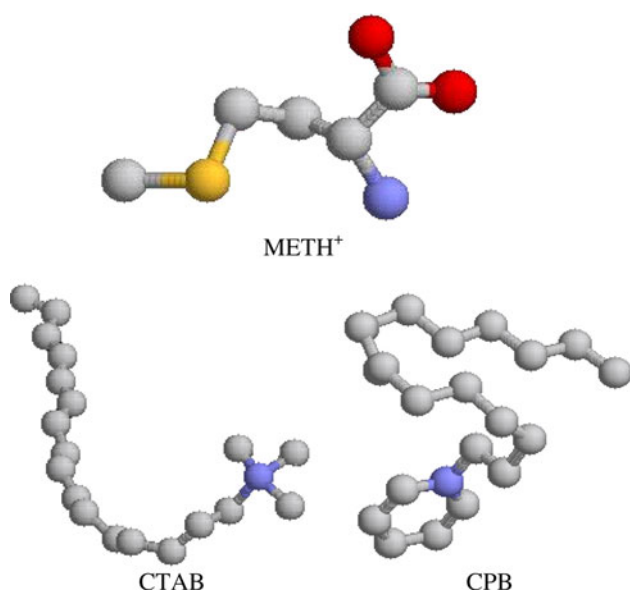
3.4 PM3 quantum chemical calculations

In aqueous solutions, the ionization of amino acids depends on pH. At the isoelectric pH, the molecules present the zwitter ion structure. The isoelectric pH of MET is 5.75, and MET exists predominantly as a protonated species METH^+ in 0.5 M HCl solution. Metal surface usually is positively charged in acidic media [27]. This leads to the limited inhibition effect for most of the amino acids on copper corrosion in acid solutions. CTAB and CPB are quaternary ammonium salts with the long alkyl chain. Quantum chemical calculations have been applied in studying the mechanistic information on corrosion and inhibition processes by many researchers [28, 29]. PM3 semi-empirical calculations were done to investigate the molecular structure parameters of METH^+ , CTAB, and CPB. Optimum conformations of METH^+ , CTAB and CPB are shown in Fig. 8. Table 3 shows the energy (in eV) of the highest occupied molecular orbital (E_{HOMO}) and the lowest unoccupied molecular orbital (E_{LUMO}) and the electron density for heteroatoms of MET, CTAB, and CPB, respectively.

It is reported that the higher the E_{HOMO} level of the inhibitor, the greater is the ease of offering electrons to the unoccupied d orbital of metallic copper and the greater is the inhibition efficiency [30]. The E_{HOMO} of the positive

Table 2 Electrochemical parameters obtained using polarization curves for copper in 0.5 M HCl containing different additives after 1 h immersion

Inhibitors (mM)	i_{corr} ($\mu\text{A cm}^{-2}$)	$-E_{\text{corr}}$ (mV)	B_a (mV dec^{-1})	η (%)
Blank	21.70	238.1	56.24	–
50 MET	5.92	327.2	65.43	72.7
10 CTAB	5.40	306.6	67.10	75.1
10 CPB	7.67	291.8	66.44	64.7
50 MET + 1CTAB	5.31	329.2	71.28	75.5
50 MET + 5CTAB	4.67	325.5	64.22	78.5
50 MET + 10CTAB	3.21	340.5	64.67	85.2
50 MET + 1CPB	5.29	323.4	71.66	75.6
50 MET + 5CPB	4.07	325.8	66.25	81.2
50 MET + 10CPB	6.07	328.9	73.55	72.0

**Fig. 8** Optimum conformations of METH^+ , CTAB, and CPB

ions of quaternary ammonium salts increased in the following order: CTAB > CPB. The present results show that CTAB has the better protection effect on copper corrosion in an acidic chloride solution and has the higher level of E_{HOMO} compared with CPB.

The inhibition of MET is related to adsorption on the copper surface by the S atom in its molecular structure. The 3d orbital of the S atom extends far from the nuclei, and the electrons in the 3d orbital can easily offer because the force

by which they are attracted to the nuclei is small [31]. The addition of halide ions has been observed to increase the adsorption of organic cations and this can greatly enhance the inhibiting action of an organic compound in acid environments [32]. We have also shown that a synergistic effect exists when glutamine and KI were used together to prevent the corrosion of copper in aerated HCl solution [33]. This study shows that the MET and quaternary ammonium salts (CTAB/CPB) have synergistic effect for copper corrosion in acidic solution, among which the mixed MET/CTAB system has a better protective effect for copper corrosion.

From Table 3, the net charge of N atom is 1.0917 for CTAB and 0.5172 for CPB. The more the positive charge density of N atom, the stronger the electrostatic interaction between N atom and negative charge moieties of MET. This may be the reason of the better inhibition for the mixed MET/CTAB compared with the mixed MET/CPB. Thus, the synergistic effect of CTAB or CPB with MET is different by their different electrostatic interaction.

4 Conclusion

The protection of MET on copper corrosion in 0.5 M HCl solution was improved by using the addition of quaternary ammonium salts. They can inhibit the copper corrosion by retarding the cathodic electrochemical process. The mixed MET/CTAB has a better protective effect for copper corrosion compared with the mixed MET/CPB. The stronger

Table 3 Quantum chemical parameters of MET, CTAB, and CPB calculated by PM3 methods

Inhibitor	E_{HOMO} (eV)	E_{LUMO} (eV)	Net charges of heteroatoms			Dipole moment (D)	
			η_{O}	η_{S}	η_{N}		
METH^+	–12.429	–4.881	–0.3663	–0.2446	–0.0595	0.8451	5.923
CTAB	–11.541	–7.375	–	–	–	1.0917	19.882
CPB	–13.619	–5.568	–	–	–	0.5172	10.422

electrostatic interaction between MET and CTAB is contributed to the better synergistic effect between them.

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