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ORIGINAL PAPER

Some environmentally friendly formulations as inhibitors for mild steel corrosion in sulfuric acid solution

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Abstract The corrosion resistance of mild steel in 1 M H_2SO_4 solution was evaluated after addition of Sn^{2+} and Zn^{2+}, *N*-acetylcystein (ACC) and *S*-benzylcystein (BzC) as a function of concentration (5–1000 μM) and solution temperature (35–50°C). Eight blends were also investigated. Both polarization resistance (R_p) and electrochemical impedance spectroscopy (EIS) were employed. For single additives, Zn^{2+} ions acted as accelerator for mild steel corrosion while the other additives showed good performance. The most effective additive was Sn^{2+}. Adsorption of Sn^{2+}, ACC and BzC obeyed the Temkin adsorption isotherm and had a very high negative value of free energy of adsorption ($-\Delta G^\circ_{ads}$). All blends provided good inhibition which increased with rise in temperature. Corrosion kinetic parameters such as activation energy (E_a) and the pre-exponential factor (λ) were calculated and discussed. EIS revealed that the interface of the uninhibited and inhibited systems can be represented by the simple equivalent circuit $R_e(R_{ct}\ Q_{dl})$.

Keywords Adsorption · Amino acids · Corrosion inhibition · EIS · Metal cations

1 Introduction

Aqueous acid solutions are widely used for the removal of undesired scale and rust in many industrial processes. Inhibitors are generally used in these processes to control metal dissolution as well as the consumption of acid. Organic compounds containing N, S or O atoms are used as acid corrosion inhibitors [1–6]. Metallic cations have been tested as inhibitors for Al and Al-alloys in chloride-containing solutions [7–11]. For mild or low-carbon steel, aluminium–thiourea mixtures have been tested as inhibitors in pure water and NaCl solution [12–14]. Few studies have been carried out on the effect of metal cations, either alone or in association with organic compounds, on the corrosion behavior of iron (or steel) in acid media. Drazic and Vorkapic [15] found that Cd^{2+}, Mn^{2+} and Zn^{2+} inhibit the hydrogen evolution reaction and corrosion of iron in 0.25 M H_2SO_4 solution. The inhibitive effect of these cations was explained in terms of the under potential deposition (upd) of the adatoms of these metals on iron. Venkatachari and colleagues [16] studied the inhibitive effect of Zn^{2+} and Mn^{2+} and Ce^{4+} ion on iron corrosion in 0.5 M H_2SO_4 solution and found that these cations inhibit iron corrosion markedly and the inhibition effect follows the order $Ce^{4+} >> Mn^{2+} > Zn^{2+}$. The role of different inorganic cations of several elements (Cr^{6+}, As^{3+}, Sn^{2+}, Cu^{2+}, Ni^{2+} and Hg^{2+}) and organic materials (phenol, formaldehyde, *o*-aminobenzoic acid and hydroquinone) in combination with different concentrations of propargyl alcohol (PA) was investigated to control the dissolution of mild steel in boiling HCl solution. Organic additives were more effective than inorganic cations. Cu^{2+}, Cr^{6+} and Ni^{2+} accelerated corrosion when used without PA but strongly reduced dissolution in its presence [17]. The effect of Cu^{2+}, Ni^{2+} and La^{3+} ions on the inhibition of mild steel corrosion in HCl solution by sodium dodecyl sulfonate (SDS) was investigated. A marked inhibition synergism of Cu^{2+} and SDS was found. Accelerated corrosion occurred in the lower concentration range of La^{3+}, but a powerful

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inhibition synergism appeared in a special concentration region of the mixture La^{3+} and SDS [18]. Hexamine (HA) was found to have a moderate inhibition effect on the corrosion of mild steel in 3 N HCl solution. Incorporation of Cu^{2+}, As^{3+}, Sb^{3+} and Sn^{2+} ions with HA improved performance [19]. Addition of Cu^{2+} (as $CuSO_4$) to dibenzyl sulfoxide (DBSO) was found to improve the inhibitive performance of the latter when used as a pickling inhibitor for mild steel in sulfuric acid solution [20]. Recently, Venkatachari and colleagues [21] found that cerium ions greatly enhance the inhibition efficiency of polyaniline (PANI) when used as inhibitor for iron in sulfuric acid.

The objective of this study is to investigate some formulations, that are non-toxic and non-hazardous, as inhibitors for the corrosion of mild steel in 1 M H_2SO_4 solution. The formulations are composed of Sn^{2+} (as $SnSO_4$), Zn^{2+} (as $ZnSO_4$), *N*-acetyl- cysteine (ACC) and *S*-benzylcysteine (BzC). Sn^{2+} ions were chosen because a comprehensive review of inorganic tin shows it to be innocuous to human health. Stannous ion is a food additive used in canned soda pop up to 12.5 ppm, canned asparagus up to 20 ppm, and canned tuna up to 1500 ppm [22]. On the other hand, Zn^{2+} ions are chosen because Zn^{2+} ions in association with phosphonic acid derivatives are considered environmentally friendly inhibitors for steel corrosion in neutral media [23–26]. Obviously, *N*- and *S*- substituted cysteine (sulfur-containing amino acids) are non-toxic compounds. Previous studies [27, 28] indicated that *S*-containing amino acids are good inhibitors for mild steel corrosion in phosphoric acid solution. In continuation of our efforts in exploring the inhibiting effect of amino acid (either alone or in association with other compounds), this work is devoted to investigating the effect of Sn^{2+} and Zn^{2+} ions on the inhibition performance of *N*- and *S*- substituted cysteine. Both polarization resistance (R_p) and impedance measurements are employed. The temperature effect on the inhibitive action of the compounds (either alone or in mixtures) is also studied.

2 Experimental

Details of mild steel composition, cell and instrumentation were given elsewhere [28]. R_p measurements were performed at $E_{corr} \pm 15$ mV with a scan rate of 1 mV s^{-1} while impedance measurements were carried out at E_{corr}. The temperature effect was studied in the range 35–50°C.

$SnSO_4$ and *S*-benzylcysteine were supplied from Aldrich while $ZnSO_4$, H_2SO_4 and *N*-acetylcysteine were supplied from Merck. All chemicals were used as received. The corrosive electrolyte (1 M H_2SO_4) was prepared by diluting concentrated acid with bidistilled water. Deaeration was achieved by passing pure O_2-free N_2 through the electrolyte for 1 h. Tests were performed in stirred solutions.

The concentration of each single additives varied from 5 μM to 1000 μM. Three types of blend were examined:

(i) Binary blends: $Sn^{2+} + Zn^{2+}$, Sn^{2+} + ACC, Sn^{2+} + BzC, Zn^{2+} + ACC and Zn^{2+} + BzC.
ii) Ternary blends: $Sn^{2+} + Zn^{2+}$ + ACCand $Sn^{2+} + Zn^{2+}$ + BzC
iii) Quaternary blend: $Sn^{2+} + Zn^{2+}$ + ACC + BzC.

The concentration of each compound in the blend was 1000 μM.

3 Results and discussion

3.1 Open circuit corrosion potential (E_{corr})

Figure 1 presents the influence of the concentration of Sn^{2+}, ACC and BzC on the corrosion potential of mild steel in 1 M H_2SO_4 solution at 35°C. The value of E_{corr} obtained in the blank solution is –476 mV versus SCE. The presence of the aforementioned additives displaces the original value of E_{corr} towards more noble values. For both Sn^{2+} and ACC, the maximum shift ($\Delta E_{corr} =$ 36 mV) occurs at 50 and 100 μM, respectively. In the presence of BzC, the positive shift in E_{corr} increases with increasing concentration, reaching a maximum value ($\Delta E_{corr} =$ 53 mV) at 1000 μM. Addition of 5–1000 μM of Zn^{2+} has negligible effect on the original value of E_{corr}.

Binary, ternary and quaternary blends shift the original value of E_{corr} in the positive direction. The maximum positive shift is exerted by Zn^{2+} + ACC ($\Delta E_{corr} =$ 53 mV). The positive shift of E_{corr} indicates that these compounds (added either alone or in blends) should predominantly

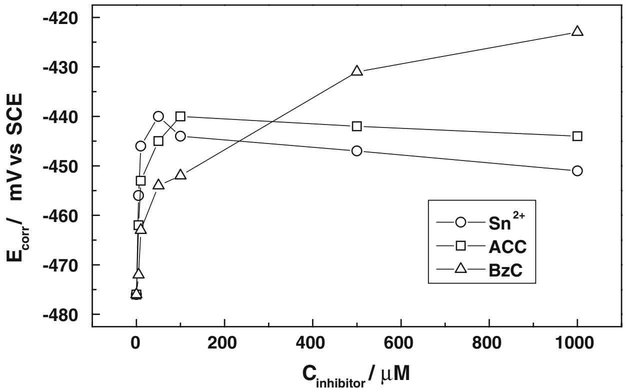

Fig. 1 Variation of the corrosion potential of mild steel with the concentration of Sn^{2+}, ACC and BzC in 1 M H_2SO_4 solution at 35°C

affect the anodic dissolution of iron. Similar results were obtained for the inhibition of mild steel corrosion in H_3PO_4 solution by sulfur-containing amino acids in the absence and presence of Cl^-, F^- and Fe^{3+} ions [27].

3.2 Electrochemical results at 35°C

3.2.1 Results with single additives

R_p studies showed that addition of 5–1000 μM Sn^{2+}, ACC and BzC greatly enhances the value of R_p obtained in the blank solution (R_p = 10.4 Ω cm^2) indicating their inhibition action. For Zn^{2+} ions, they decrease the original value of R_p by ~24% and thus act as stimulator for mild steel corrosion in H_2SO_4 solution. This result is in contradiction to those obtained by Drazic and Vorkapic [12] and Venkatachari and colleagues [21] where Zn^{2+} ions acted as inhibitor for iron corrosion in H_2SO_4.

Figure 2 shows the impedance diagrams obtained for Sn^{2+} ions. For the uninhibited solution, the Nyquist plot is composed of a capacitive loop covering most of the frequency range, followed by a small inductive loop below 1 Hz. The inductive loop is commonly associated with the relaxation process of adsorbed species at the metal/solution interface. The capacitive loop can be ascribed to the charge transfer process. In the presence of 5–1000 μM Sn^{2+} ions, only one semicircle is observed. The diameter of the semicircle increases (and hence the value of charge transfer resistance R_{ct}) with increasing concentration of Sn^{2+} indicating their inhibition effect. Both ACC and BzC show the same impedance behavior. In the presence of Zn^{2+} ions, one capacitive loop is obtained but its diameter decreases with increasing Zn^{2+} concentration indicating accelerating action. The above result agrees well with that obtained from R_p measurements. Regardless of the inductive loop which appeared in the blank solution, the experimental impedance data can be represented by an equivalent circuit [29]. The impedance parameters, R_{ct} and the constant phase element (Q_{dl}) related to the capacity of the double layer were calculated from the non-linear least squares fit (NLSF) of the above mentioned circuit. Values of R_{ct} and R_p were used to compare the inhibition efficiency (IE%) of the investigated compounds. Values of IE% were calculated according to the following equations:

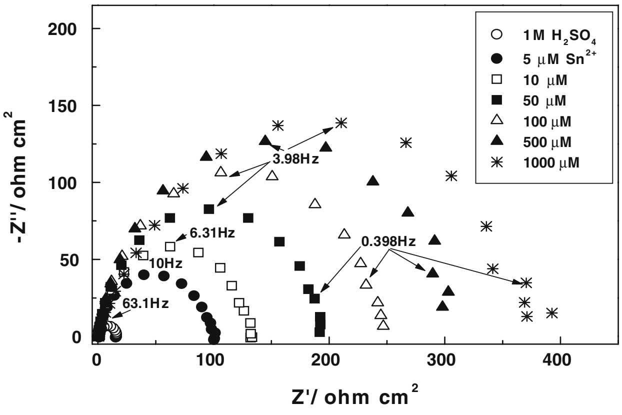

Fig. 2 Complex plane impedance of mild steel in 1 M H_2SO_4 solution without and with Sn^{2+}ions. Spectra recorded at E_{corr} (35°C)

$$\mathrm{IE\%} = [(R_p^1 - R_p^0)/R_p^1] \times 100 \qquad (1)$$

$$\mathrm{IE\%} = [(R_{ct}^1 - R_{ct}^0)/R_{ct}^1] \times 100 \qquad (2)$$

where $R^0{}_p$, $R^0{}_{ct}$ and $R^1{}_p$, $R^1{}_{ct}$ are the polarization and charge transfer resistances in the absence and presence of the additive.

Figure 3 shows the variation of IE% obtained from R_p (Fig. 3a) and R_{ct} (Fig. 3b) with the concentration of Sn^{2+}, ACC and BzC. Both figures have approximately the same features where IE% follows the order: Sn^{2+} > ACC » BzC.

3.2.2 Adsorption isotherms

The nature of the inhibitor interaction on the corroding surface during corrosion inhibition of metals and alloys has been deduced in terms of the adsorption characteristics of the inhibitor [30]. Surface coverage (θ) data are very useful in discussing the adsorption process. Values of θ can be obtained from the following equations:

$$\theta \quad = [(R_p^1 - R_p^0)/R_p^1] \qquad (3)$$

$$\theta \quad = [(R_{ct}^1 - R_{ct}^0)/R_{ct}^1] \qquad (4)$$

Attempts were made to fit θ values to various adsorption isotherms. Adsorption of both Sn^{2+} ions and ACC obeys Temkin's isotherm while adsorption of BzC follows that of Frumkin. Figure 4 shows these isotherms. As the isotherm of the Sn^{2+} ion is similar to that of ACC, and for the sake of clarity, only the isotherm of ACC is shown. It is clearly observed that data obtained from R_p and EIS are in good agreement. The adsorption parameters, standard free energy of adsorption $\Delta G°_{ads}$ and the equilibrium constant of adsorption K_{ads}, and a constant f which describes the interaction between the molecules in the adsorption layer, were calculated and are given in Table 1. The large negative values of $\Delta G°_{ads}$ indicate the spontaneous adsorption of the additives and are usually characteristic of strong interaction with the steel surface. The results of Table 1 indicate that values of $\Delta G°_{ads}$ and K_{ads} follow the order: Sn^{2+} > ACC >> BzC. This suggests that Sn^{2+} ions are the most effective additive while BzC is the least effective.

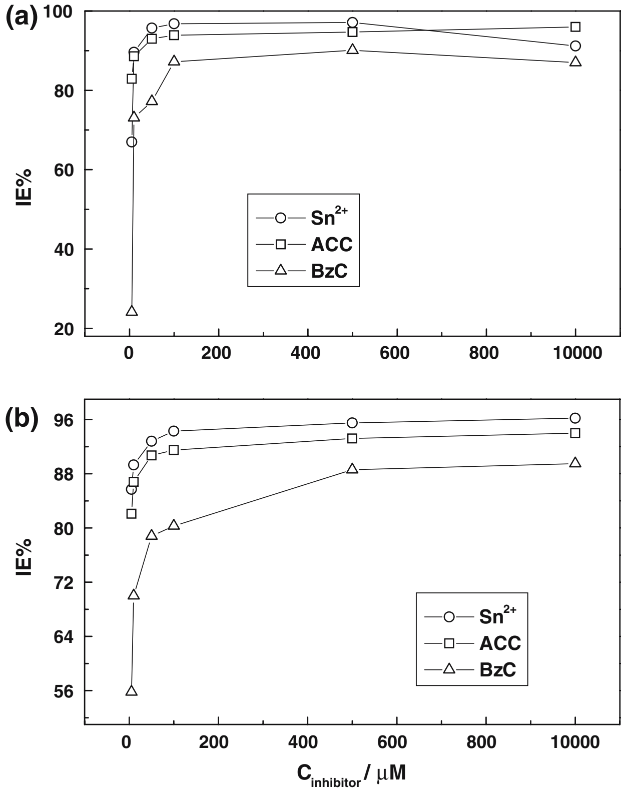

Fig. 3 Variation of the inhibition efficiency with the concentration of Sn^{2+} ions in 1 M H_2SO_4 solution. (**a**) from R_p values (**b**) from R_{ct} values

It is of interest to analyze the values obtained for the constant ***f***. The negative values of ***f*** obtained for BzC by R_p and EIS are evidence for the existence of repulsive forces between BzC molecules in the adsorbed layer. The repulsive forces arise from the benzyl group attached to the S atom (adsorption center) lead to desorption of the molecules and hence exerts the lowest inhibition efficiency. The large and positive values of ***f*** obtained in the case of Sn^{2+} ions and ACC indicate no interaction of the adsorbed species.

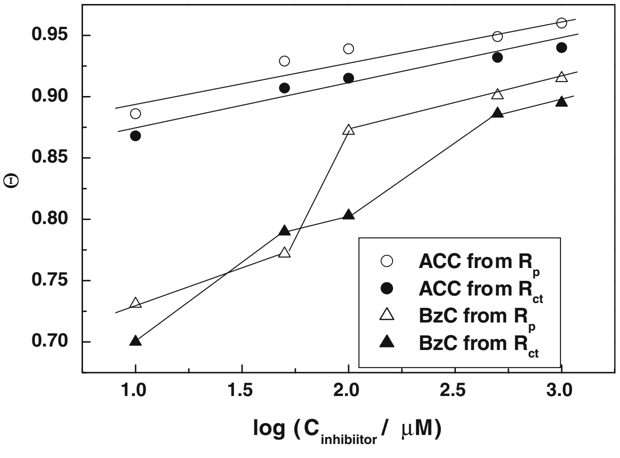

Fig. 4 Adsorption isotherms of cysteine derivatives on mild steel surface in 1 M H_2SO_4 solution at 35°C

3.2.3 Results in the presence of blends

The effect of Sn^{2+} and Zn^{2+} ions (1000 µM) on the inhibition efficiency of ACC and BzC was studied using three mixtures of different ratios: 100:1, 10:1 and 1:1. Table 2 shows the efficiency of these mixtures as deduced from R_p and R_{ct} values. The results demonstrate that the presence of Sn^{2+} ions slightly improves the efficiency of ACC and enhances the efficiency of BzC in all mixtures (Fig. 5a, b). The presence of Zn^{2+} ions slightly lowers the efficiency of ACC in 100:1 and 10:1 mixtures and has no influence in the 1:1 blend. When present with BzC, Zn^{2+} ions largely suppress the efficiency of BzC in the 100:1 blend and have no influence in the remaining blends.

The efficiency of the binary mixture Sn^{2+} + Zn^{2+} (1:1) is slightly lower than that obtained in the presence of 1000 µM Sn^{2+} ions alone. For ternary (1:1:1) and quaternary (1:1:1:1) mixtures, the results can be summarized as follows:

(i) The efficiency of the inhibitive mixture Sn^{2+} + Zn^{2+} + ACC is slightly lower than the binary mixtures
(ii) The efficiency of the ternary blend Sn^{2+} + Zn^{2+} + BzC and that of the quaternary blend are the same as that obtained in the presence of the binary blend Sn^{2+}+ BzC (1:1).
In all cases, the efficiency of the blends ranges from 90% to 96% which is approximately the same as that obtained in the presence of 1000 µM Sn^{2+} ions alone.

3.3 Effect of temperature

To ensure the effectiveness of the studied compounds, electrochemical measurements were performed at different temperatures (35–50°C). The concentration used for the additive was 1000 µM whether single or in a mixture. Figure 6 show the Nyquist plots traced for the blank solution at different temperatures. The diameter of the capacitive loop (and hence the value of R_{ct}) decreases with increasing temperature. The corrosion rate is thus increased. Nyquist plots obtained at 40–50°C have almost the same shape as that at 35°C. Thus, charge transfer controls the corrosion process and the equivalent circuit representing the system mild steel/1 M H_2SO_4 at 35°C is still valid. Figure 7 shows the influence of temperature on the complex plane impedance (representative one) obtained for the corrosion of mild steel in the presence of

Table 1 Parameters of adsorption of Sn^{2+} ions, ACC and BzC on mild steel in 1 M H_2SO_4 at 35°C

Inhibitor	f	R_p		f	R_{ct}	
		K_{ads}/M^{-1}	$\Delta G°_{ads}$/kJ mol^{-1}		K_{ads}/M^{-1}	$\Delta G°_{ads}$/ kJ mol^{-1}
Sn^{2+}	55.6	4.18×10^{26}	–167.1	64	1.38×10^{30}	–187.9
ACC	66.7	2.65×10^{25}	–160.1	67.6	3.44×10^{24}	–154.9
BzC	–13.8	5.22×10^{9}	–67.55	–16	1.86×10^{10}	–70.8

Table 2 Values of inhibition efficiency of Sn^{2+} and Zn^{2+} ions in absence and presence of ACC and BzC obtained at 35°C from R_p and EIS techniques

Additive	IE/%	
	R_p	R_{ct}
1000 μM Sn^{2+} (A)	91.2	96.2
A + 10 μM ACC	90.5 (88.6)	92.8 (86.8)
A + 100 μM ACC	95.8 (94)	95 (91.5)
A + 1000 μM ACC	97.1 (96)	95.8 (94)
A + 10 μM BzC	88 (73.1)	90.1 (70)
A + 100 μM BzC	93.7 (87.2)	92.9 (80.3)
A + 1000 μM BzC	96.4 (87)	95.3 (89.5)
1000 μM Zn^{2+} (B)	–23.8	–17.5
B + 10 μM ACC	81	78.1
B + 100 μM ACC	91.3	88.8
B + 1000 μM ACC	95.3	93.8
B + 10 μM BzC	50	54
B + 100 μM BzC	79.7	78.6
B + 1000μM BzC	92.9	89.5

Values between brackets are those obtained in presence of amino acid alone

Sn^{2+} + Zn^{2+} + ACC +BzC mixture. Although the diameter of the capacitive loop is decreased with increasing temperature, it is still much larger than the corresponding one for the pure medium at the same temperature indicating the high performance of the blend. At each temperature, impedance parameters were calculated for all compounds and those obtained at 50°C are given in Table 3. Values of R_{ct} obtained in the presence of the additives are much higher than that obtained in the blank solution. From values of R_{ct}, the best additives are:

Sn^{2+} + BzC > Sn^{2+} + Zn^{2+} + BzC > Sn^{2+} + Zn^{2+} + ACC + BzC. On the other hand, values of the Q_{dl} obtained in the presence of the additives are lower than that obtained in pure acid. The decrease in Q_{dl} indicates a decrease in steel surface area exposed to the corrosive medium as a result of additive adsorption.

Values of IE% were calculated and plotted as a function of temperature as shown in Figs. 8–10. The common feature of these figures is that the inhibition efficiency of the additives (single compounds or blends) is always increased with rise in temperature. This behavior reflects the chemical nature of adsorption (chemisorption). These figures demonstrate that the most efficient compounds are Sn^{2+}, Sn^{2+} + BzC and Sn^{2+} + Zn^{2+} + BzC.

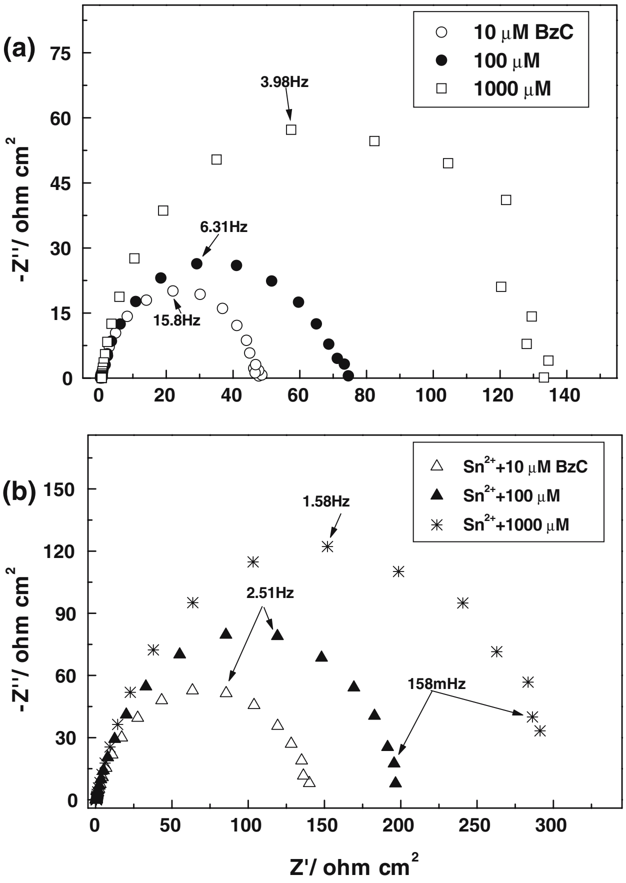

Fig. 5 Complex plane impedance of mild steel in 1 M H_2SO_4 solution without (**a**) in presence of BzC (**b**) in presence of Sn^{2+}+ BzC blends. Spectra recorded at E_{corr} (35°C)

As values of R_t are inversely proportional to the corrosion rate, the logarithm of ($1/R_{ct}$) was calculated at various temperatures in the absence and presence of additives.

The dependence of corrosion rate on temperature can be expressed by the Arrhenius equation:

$$\log(1/R_{ct}) = \log\lambda - (E_a/2.303RT) \qquad (5)$$

λ is the pre-exponential factor and E_a is the apparent activation energy of the corrosion process. Arrhenius plots obtained for the corrosion of mild steel in uninhibited and

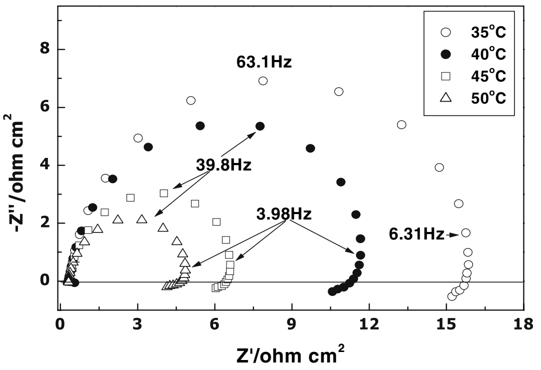

Fig. 6 Effect of temperature on the complex plane impedance of mild steel in 1 M H_2SO_4 solution spectra recorded at E_{corr}

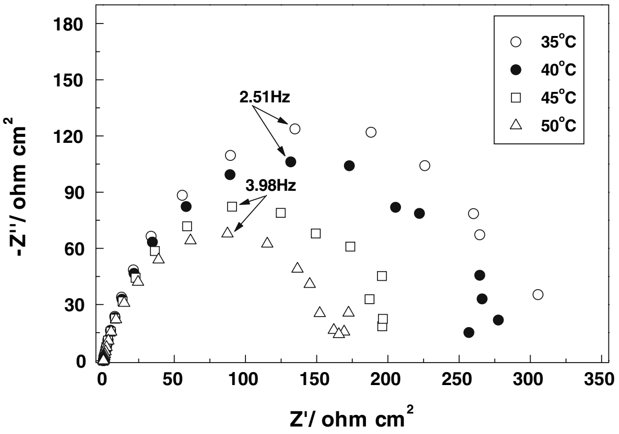

Fig. 7 Effect of temperature on the complex plane impedance of mild steel in 1 M H_2SO_4 solution containing Sn^{2+}+ Zn^{2+}+ ACC + BzC blend (1000 μM for each component). Spectra recorded at E_{corr}

inhibited acid solutions are shown in Figs. 11, 12 for the single compounds and binary blends, respectively while Fig. 13 represents Arrhenius plots for ternary and quaternary blends. Values of λ and E_a were calculated by regression between log ($1/R_{ct}$) and ($1/T$). The linear regression coefficient in all cases was found to be > 0.99.

The value of E_a obtained in the uninhibited solution was –68.8 kJ mol^{-1}. For single compounds values of E_a were –67.9, –51.4 and –38.3 kJ mol^{-1} for Sn^{2+}, ACC and BzC, respectively. For binary, ternary and quaternary blends values of E_a range from –28.4 kJ mol^{-1} to –40.5 kJ mol^{-1}. The lower values of apparent activation energy obtained in the presence of the inhibitors compared with that obtained in their absence can be attributed to surface chemisorption [31, 32]. Hoar and Holliday [33] attributed the decrease in activation energy of the corrosion process in the inhibited state to the slow rate of inhibitor adsorption with a resultant closer approach to equilibrium during experiments at higher temperature. On the other hand, Riggs and Hurd [34] ascribed the decrease in activation energy at high levels of inhibition to the shift of the net corrosion reaction from that of the uncovered part on the substrate surface to the covered one.

The pre-exponential factor λ is connected with the number of active centers in heterogeneous chemical reactions. The presence of adsorbed inhibitor molecules blocks a significant number of active sites on the metal surface which is energetically non-homogeneous. In general [31] the adsorbed inhibitor species block the most active sites, i.e. those with the lowest E_a value. Thus, sites of higher E_a, which are in fact greater in number (λ is of larger value in the presence of inhibitor) take part in the subsequent corrosion process. However, the value of λ obtained in inhibitor-free H_2SO_4 solution was found to be 2.95×10^{10}. In the presence of single additives λ was 9.5×10^8, 3.1×10^6 and 5.6×10^4 in the presence of Sn^{2+}, ACC and BzC, respectively. For binary, ternary and quaternary blends values of λ ranged from 8.7×10^2 to 9.1×10^3. The trend of λ values is the same as those of E_a. The results can be explained by the fact that the presence of all

Table 3 Parameters deduced from Nyquist plots obtained at E_{corr} for mild steel in 1 M H_2SO_4 solution without and with 1000 μM additive, 50°C

Additive	R_e/Ω cm^2	R_{ct}/Ω cm^2	$Q_{dl} \times 10^{-4}$/Ω^{-1}cm^{-2} s^n	n
0	0.32	4.6	8.14	0.96
Sn^{2+}	0.35	110.3	7.16	0.79
ACC	0.28	64.4	4.67	0.88
BzC	1.9	27.4	5.92	0.90
Sn^{2+}+ Zn^{2+a}	0.28	122	6.26	0.80
Sn^{2+} + ACC^a	0.36	111.6	7.52	0.83
Sn^{2+} + BzC^a	0.29	202	3.8	0.84
Zn^{2+} + ACC^a	0.33	77.1	3.6	0.89
Zn^{2+} + BzC^a	0.29	33.7	5.8	0.88
Sn^{2+} + Zn^{2+} + ACC^a	0.33	152.8	7.24	0.81
Sn^{2+} + Zn^{2+} + BzC^a	0.36	189.2	3.03	0.83
Sn^{2+} + Zn^{2+} + ACC + BzC^a	0.35	166.8	3.46	0.87

[a] Each mixture contains 1000 μM from each of its composition

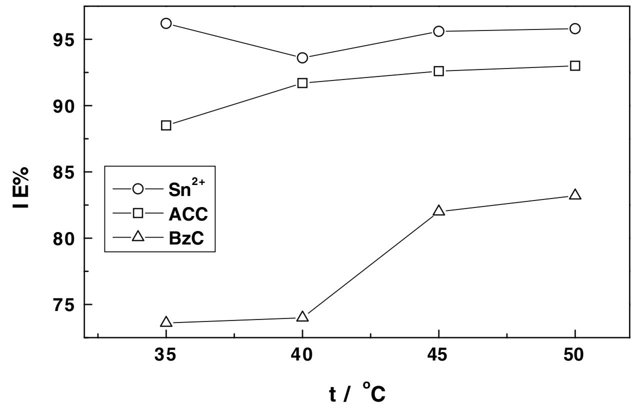

Fig. 8 Effect of temperature on the inhibition efficiency (as calculated from R_{ct} values) of Sn^2, ACC and BzC

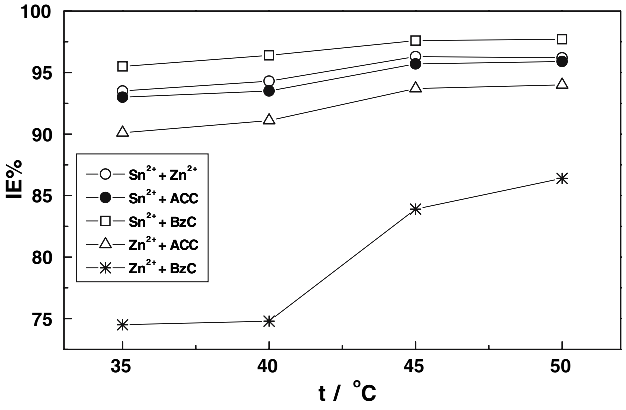

Fig. 9 Effect of temperature on the inhibition efficiency (as calculated from R_{ct} values) of binary blends

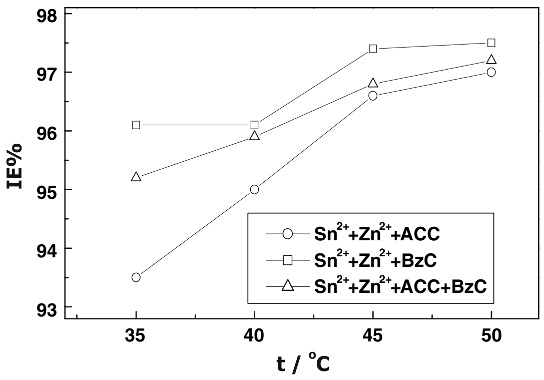

Fig. 10 Effect of temperature on the inhibition efficiency (as calculated from R_{ct} values) of ternary and quaternary blends

investigated compounds and blends results in a low number of active centers remaining uncovered by the inhibitor. Similar results were obtained for the inhibition of mild steel corrosion in acid solutions by several organic compounds [35–39]. The effect of temperature on the inhibition efficiency is not sufficient to judge the applicability of these additive in the practical field but short and long term corrosion test must be performed. This issue is under investigation.

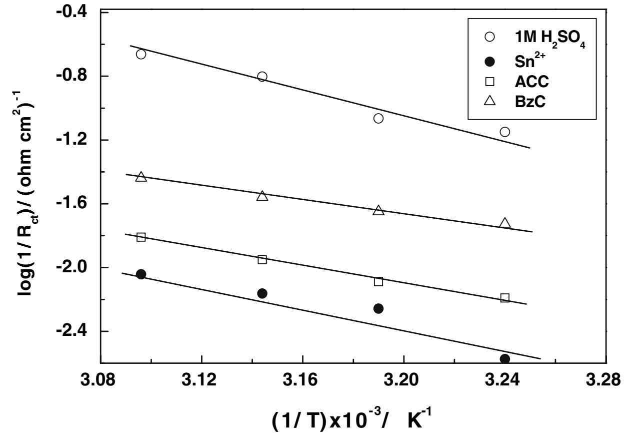

Fig. 11 Arrhenius plots (as calculated from R_{ct} values) of Sn^2, ACC and BzC

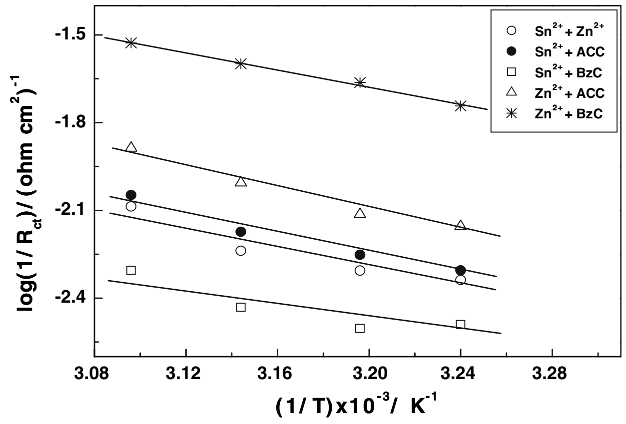

Fig. 12 Arrhenius plots (as calculated from R_{ct} values) of binary blends

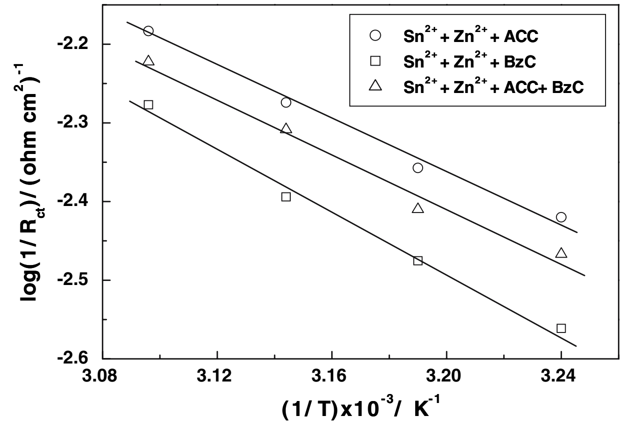

Fig. 13 Arrhenius plots (as calculated from R_{ct} values) of ternary and quaternary blends

3.4 General discussion

An iron surface attains a positive charge in aqueous H_2SO_4 solution as its potential of zero charge ($E_{q=0}$ is –550 mV versus SCE) lies 74 mV more positive than its corrosion potential (E_{corr} = –476 mV versus SCE). So, adsorption of the anionic species is favorable. In the presence of $SnSO_4$ or $ZnSO_4$, SO_4^{2-} ions are firstly adsorbed followed by adsorption of Sn^{2+} or Zn^{2+}. Values of E_{corr} obtained in the presence of 1000 μM Sn^{2+} and Zn^{2+} are –442 and –476 mV versus SCE, respectively. Therefore, the potential of the interface is more negative in the presence of Zn^{2+} than Sn^{2+} ions. On the other hand, the ionic radius of Sn^{2+} is 0.68 Å whereas that of Zn^{2+} is 0.74 Å [40]. Thus the divalent cations Sn^{2+} and Zn^{2+} showed different behavior. The former has a strong inhibition effect while the later is an accelerator. Because of the large ionic size of Zn^{2+} and the higher negative potential of the interface, it is expected, for Zn^{2+} ions, to be repelled strongly from the interface and remain in solution to act as depolarizer.

In acid solutions, amino acids exist as protonated species (as a result of the presence of the $–NH_2$ group) which are not likely to be adsorbed on the positively charged steel surface. The very high IE% of these compounds can be explained in the light of adsorption on anodic sites through the sulfur atom. This explanation is supported by the relatively large positive shift of E_{corr} obtained in the presence of these additives. Improvement in the inhibition efficiency of the binary, ternary and quaternary blends (Figs. 9 and 10) can be attributed to changes in the structure of the double layer at elevated temperatures. Rise in temperature causes the interface to be more favorable for the adsorption of the charged molecules of cysteine derivatives, making it more compatible for co-adsorption with the metal cations [17].

4 Conclusions

At 35°C, Zn^{2+} ions accelerate mild steel corrosion in 1 M H_2SO_4 solution while Sn^{2+}, ACC, and BzC provide good corrosion inhibition. Adsorption of Sn^{2+}, ACC and BzC follow the Temkin adsorption isotherm with very high negative value of ΔG°_{ads}. Binary, ternary and quaternary blends of the additives are efficient inhibitors.

Sn^{2+} ions slightly improve the efficiency of ACC and enhance the efficiency of BzC in all mixtures. The presence of Zn^{2+} ions slightly lowers the efficiency of ACC in 100:1 and 10:1 mixtures and has no influence in the 1:1 blend. When present with BzC, Zn^{2+} ions largely suppress the efficiency of BzC in the 100:1 blend and have no influence in the remaining blends. The inhibition efficiency of all the investigated single additives and their blends increases with increase in temperature. EIS results show that charge transfer controls the corrosion process in both the blank solution and in the presence of additives and all systems can be represented by the simple equivalent circuit $R_e(R_{ct}Q_{dl})$. The results obtained by R_p and EIS techniques are in good agreement.

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