

Malonic Acid as Transporter of Zn^{2+} Towards Carbon Steel Surface

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Abstract

The inhibition efficiency (IE) of malonic acid (MA)- Zn^{2+} system in controlling corrosion of carbon steel immersed in well water has been evaluated by weight-loss method. The formulation consisting of 50 ppm of MA and 50 ppm of Zn^{2+} has 85% IE. The influence of N-cetyl-N,N,N-trimethylammonium bromide (CTAB) and N-cetyl pyridinium chloride (CPC) on the IE of the MA- Zn^{2+} system has been studied. At lower pH value (pH=6) IE decreases and in alkaline medium (pH=8) IE increases. Polarization study reveals that MA- Zn^{2+} system functions as a mixed inhibitor. AC impedance spectra reveal that a protective film is formed on the metal surface. FTIR spectra reveal that the protective film consists of Fe^{2+} -MA complex and $Zn(OH)_2$.

Keywords: carbon steel, corrosion inhibition, malonic acid, well water.

Introduction

Several carboxylates such as sodium salicylate [1], sodium cinnamate [2], anthranilate [3], and adipate [4] have been used as inhibitors. These inhibitors are described by the formula $R(COO^-)_n$ where R can be alkyl or aryl and n is usually 1 or 2 but can be 3 – 6. A very wide range of such chemicals have been shown to be effective inhibitors of the corrosion of mild steel. The chief requirement seems to be that the R.COOH acid should have a pK_a value of at least 4. Thus, in the straight chain monocarboxylic acids the sodium salt of

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formic H.COOH acid with $pK_a = 3.75$ is not inhibitive, whereas the higher members of the series, beginning with acetate, $pK_a = 4.76$, are inhibitive. Similarly with the dicarboxylates $(CH_2)_n (COO^-)_2$ oxalate with $n = 0$ and $pK_a = 1.23$ and malonate with $n = 1$ and $pK_a = 2.54$ are non-inhibitive, whereas higher members of the series, i.e., succinate ($pK_a = 4.17$), azelate ($pK_a = 4.54$) and sebacate ($pK_a = 4.55$), are very good inhibitors [1]. It has also been shown [1] that for aryl carboxylates ortho substituted benzoates are less effective than meta- or para- substituted compounds. This effect is also presumably associated with the lower pK_a value of the ortho- compounds since there is little difference in efficiency between ortho- and para- substituted cinnamates for which the pK_a values are similar. This observation on the acid strength is probably the only reliable statement that can be made in predicting whether a carboxylate will be an inhibitor and even this prediction may relate only to mild steel. The inhibitive properties of carboxylates to other metals and alloys are, so far, impossible to predict. Benzoate is a good inhibitor of corrosion of mild steel but not of cast iron or zinc [1], whereas the structurally related cinnamate is effective for these other metals. A ring structure for the inhibitor molecules is not essential for the protection of cast iron since some aliphatic dicarboxylates have this property [2]. Generally the substituted cinnamates are better than substituted benzoates as inhibitors. Experience with benzoate suggests that carboxylates are 'safe' inhibitors in the sense that they are less likely to promote localized attack than some other anodic inhibitors in the presence of excess chloride or sulphate. Further work is needed to confirm this property with other carboxylates. Reviews of carboxylates as corrosion inhibitors have appeared from time to time [1, 3-7]. More detailed studies of particular carboxylates have also been published. Some examples included sodium salicylate [[8], sodium cinnamate [9], sodium phenyl acetate [10], anthranilate [11], thiodivaleric [12] and adipate [13]. Corrosion of tin in citric acid solution and effect of some inorganic anions have been studied [14]. Inhibition of corrosion of carbon steel by sodium potassium tartrate [15] and also by adipic acid [16] has been studied. The present work is undertaken: (i) to evaluate the inhibition efficiency of malonic acid (MA) as its sodium salt in controlling corrosion of carbon steel in well water, in the absence and presence of Zn^{2+} , (ii) to study the influence of N-cetyl-N,N,N-trimethyl ammonium bromide (CTAB), N-cetyl pyridinium chloride (CPC) and various pH values on the IE of the MA- Zn^{2+} system, (iii) to analyze the protective film by FTIR, (iv) to make use of polarization study and AC impedance spectra to know the mechanistic aspects of corrosion inhibition, and (v) to propose a suitable mechanism of corrosion inhibition based on the results from the above studies.

Experimental

Preparation of the specimens

Carbon steel specimens (0.026% S, 0.06% P, 0.4% Mn, 0.1% C and the rest iron) of the dimensions 1.0x4.0x0.2 cm were polished to a mirror finish and

degreased with trichloroethylene, and used for the weight-loss method and surface examination studies.

Weight-loss method

The parameters of well water used in the present study are given in Table 1. Carbon steel specimens in triplicate, were immersed in 100 mL of the solutions containing various concentrations of the inhibitor in the presence and absence of Zn^{2+} for one day. The weight of the specimens before and after immersion were determined using a balance, Shimadzu AY62 model. The corrosion products were cleansed with Clarke's solution [17]. The corrosion inhibition efficiency (IE) was then calculated using the equation

$$IE = 100[1 - (w_2/w_1)]\%$$

where w_1 = corrosion rate in absence of inhibitor and w_2 = corrosion rate in presence of inhibitor.

Table 1. Physico-chemical parameters of well water.

Parameters	Value
pH	8.38
Conductivity	3111 μ mhos/cm
TDS	2018 ppm
Chloride	665 ppm
Sulphate	14 ppm
Total hardness	1100 ppm

Surface examination study

The carbon steel specimens were immersed in various test solutions for a period of one day. After one day, the specimens were taken out and dried. The nature of the film formed on the surface of metal specimens was analyzed by surface analysis technique.

FTIR spectra

These spectra were recorded in a Perkin-Elmer 1600 spectrophotometer. The film was carefully removed, mixed thoroughly with KBr and made into pellets, and the FTIR spectra were recorded.

Potentiostatic polarization study

This study was carried out using EG & G electrochemical impedance analyzer model 6310. A three-electrode cell assembly was used. Carbon steel was used as working electrode, platinum was used as counter electrode and saturated calomel electrode (SCE) was used as reference electrode. Corrosion potential, corrosion current and Tafel slopes were calculated.

AC impedance measurements

EG & G electrochemical impedance analyzer model 6310 has introduced a very effective approach to AC impedance measurements. The cell set up was the same as that used for polarization measurements. A time interval of 5 to 10 min

was given for the system to attach a steady state open circuit potential. Then over this steady state potential, AC potential of 10 mV was superimposed. The real part (z') and imaginary part (z'') of the cell impedance were measured in ohms for various frequencies. The R_t (charge transfer resistance) and C_{dl} (double layer capacitance) values were calculated.

Results and discussion

Weight-loss study

The inhibition efficiencies (IE) of carbon steel immersed in well water for one day, in the absence and presence of inhibitor at various concentrations have been measured by weight-loss study. The corrosion inhibition efficiencies of malonic acid (MA)- Zn^{2+} systems are given in Table 2. It is found that the IE increases as the concentration of MA increases. As the concentration of Zn^{2+} increases, IE also increases. A synergistic effect exists between MA and Zn^{2+} . For example, 50 ppm of MA has 43% IE; 50 ppm of Zn^{2+} has 22% IE. However, the formulation consisting of 50 ppm of MA and 50 ppm of Zn^{2+} has 85% IE. That is, mixture of inhibitors shows better inhibition efficiency than the individual inhibitors.

Table 2. Inhibition efficiency (%) of various MA- Zn^{2+} system, when carbon steel is immersed in well water for one day.

MA ppm	Zn^{2+} (ppm)				
	0	5	10	25	50
0	-	3	5	8	22
50	43	66	75	80	85
100	44	66	76	81	85
150	45	67	77	82	87
200	45	68	78	82	88
250	46	68	78	84	90

Influence of CTAB on the IE of MA- Zn^{2+} system

The influence of CTAB on the inhibition efficiency of MA (50 ppm)- Zn^{2+} (5 ppm) system is given in Table 3. It is observed that as the concentration of CTAB increases, the IE also increases. It seems that as the concentration of CTAB increases, the transport of Zn^{2+} -MA complex towards the metal surface also increases and hence the increase in the IE.

Table 3. Influence of CTAB on the inhibition efficiency of the MA (50 ppm)-Zn²⁺(5 ppm) system. Inhibitor system: MA+Zn²⁺+CTAB. Immersion period: one day.

MA (ppm)	Zn ²⁺ (ppm)	CTAB (ppm)	IE (%)
50	5	0	66
50	5	50	70
50	5	100	78
50	5	150	85
50	5	200	90
50	5	250	95

Influence of CPC on the IE of MA- Zn²⁺ system

The influence of CPC on the inhibition efficiency of MA (50 ppm)- Zn²⁺(5 ppm) system is given in Table 4. It is observed that as the concentration CPC increases, the IE decreases. It is due to the fact that as the concentration of CPC increases the chloride ion concentration (present in CPC) also increases and hence IE decreases.

Table 4. Influence of CPC on the inhibition efficiency of the MA (50 ppm)-Zn²⁺(50 ppm) system. Inhibitor system: MA+Zn²⁺+CPC. Immersion period: one day.

MA (ppm)	Zn ²⁺ (ppm)	CPC (ppm)	IE (%)
50	5	0	66
50	5	50	65
50	5	100	64
50	5	150	62
50	5	200	60
50	5	250	58

Influence of pH on the IE of MA- Zn²⁺ system

The influence of pH (addition of H₂SO₄ or addition of NaOH) on the IE of MA and MA-Zn²⁺ system is given in Tables 5 and 6. It is found that when pH =6 (acidic), the IE decreases. This is due to the fact that in acidic medium the protective film is broken by the acid; moreover in acid medium malonic acid exists in unionized form. So it can not easily coordinate with Fe²⁺ to form Fe²⁺-MA complex on the metal surface. When pH is increased,

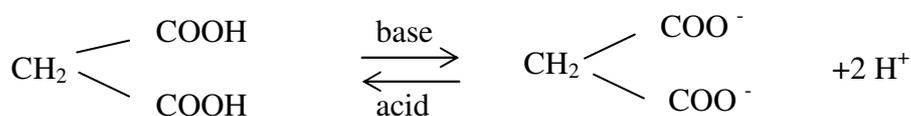


Table 5. Influence of various pH on the inhibition efficiency of the malonic acid (50 ppm) system. Inhibitor system: MA. Immersion period: one day.

pH	6	8	9	11
IE (%)	38	43	45	47

Table 6. Influence of various pH on the inhibition efficiency of the MA (50 ppm)-Zn²⁺(5 ppm) system. Inhibitor system : MA +Zn²⁺. Immersion period: one day.

pH	6	8	9	11
IE(%)	58	66	45	47

IE slightly increases for MA system. This is due to the fact that ionization of MA is increased by the presence of OH⁻ in solution, and hence coordination of MA with Fe²⁺ is enhanced. When pH is increased IE slightly decreases for the MA- Zn²⁺ system. This is due to the fact that when NaOH is added to the MA-Zn²⁺ system Zn(OH)₂ is precipitated in the bulk of the solution. Zn²⁺ is not free to transport MA towards the metal surface. Hence a decrease in the IE is noticed. However when more NaOH is added (at pH 11) sodium zincate is formed under a solubilized form. Now Zn²⁺ is free transport MA towards metal surface to form Fe²⁺-MA complex on the metal surface and hence an increase in IE is noticed. There is competition for Zn²⁺. The Zn²⁺ ion experiences a pull towards the bulk of the solution and at the same time there is a strong pull towards the metal surface. Zn²⁺ escapes from the bulk and diffuses towards the metal surface.

Surface analysis

The protective film formed on the surface of the metal in the presence of MA-Zn²⁺ system has been analyzed by FTIR spectroscopy.

Analysis of FTIR spectra

FTIR spectrum (KBr) of pure malonic acid (MA) is shown in Fig. 1a. The C=O stretching frequency of carboxyl group appears at 1720 cm⁻¹. The FTIR spectrum (KBr) of film formed on the surface of metal after immersion in well water containing 50 ppm of MA and 50 ppm of Zn²⁺ is shown in Fig. 1b. The C=O stretching frequency of carboxyl group has shifted from 1720 cm⁻¹ to 1700 cm⁻¹ [18]. This indicates that the oxygen atom of carboxyl group has coordinated with Fe²⁺, resulting in the formation of Fe²⁺-MA complex on the anodic sites of the

metal surface. The peak at 1350 cm^{-1} is due to $\text{Zn}(\text{OH})_2$ formed on the cathodic sites[19].

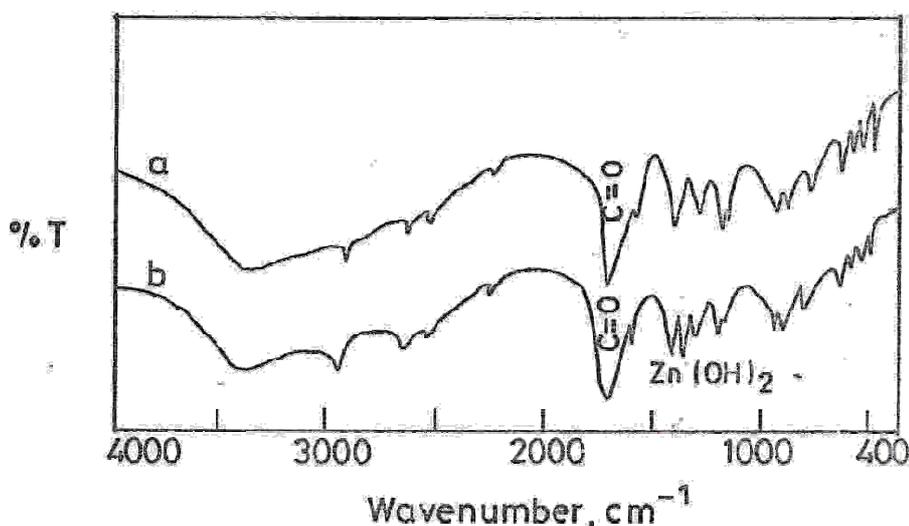


Figure 1. FTIR spectra. (a) Pure malonic acid (KBr). (b) Film formed on carbon steel after immersion in well water containing 50 ppm of malonic acid and 50 ppm of Zn^{2+} .

Analysis of potentiostatic polarization curves

The potentiostatic polarization curves of carbon steel immersed in various solutions are shown in Fig. 2. The corrosion parameters are given in Table 7. When carbon steel is immersed in well water, the corrosion potential is -511 mV vs. saturated calomel electrode (SCE). The formulation consisting of 50 ppm of MA and 50 ppm of Zn^{2+} has corrosion potential of -516 mV vs. SCE. The corrosion potential shift is very small. The Tafel slopes b_a and b_c for this system are almost equal (33 mV and 35 mV). These results suggest that the MA- Zn^{2+} formulation functions as a mixed inhibitor controlling the anodic reaction of formation Fe^{2+} and cathodic reaction of formation of OH^- , to the same extent.



The corrosion current for well water is $2.6 \times 10^{-8}\text{ A/cm}^2$. The corrosion current for formulation consisting of MA (50 ppm)-Zn (50 ppm) has decreased to $0.11 \times 10^{-8}\text{ A/cm}^2$. These observations suggest that a protective film is formed on the metal surface.

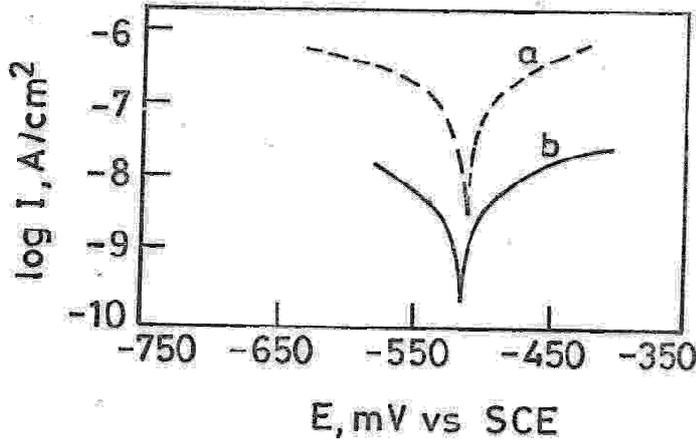


Figure 2. Polarization curves of carbon steel immersed in various test solution. (a) Well water. (b) Well water containing 50 ppm of malonic acid and 50 ppm of Zn^{2+} .

Table 7. Corrosion parameters of carbon steel immersed in well water in the presence and absence of inhibitor obtained by polarization method.

MA (ppm)	Zn^{2+} (ppm)	E_{corr} (mV vs. SCE)	I_{corr} (A/cm ²)	b_a (mV)	b_c (mV)
0	0	-511	2.6×10^{-8}	32.00	31.50
50	50	-516	0.11×10^{-8}	35.00	33.00

Analysis of AC impedance spectra

The AC impedance spectra of carbon steel immersed in various solutions are shown in Fig. 3. The AC impedance parameters, namely, charge transfer resistance (R_t) and double layer capacitance (C_{dl}) are given in Table 8. Well water has R_t value of $0.04 \times 10^3 \Omega \text{ cm}^2$ and C_{dl} value of $9.999 \times 10^{-5} \mu \text{ F cm}^{-2}$. When MA and Zn^{2+} are added to well water, R_t value increases tremendously from $0.04 \times 10^3 \Omega \text{ cm}^2$ to $2.21 \times 10^3 \Omega \text{ cm}^2$. The C_{dl} decreases from $9.999 \times 10^{-5} \mu \text{ F cm}^{-2}$ to $0.1142 \times 10^{-5} \mu \text{ F cm}^{-2}$. This suggests that a protective film is formed on the surface of the metal. This accounts for the very high IE of MA- Zn^{2+} system.

Table 8. Impedance parameters of carbon steel in well water in the presence and absence of inhibitor obtained by AC impedance method.

MA (ppm)	Zn^{2+} (ppm)	R_t ($\Omega \text{ cm}^2$)	C_{dl} ($\mu \text{ F cm}^{-2}$)
0	0	0.04×10^3	9.999×10^{-5}
50	50	2.21×10^3	0.1142×10^{-5}

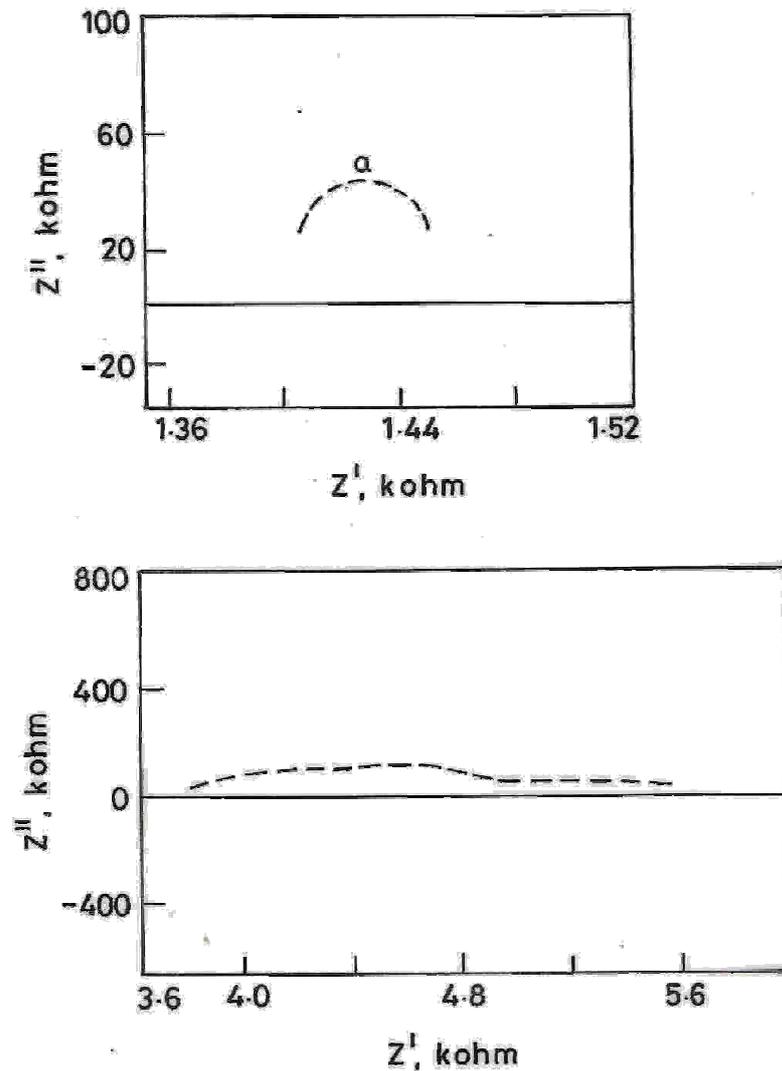


Figure 3. AC impedance spectra of carbon steel immersed in various test solutions. (a) Well water. (b) Well water containing 50 ppm of malonic acid and 50 ppm of Zn^{2+} .

Conclusions

The present study leads to the following conclusions:

- The inhibition efficiency (IE) of malonic acid (MA)- Zn^{2+} system in controlling corrosion of carbon steel immersed in well water has been evaluated by weight-loss method.
- The formulation consisting of 50 ppm of MA and 50 ppm of Zn^{2+} has 85% IE.
- Addition of N-cetyl-N,N,N-trimethylammonium bromide increases IE.
- Addition of N-cetyl pyridinium chloride lowers the IE of the MA- Zn^{2+} system.
- At lower pH value (pH=6) IE decreases and in alkaline medium (pH=8) IE increases.
- AC impedance spectra reveal that a protective film is formed on the metal surface.

- FTIR spectra reveal that the protective film consists of Fe²⁺-MA complex and Zn(OH)₂.
- Polarization study reveals that MA- Zn²⁺ system functions as a mixed inhibitor.

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