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Synergistic effect of benzyl tri methyl ammonium chloride and KI on the corrosion inhibition of stainless steel

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ABSTRACT

The inhibition of corrosion of stainless steel in acidic medium by the inhibitor Benzyl tri methyl ammonium chloride has been investigated by weight loss method. The synergism between KI and Benzyl tri methyl ammonium chloride is also established. The combination consists of 0.0025 M Benzyl tri methyl ammonium chloride and 0.0018 M of KI offers good inhibition efficiency of 96%. Polarisation study reveals that this combination functions as a mixed inhibitor. Impedance spectra reveal that a protective film is formed on the metal surface. The surface morphology has been analysed by SEM.

Key words: Stainless steel, Corrosion inhibition, electrochemical measurements, SEM.

INTRODUCTION

Stainless Steel is a material frequently used for its properties of resistance to corrosion in both the industrial and maritime field, Chromium is the main alloying element, and the steel should contain at least 11% of chromium. Chromium is a reactive element, but it and its alloys passivate and exhibit excellent resistance to many environments. Type 430 stainless steel can be readily formed and has good corrosion resistance to the atmosphere. This is one reason why it is most widely used in the automobile trim. The first chemical plant application of stainless steel was a type 430 tank for shipping nitric acid [1]. The Corrosion of stainless steel in acidic solutions is a fundamental academic and industrial concern that has received a considerable attention [2]. The use of inhibitors is one of the most practical methods of protecting corrosion. Most of the acid inhibitors are organic compounds containing nitrogen, sulphur and oxygen atoms [3]. Inhibition of metal corrosion by organic compounds is a result of adsorption of organic molecules or ions at the metal surface forming a protective layer [4-9]. The heteroatom's present in the inhibitor having lone pair of electrons are responsible for adsorption by the metal surface.

In the present study, BTMAC, a quaternary ammonium compound is chosen as a new inhibitor to prevent the corrosion of stainless steel in HCl. Benzyl Tri Methyl Ammonium Chloride is widely used as a solvent for cellulose, a gelling inhibitor in polyester resins, a chemical intermediate, paint dispersant, and an acrylic dyeing agent. It is also used in plant growth regulator compositions and synthetic processes BTMAC has strong positively charge N^+ ion and π electrons from aromatic benzyl group for adsorption to take place on the stainless steel surface. The aim of this work is to study the effectiveness of BTMAC with KI as a corrosion inhibitor for stainless steel in 1.0 M HCl solution.

MATERIALS AND METHODS

Material preparation
The composition of the stainless steel is as follows 0.12% C, 1.00% Si, 1.00% Mn, 16.00% Cr, 0.75% Ni, 0.04% P, 0.03% S and the balance is Fe. The 430 stainless steel has the dimensions of 4.5cm×1.7cm×0.0457cm. They were polished to mirror finish and degreased with acetone and used for the present study.

Weight – Loss Method
Stainless steel specimens were immersed in 100 mL of the 1.0 M HCl solution with and without inhibitor for 1h. The weight of metal specimens before and after immersion was determined by using Shimadzu Ay 220 model digital balance. From the weight loss data, percent inhibition efficiency (IE %) and corrosion rate was calculated.

$$IE\% = \frac{CR_0 - CR_t}{CR_0} \times 100 \qquad (1)$$

Where, CR_0 and CR_t are the corrosion rates of the stainless steel in the absence and the presence of the inhibitor respectively.

Corrosion Rate = Weight loss / (surface area x time in hrs) (2)

Electrochemical measurements
The stainless steel coupons, were prepared as detailed above, was used as working electrode. Before each experiment, the exposed area of the working electrode was polished with soft 3M 1500 sand paper, to a metallic shine. Then it was washed with distilled water, degreased with acetone, and finally dried with soft paper. The electrochemical measurements were performed in a conventional three electrode glass cell which consists of stainless steel as working electrode (WE), Calomel as reference electrode, platinum as counter electrode. Potential was allowed to stabilize 60 min before starting the measurements. Measurements were performed using Digital LCRZ bridge model TH 2816 A. Tafel polarization curves were obtained. Impedance measurements were carried out in frequency ranges from200kHz to 50 Hz.

Scanning electron microscopy (SEM)
The surface morphology of the stainless steel immersed in 1.0 M HCl in the presence and absence of the BTMAC with KI was studied by using scanning electron microscopy. The immersion time of the electrodes for the SEM analysis was 1h.

RESULTS AND DISCUSSION

Weight Loss method
Corrosion rates (CRs) of stainless steel immersed in 1.0 M HCl in the absence and presence of inhibitor BTMAC are given in Tables 1and 2. The inhibition efficiencies (IE) are also given in these Tables. It is observed from Table 1 that 0.0005 M of BTMAC has 55 percent IE. As the concentration of BTMAC increases the IE also increases.

Influence of KI on the Inhibition Efficiencies of BTMAC
The influence of KI on the inhibition efficiency of BTMAC is given in Table 2. It is observed that as the concentration of BTMAC increases the IE increases. Similarly, for a given concentration of BTMAC the IE increases as the concentration of KI increases. It is also observed that a synergistic effect exists between BTMAC and KI. For example, 0.0018 M of KI has 75 percent IE; 0.0025 M of BTMAC has 70 percent IE. Interestingly their combination has a high IE, namely, 96 percent. On Further addition of KI decreases the combined inhibition efficiency.

Table1: Corrosion Rates (CRs) of Stainless Steel immersed in 1.0 M HCl in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method

BTMAC $\times 10^{-3}$ M	KI $\times 10^{-3}$ M	CR$\times 10^{-2}$, g cm^{-2} min^{-1}	IE%
0	0	4.83	-
0.5	0	2.17	55
1.0	0	1.79	62
1.5	0	1.75	63
2.0	0	1.71	64
2.5	0	1.42	70

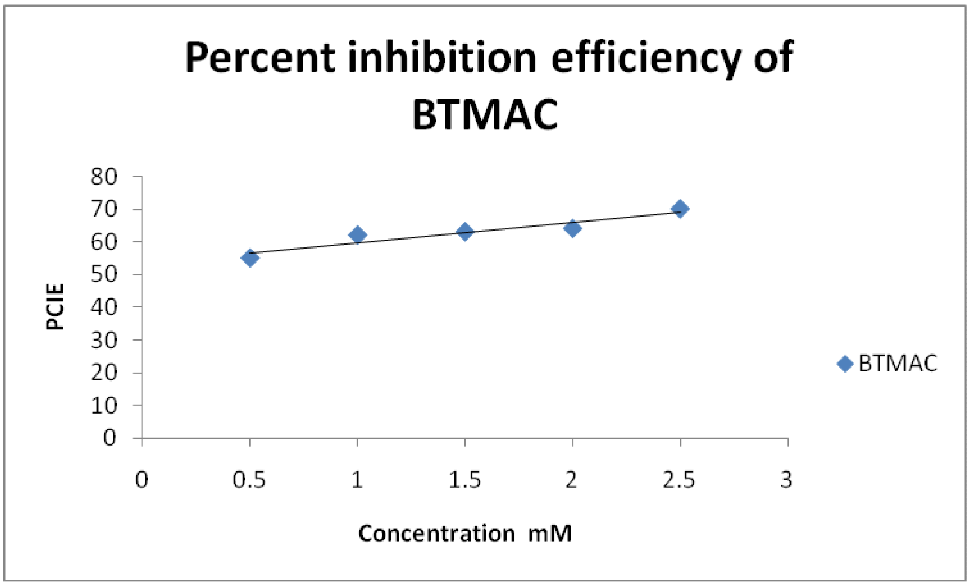

Figure: 1 shows the increase in the PCIE

Table 2: corrosion rates (CRs) of stainless steel immersed in 1.0 M HCl in the presence and absence of inhibitor system at various concentrations and the inhibition efficiencies (IEs) obtained by weight loss method

BTMAC× 10^{-3} M	KI ×10^{-3} M	CR×10^{-2}, g cm^{-2} min^{-1}	IE%
0	0	4.83	-
2.5	0.6	0.36	90
2.5	1.2	0.29	92
2.5	1.8	0.14	96
2.5	2.4	0.18	95
2.5	3.0	0.18	95

Synergism parameter (S_θ) has been used to know the synergistic effect existing between two inhibitors [10-16]. Synergism parameter (S_θ) can be calculated using the following relationship:

$$\text{Synergism parameter } (S_\theta) = \frac{1-\theta_{1+2}}{1-\theta'_{1+2}}, \qquad (3)$$

Table3: Inhibition efficiencies and synergism parameters for various concentrations of Benzyl tri methyl Ammonium chloride-KI, when Stainless Steel is immersed in 1.0 M HCl

BTMAC ×10^{-3} M	Inhibition efficiency IE (%)	Surface Coverage θ_1	KI ×10^{-3} M	Inhibition efficiency IE (%)	Surface Coverage θ_2	Combined IE % I'_{1+2}	Combined Surface Coverage θ'_{1+2}	Synergism Parameter S_θ
2.5	70	0.70	0.6	61	0.61	90	0.90	1.17
2.5	70	0.70	1.2	70	0.70	92	0.92	1.13
2.5	70	0.70	1.8	75	0.75	96	0.96	1.89
2.5	70	0.70	2.4	77	0.77	95	0.95	1.38
2.5	70	0.70	3.0	81	0.81	95	0.95	1.14

Where
$\theta_{1+2} = (\theta_{1+}\,\theta_2)-(\theta 1\ \theta_2)$
θ_1 = surface coverage by Benzyl Tri Methyl Ammonium chloride,
θ_2 =surface coverage by KI,
θ'_{1+2} =surface coverage by both Benzyl Tri Methyl Ammonium chloride and KI,

The synergism parameters of BTMAC and KI are given in Table 3. For different concentrations of inhibitors, S_θ approaches 1 when no interaction between the inhibitor compounds exists. When S_θ >1, it points to synergistic effects. In the case of S_θ < 1, it is an indication that the synergistic effect is not significant [17]. From Table 2, it is observed that values of synergism parameters (S_θ) calculated from surface were found to be one and above.

This indicates that a synergistic effect exists between BTMAC and KI [18-20]. Thus, the enhancement of the inhibition efficiency caused by the addition of KI to BTMAC is due to the synergistic effect.

Analysis of polarisation study

Polarisation study has been used to confirm the formation of protective film formed on the metal surface during corrosion inhibition process [21-23]. If a protective film is formed on the metal surface, the corrosion current value (I_{corr}) decreases. The potentiodynamic polarisation curves of stainless steel immersed in 1.0 M HCl in the absence and presence of inhibitor are shown in Figure 2, the corrosion parameters are given in Table 4. When stainless steel was immersed in 1.0 M HCl the corrosion potential was – 494.171 mV versus SCE. When BTMAC (0.0025 M) and KI (0.0018 M) were added, the corrosion potential shifted to noble side -477.446 mV versus SCE. There is slight shift in E_{corr} value, denotes that it act as mixed inhibitor. The large shift in cathodic Tafel slope β_c [24], from 70.674 to 128.806 mV shows that it predominantly controls the cathodic reaction.

Table4: Corrosion parameters of stainless steel immersed in 1.0 M HCl in the absence and presence of inhibitor from polarisation study

Concentration in M	E_{corr}, mv	I_{corr}, µA	β_c, mV	β_a, mV	IE %
Blank	-494.171	-329.836	70.674	53.767	-
0.0025 M BTMAC + 0.0018 M KI	-477.446	-89.514	128.806	37.014	73

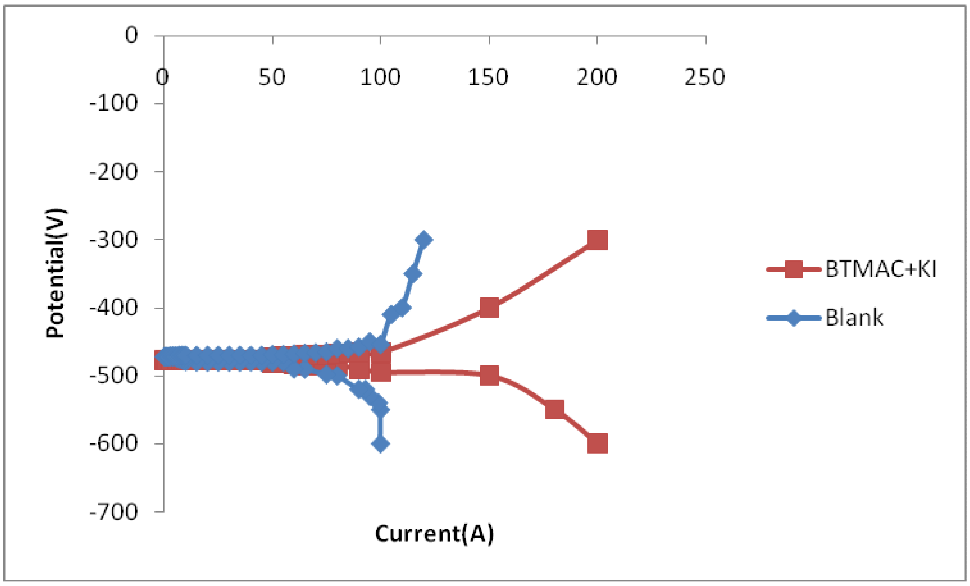

Figure 2: Polarisation spectra of Stainless Steel immersed in 1 M HCl in the absence and presence of inhibitor (0.0025 M BTMAC + 0.0018 M KI)

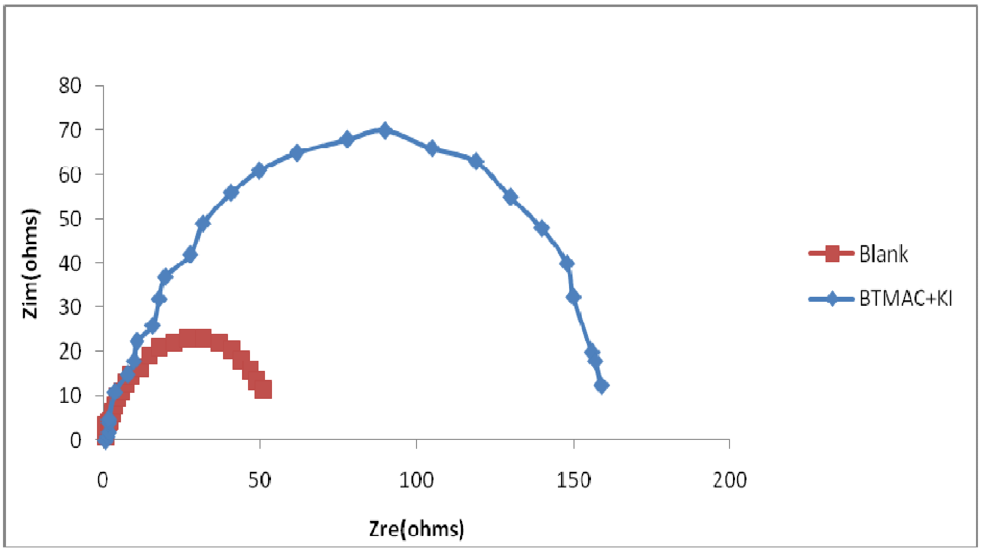

Figure3: Impedance spectra of Stainless steel immersed in 1 M HCl in the absence and presence of inhibitor (0.0025 M BTMAC +0.0018 M KI)

Analysis of Impedance Spectra

Impedance spectra have been used to confirm the formation of protective film on the metal surface, charge transfer resistance (R_{ct}) increases, double layer capacitance value (C_{dl}) decreases[25]. The AC impedance spectra of stainlesssteel immersed in 1 M HCl in the absence and presence of inhibitors BTMAC-KI are shown in Figure 3. The R_{ct} and C_{dl}values obtained from impedance spectra are give in Table5.

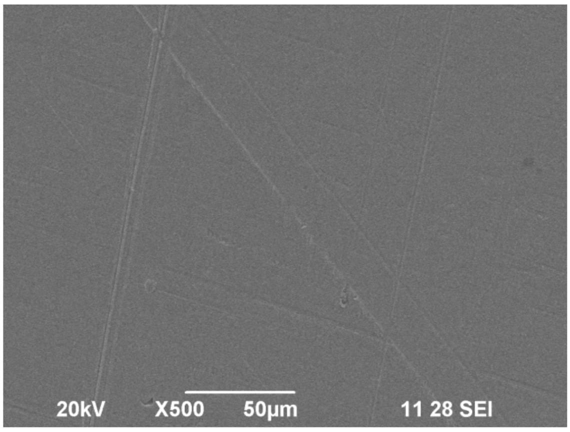

Fig-4(a)

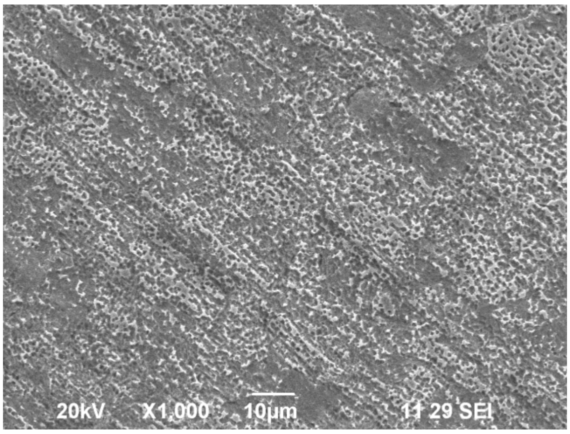

Fig-4(b)

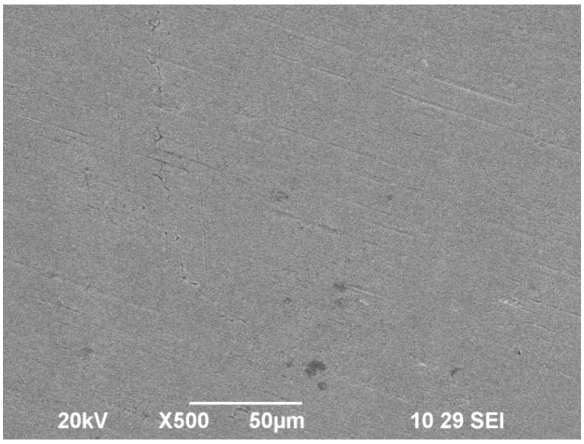

Fig-4 (c)

Figure 4 (a) SEM analysis of stainless steel before immersion, (b) Stainless steel immersed in 1.0 M HCl (Blank), (c) Stainless steel immersed in 1.0 M HCl+0.0025 M BTMAC + 0.0018 M KI

Table 5: Corrosion parameters of stainless steel immersed in 1 M HCl in the absence and presence inhibitor obtained from impedance spectra

Concentration in M	R_{ct}, Ohm	C_{dl} 10^{-3}, F	IE%
Blank	50	7.2380	-
0.0025 M BTMAC+ 0.0018 M KI	155	2.2747	67

The increase in the charge transfer resistance (R_{ct}) value from 50 to 155 ohm and the decrease in the double layer capacitance value (C_{dl}) from 7.2380 F to 2.2747 F on the addition of inhibitor system confirms the formation of a protective layer on the surface of the metal.

SEM Analysis

The SEM photograph of polished stainless steel, stainless steel dipped in 1.0 M HCl, and in 1.0 M HCl with the inhibitors is shown in fig 4a, 4b and 4c respectively. Figure 4(a) shows the smooth surface of the metal. The SEM photograph in figure 4(b) has shown the roughness of the metal due to corrosion by 1.0 M HCl. Figure 4(c) clearly shows the formation of a film by the adsorption of BTMAC and KI on the stainless steel surface which has made the surface smooth.

CONCLUSION

Based on the results obtained from this study, the following conclusions can be deduced BTMAC controls the corrosion of stainless steel in acidic medium. The inhibition efficiency of BTMAC increases with the increase in inhibitor concentration. Addition of KI to inhibitor shows synergistic effect on the corrosion inhibition efficiency towards stainless steel in acidic medium. Polarisation studies reveal that the inhibitor functions as a mixed inhibitor. However the large shift in the cathodic slope reveals that it controls the cathodic process more predominantly. SEM analysis and impedance spectra confirm the formation of the protective film on the metal surface.

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