Benzyl Triethylammonium Chloride As An Inhibitor For The Corrosion Of 430 Stainless Steel In Hcl Solution

M. Kalpana Devi, Felicia Rajammal Selvarani

Abstract: The inhibition effect of Benzyl Tri ethyl ammonium chloride on the corrosion behavior of 430 stainless steel in 1.0 M HCl as corrosion medium is investigated by mass loss method. The maximum inhibition efficiency is found to be 79% at 303 K. The investigation of adsorption isotherms indicates that the inhibition process fit Langmuir isotherm, fairly well. The surface morphology has been analysed by SEM and EDAX.

Keywords: Benzyl Tri ethyl ammonium chloride, physisorption, Stainless steel

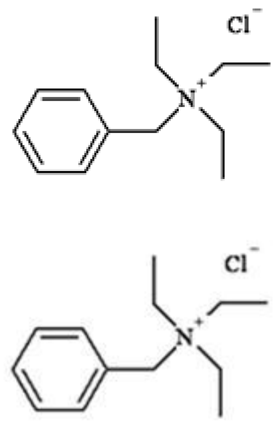
1 Introduction

The Pitting corrosion of 430 stainless steel is a destructive form of corrosion. Most equipment failures in stainless steel are due to pitting corrosion, [1, 2]. Hydrochloric acid is Widely-used in pickling solutions. The addition of an inhibitor is necessary to prevent corrosion i.e. to reduce the dissolution of metals in these acidic environments [3]. Corrosion inhibitors play an important role in corrosion prevention in many industries. Most commercial inhibitors used are organic compounds containing elements such as sulphur, oxygen, phosphorus and nitrogen [4-6]. Organic inhibitors are adsorbed on to the metal surface and consequently decrease corrosion attack. Quaternary ammonium compounds are considered the most potential inhibitor for corrosion control, especially on the carbon steel materials. Several studies of n-alkyl quaternary ammonium compounds such as benzyl tri methyl ammonium iodide [7], cetyl benzyl di methyl ammonium chlorides [8] on metals have been carried out. The adsorption process of quaternary ammonium compounds and other organic inhibitors have been investigated as function of the nature and surface charge of metallic materials, adsorption mechanism steps, chemical structures and electrolyte solution types [9-11]. In this present study, BTEAC, a n-alkyl quaternary ammonium compound is studied as a new inhibitor to prevent the corrosion of stainless steel in HCl. BTEAC has a strong positively charged N+ ion and π electron from aromatic benzyl group for adsorption to take place on stainless steel surface.

2 Materials and Method

Commercially pure 430 stainless steel samples, are used for preparing SS coupons for mass loss study. The corrosion medium, 1.0 M HCl solution, was prepared from analytical reagent HCl (37%) using double distilled water. Commercially available Benzyl tri ethyl ammonium chloride ($C_{13}H_{22}Cl\ N$) is used as such.

- *M.kalpana Devi is currently pursuing Ph.D in Chemistry,in Holy cross college, Trichy, Tamilnadu,India. E-mail: knehan2009@gmail.com*
- *Felicia Rajammal selvarani, Associate professor, Department of Chemistry Holycross college,Trichy, Tamil nadu, India.*



Benzyltriethyl ammoniumchloride

2.1 MASS LOSS STUDY

Rectangular specimens of SS, having the dimension 4.0cm×1.5 cm×0.0457 cm and containing a small holes of about 1 mm diameter near the upper edge are taken. Specimens are cleaned by buffing to produce a mirror finish and are then degreased with acetone. Initial Weight of specimen is taken up to the four decimal of gram with a digital balance. The solution of 1.0 M HCl is prepared using double distilled water. Each specimen is suspended by hooks to the surface of the 100 mL solution for all experiments. After the sufficient exposure time the, specimen is retrieved, cleaned by running water and then dried by hot dryer and then final weight is taken. From the Weight loss results, corrosion rates, CR degree of surface coverage θ and the inhibition efficiency (%IE) of the inhibitor, are calculated using equations 1, 2and3 respectively.

$$\mathbf{CR}\ (\mathrm{g\ cm^{-2}\ min^{-1}}) = \frac{\Delta m}{A} \qquad (1)$$

$$\boldsymbol{\theta} = \left(1 - \frac{CRo}{CRi}\right) \qquad (2)$$

$$\mathbf{IE\%} = \left(1 - \frac{CRo}{CRi}\right) \times 100 \qquad (3)$$

Where, CR_0 and CR_i are the Corrosion rates for SS in the absence and the presence of the inhibitor in 1.0 M HCl solution, respectively. **θ** is the degree of surface coverage by the inhibitor, A is the surface area of the SS coupons (cm^2), t is the time of immersion and Δm is the weight loss of SS after time t.

2.2SEM Analysis

Scanning Electron Microscope (SEM) images are taken in order to study the changes during the corrosion of stainless steel in the presence and the absence of inhibitor. The stainless steel specimens used for surface morphological studies are immersed in 1.0 M HCl containing optimum concentration of inhibitor and blank for 1 h. Then, they are removed, rinsed quickly with rectified spirit and dried. The analysis is performed on scanning electron microscope

2.3 Energy Dispersive Analysis of X-Rays (EDAXs)

The stainless steel specimen immersed in blank and in the inhibitor solution for 1 h is Removed, rinsed with water and dried to examine the elements present on the metal surface.

3. RESULT AND DISCUSSION

Table1: *Inhibition of corrosion of SS by Benzyltriethylammoniumchloride in 1.0 M HCl at 303 K and 313K*

[BTEAC], mM	Corossion rate×10^{-2}		%Inhibition Efficiency		E_a KJ mol^{-1}	Q_{ads} KJ mol^{-1}
	303 K	313K	303K	313K		
Blank	4.8322	8.6433			45.79	
0.4	1.8599	6.9657	61	18	104.13	-149.62
1.2	1.7140	6.4916	64	24	105.02	-136.28
2.0	1.5317	6.1451	68	28	109.56	-133.92
2.4	1.4223	6.0175	70	29	113.75	-137.40
3.2	1.0940	5.8350	76	32	132.01	-150.33
4.0	0.9847	5.3970	79	37	134.16	-146.45

Table 2: *values of $\Delta G°_{ads}$ for corrosion inhibition by BTEAC*

[BTEAC] mM	**Surface coverage θ** 303 K	**Surface coverage θ** 313 K	$\Delta G°_{ads}$ k J mol^{-1} 303 K	$\Delta G°_{ads}$ k J mol^{-1} 313 K
0.4	**0.61**	0.18	**-25.160**	**-21.052**
1.2	**0.64**	**0.24**	**-22.715**	**-18.967**
2.0	**0.68**	**0.28**	**-21.877**	**-18.179**
2.4	**0.70**	**0.29**	**-21.654**	**-17.832**
3.2	**0.76**	**0.32**	**-21.698**	**-17.452**
4.0	**0.79**	**0.37**	**-21.570**	**-17.448**

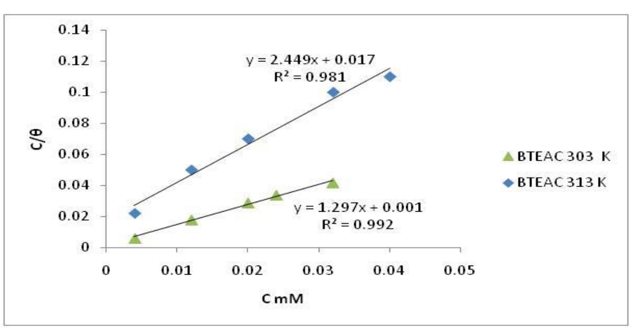


Fig-1 *Langmuir Adsorption isotherm*

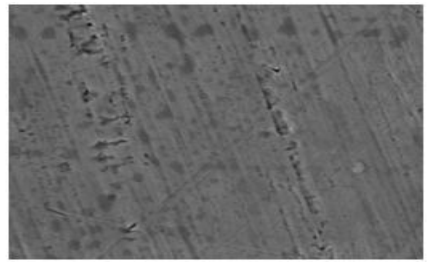


Fig.2a *SEM photograph of stainless steel before immersed in 1.0 M HCl solution*

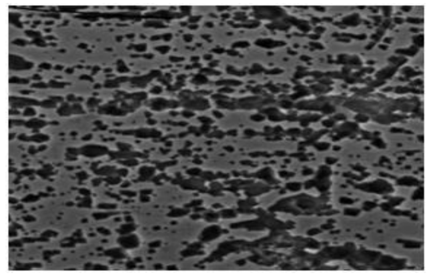


Fig .2b *SEM photograph of stainless steel immersed in 1.0 M HCl solution*

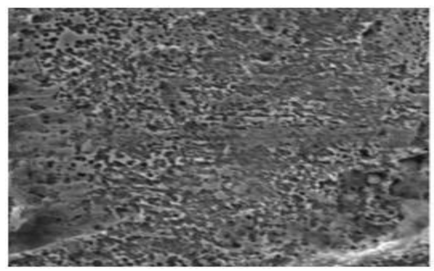


Fig .2c *SEM photograph of stainless steel after immersed in1.0 M HCl solution with BTECA.*

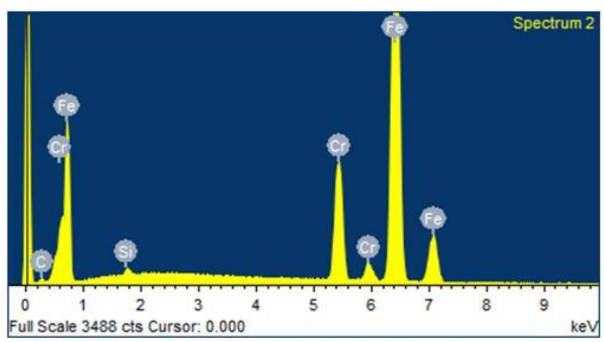


Fig-3a *EDAX spectrum of stainless steel*

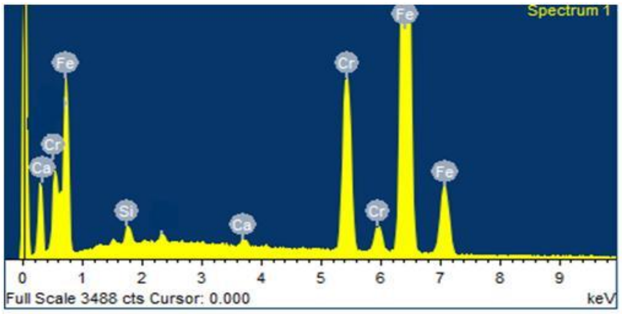


Fig-3b *EDAX spectrum of stainless steel Immersed in 1.0 M HCl*

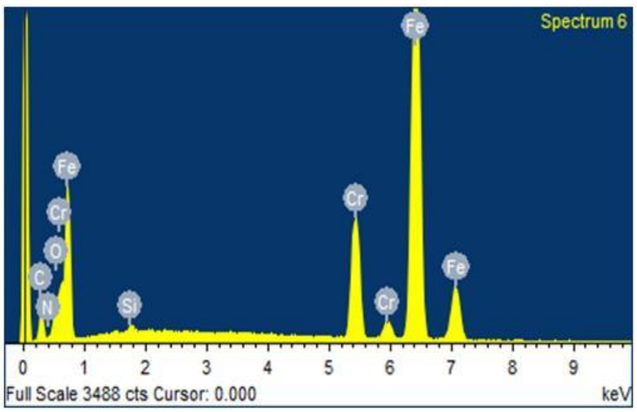


Fig-3c *EDAX Spectrum of SS immersed in 1.0 M HCl with BTEAC*

Table: 3 *EDAX spectrum of stainless steel immersed in 1.0 M HCl in the presence and the absence of BTEAC.*

Sample	Fe % Wt	Cr % Wt	N % W
Polished Stainless steel	81.15	16.16	-
Blank in1 M HCl	62.04	13.05	-
With BTEAC in 1 M HCl Solution	71.38	13.06	0.32

Discussion

Mass loss method

Values of the inhibition efficiencies of stainless steel in the absence and in the presence of the inhibitor at 303 K and 313 K are recorded in Table 1. The Corrosion rate of stainless steel in 1.0 M HCl decreases with increase in the concentration of inhibitor. The inhibition efficiency obtained at 313 K are relatively lower than the values obtained at 303 K, indicating that the inhibition efficiency of BTEAC decreases with increase in temperature.

Study of Adsorption isotherm

The surface coverage values θ are determined from the mass loss studies. Langmuir isotherm, is studied with the surface coverage values θ.

The Langmuir isotherm equation is of the form:

C/θ = 1/Kads + C ------------------------- (4)

The plot of C/θ against C is a straight line graph.

the best –fit adsorption isotherm is the Langmuir adsorption isotherm, for adsorption of BTEAC on stainless steel surface with the mean R^2 value is 0.948.

The values of ΔG°ads for the adsorption process are calculated at each θ value, using Langmuir isotherm.

K ads= θ/C (1-θ) ---------------------------------- (5) and tabulated in Table-2.

The equilibrium constant of adsorption is related to the free energy of adsorption (ΔGads) according to equation. (6)[12, 13].

ΔGads = -2.303RT log (55.5 Kads) -------------------- (6)

Where R is the gas constant, T is the temperature; K is the equilibrium constant of adsorption The values of ΔG°ads (Table-2) are negatively lower than the threshold values of -40 kJ mol-1 required for chemical adsorption. The negative values of ΔG°ads show that the adsorption of inhibitor on stainless steel surface is spontaneous and favours the mechanism of physical adsorption [14].

Effect of temperature

The activation energies for the corrosion processes are calculated using the Arrhenius equation:

CR = A exp (-Ea/RT) ------------------ (7)

The reduction of inhibition efficiency with rise in temperature (Table 1) is suggestive of the physical adsorption mechanism on the metal surface [15]. Within the temperature range of 303(T1) to 313 K (T2),

Equation (7) can be written as

Log (CR2/CR1) = Ea/ R (1/T1- 1/T2) -------------- (8)

Where Ea is the activation energy, CR2 and CR1 are the corrosion rates at the temperature T1 (303 K) and T2 (313K), respectively, Values of Ea calculated from the equation (8) are recorded. The values (Table 3) are less than -80 kJ mol-1 indicating physisorption [16-18]. The activation energies Ea are also observed to increase with increasing in the concentration of inhibitor, indicating that there is decreasing the adsorption of the inhibitor with increasing concentration. The heat of adsorption (Qads) is calculated using equation [19].

Qads = 2.303R [log (θ2/ (1- θ2) - log (θ1/(1- θ1)] x (T1 × T2/ T2- T1) kJ mol-1 ------ (9)

Where θ1 and θ2 are the degrees of surface coverage at the temperatures T1 (303 K) and T2 (313 K), respectively. Values of Qads calculated from equation (9) are recorded. (Table 2) These values are negative, indicating that the adsorption is exothermic [20].

Microscopic study
Microphotograph's (Fig. 2a, 2b, and 2c) for stainless steel in 1.0 M HCl without and with BTEAC At 200 x magnification are shown. Comparison micrographs seem to indicate that in the presence of the inhibitor, the smoothness of the surface of stainless steel sample has improved considerably. The Smoothening of the metal surface would have probably, resulted from the inhibitor adsorption on the metal surface.

EDAX-Energy Dispersive Analysis X-ray Analysis
The EDAXs survey spectra are used to determine the elements present on the metal surface before and after exposure to the inhibitor solution [21]. EDAX spectrum of stainless steel is shown in Figure 3(a). They show the characteristic peaks of the elements. Figure 3(b) shows the EDAX spectrum of stainless steel immersed in 1.0 M HCl. The EDAX spectrum of stainless steel immersed in 1.0 M HCl solution containing 0.028 M of BTEAC is shown in Figure 3(c). It shows the additional line characteristic for the existence of N. In addition, the intensity of Fe signal is enhanced. The appearance of the N signal and enhancement in Fe signal is due to the presence of inhibitor. The increase in the % of Fe on the surface shows the reduction of corrosion in the presence of inhibitor.

CONCLUSION
Corrosion of stainless steel in 1.0 M HCl is found to decrease with increasing concentration of the Inhibitor, BTEAC The type of corrosion is found to be physisorption. SEM and EDAX confirm the presence of a protective film on the metal surface.

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