

Ethylbenzotriazolium Bromide Ionic Liquid: A New Water Soluble Inhibitor for Corrosion of Mild Steel in Acid Media

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The inhibiting effect of 1-ethyl-3-ethylbenzotriazolium bromide ionic liquid, [C₂Et]Br, on the corrosion behaviour of mild steel in 5 wt. % HCl was investigated by using various techniques such as weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy. All studies showed that the increase in inhibition efficiency and decrease in the corrosion rate by increasing the inhibitor concentration. Polarization measurements indicated that the [C₂Et]Br acted essentially as a mixed-type inhibitor. The electrochemical impedance study showed that corrosion inhibition took place by adsorption.

Key Words: Benzotriazolium ionic liquid, Corrosion, Steel, Polarization, EIS, Acid solution.

INTRODUCTION

Acid solutions are commonly used in the chemical industry to remove the scales from the metallic surfaces. The addition of inhibitors secures the metal against an acid attack effectively. The applicability of organic compounds as corrosion inhibitors for metals in acidic media has been recognized for a long time. The existing data show that most of the organic inhibitors act by adsorption on the metal surface¹⁻⁶. The adsorption of inhibitors occurs through heteroatoms such as nitrogen, oxygen, phosphorus and sulphur as well as a triple bond or an aromatic ring.

It has been observed that adsorption depends mainly on certain physicochemical properties of the inhibitor group, such as electron density at the donor atom, π -orbital character and the electronic structure of the molecule. Imidazolium compounds and benzotriazole derivatives are reported to show corrosion resistant behaviour on copper, mild steel and aluminium. It was found that the action of such inhibitors depends on the specific interaction between the functional groups and the metal surface, due to the presence of the -C=N-group, -N=N-group and electronegative nitrogen in the molecule.

Ionic liquids are molten salts, which are made up only from two asymmetrical ions of opposite charges and have a melting point of <100 °C or are ideally, even liquid at ambient temperature. They have found their application in different areas as organic synthesis, catalysts, energy storage devices, etc.⁶. How-

ever, ionic liquids were used as metallic corrosion inhibitors. Up to date, there was little information on imidazolium ionic liquids used as corrosion inhibitors in acid medium¹⁻³.

Our previous work⁷ showed that the benzotriazolium ionic liquids could be used as a corrosion inhibitor in acid medium. The aim of this work is to investigate the inhibiting influence of 1-ethyl-3-ethylbenzotriazolium bromide, [C₂Et]Br, on mild steel (MS) corrosion in 5 wt. % hydrochloric acid solution. This has been studied by weight loss, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) techniques. To our best knowledge, the benzotriazole ionic liquid, [C₂Et]Br has been firstly used as corrosion inhibitors in acid medium.

EXPERIMENTAL

The synthetic route of [C₂Et]Br is depicted in Fig. 1. First 1-ethylbenzotriazole was synthesized by a reaction of benzotriazole and ethylbromide in aqueous sodium hydroxide solution using tetrabutylammonium bromide as phase transfer reagent and then 1-ethylbenzotriazole was further quaternized with ethylbromide. The specific steps were similar to those described previously⁸. The chemical structure of product was checked by IR (Aratar-360, American) and ¹H NMR [Avance(III), Bruker]. The corresponding spectral characteristics were described as following. IR (KBr, $\nu_{\max}$, cm⁻¹ pellet): 3484, 3038, 2969, 2873, 1607, 1453, 1379, 1255, 1146, 772, 754. ¹H NMR (400 MHz, CDCl₃) 1.71 (t, 6H), 5.16 (q, 4H), 7.84 (m, 2H), 8.47 (d, 2H).

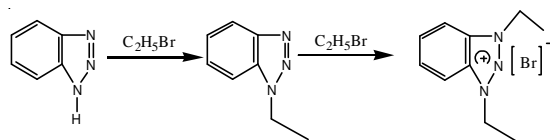


Fig. 1. Structure and synthesis of 1-ethyl-3-ethylbenzotriazolium ionic liquid

Prior to all measurements, the mild steel samples are polished successively with fine grade emery papers from 400 to 1200 grade. The specimens are rinsed thoroughly with double-distilled water, degreased in absolute ethanol and dried by compressed air at room temperature. The aggressive solution 5 wt. % HCl is prepared by dilution of AR grade 37 wt. % HCl with double distilled water. The concentration range of inhibitor employed was 2–40 mmol/L in acid solutions.

Weight loss experiments were performed on mild steel samples with a rectangular form in 5 wt. % HCl with and without addition of different concentrations of inhibitor. Every sample was weighted by an electronic balance and then placed in the acid solution (100 mL). The duration of the immersion was 5h at 323 K, the solution temperature was by thermostatically controlled. After immersion, the surface of the specimen was cleaned by anhydrous alcohol rinsing and the sample was reweighted in order to calculate the corrosion rate.

Electrochemical experiments were carried out using an electrochemical workstation (CHI660D, ShangHai). A conventional three-electrode arrangement at 323 K under atmospheric condition was used for electrochemical studies. Working electrode was prepared from a MS sheet, mounted in polyester so that the area exposed to corrosive solution was 1 cm². A saturated calomel electrode (SCE) and a 1 cm × 1 cm platinum electrode were used as the reference and counter electrodes, respectively. For potentiodynamic polarization measurements the potential sweep rate was 10 mVs⁻¹ in the potential range from 150 mV below the open circuit potential to 150 mV above the open circuit potential. The impedance measurements were carried out in the frequency range of 100 kHz to 1 Hz with a signal amplitude perturbation of 5 mV at the open circuit potential (OCP). All potentials were recorded with respect to the saturated calomel electrode.

RESULTS AND DISCUSSION

Weight loss measurements: The weight loss results regarding the corrosion parameters for mild steel in 5 wt. % HCl solution in the absence and presence of different concentrations of inhibitor are summarized in Table-1.

TABLE-1
WEIGHT LOSS DATA OF MILD STEEL IN 5 wt. % HCl FOR
VARIOUS CONCENTRATION OF [C₂Et]Br

Inhibitor conc. (mmol/L)	CR _{corr} (gm ² h ⁻¹)	IE (%)
Blank	13.770	-
2	7.340	46.7
4	5.811	57.8
10	4.943	64.1
20	3.924	71.5
40	2.700	80.4

The inhibition efficiency was calculated by using the following eqn.(1)³, where CR₀ and CR_{inh} are the corrosion rates

of mild steel with and without the inhibitor, respectively. It can be observed that corrosion rate values of mild steel decrease when the inhibitor concentration increases. The inhibition (IE) increases with increasing the concentrations, reaching a maximum value (80.4 %) of 40 mmol/L of [C₂Et]Br. Gravimetric measurements confirm the protection property of [C₂Et]Br in 5 wt. % HCl. The inhibition may be due to adsorption of [C₂Et]⁺ on the mild steel surface.

$$IE = \frac{CR_0 - CR_{inh}}{CR_0} \times 100\% \quad (1)$$

Electrochemical experiment

Potentiodynamic polarization curves: Fig. 2a shows the influence of C₂EtBr on the cathodic and anodic potentiodynamic polarization curves of mild steel in 5 wt.% HCl. It is observed that in the presence of [C₂Et]Br, the curves were shifted to more positive or negative potential region and the shift was found dependent on concentration of the inhibitor. The increase in concentration of the inhibitor increase the shift and the decreases. The curves are displaying a preferential suppression of the anodic half reaction.

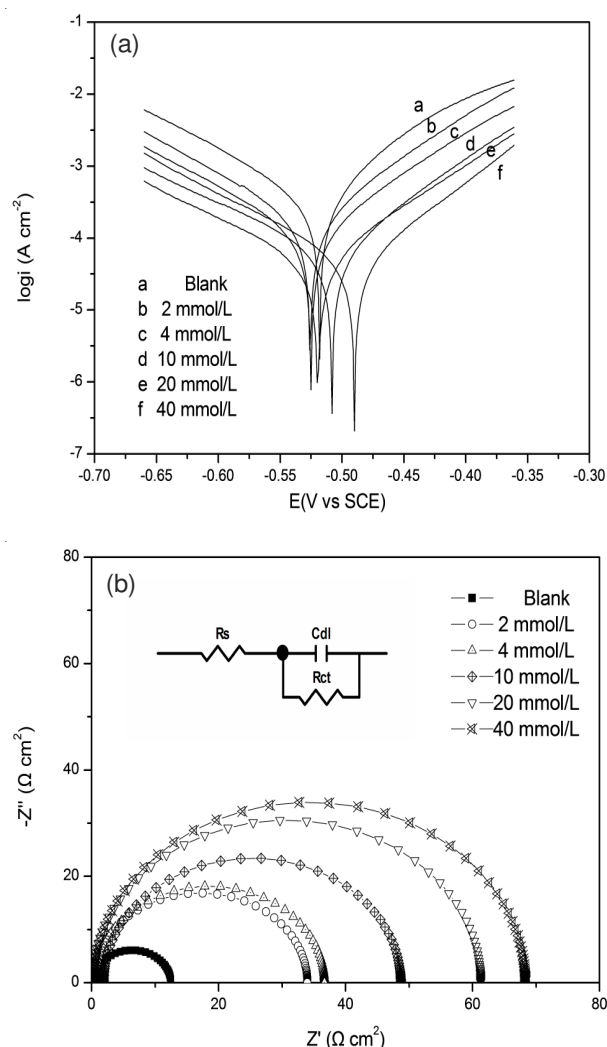


Fig. 2. (a) Potentiodynamic polarization curves for corrosion of MS in 0.5 wt. % HCl containing different concentrations of [C₂Et]Br; (b) Nyquist plots and the corresponding equivalent circuit for MS in 5 % HCl in the absence and presence of [C₂Et]Br

TABLE-2
ELECTROCHEMICAL PARAMETERS FOR CORROSION OF MILD STEEL IN 5 wt. %
HCl IN THE PRESENCE OF DIFFERENT CONCENTRATIONS [C₂Et]Br

Inhibitor conc. (mM)	Potentiodynamic polarizations parameters						Impedance parameters	
	E _{corr} (mV/SCE)	b _a (mVdec ⁻¹)	b _c (mVdec ⁻¹)	I _{corr} (mAcm ⁻²)	IE (%)	R _{ct} (Ω cm ²)	C (μF/cm ²)	IE (%)
Blank	-518	72	-106	0.416	-	12.2	176	-
2	-526	80	-103	0.227	45.4	33.8	48	64.1
4	-525	86	-108	0.149	64.1	36.5	35	66.3
10	-490	77	-104	0.619	85.2	46.8	33	73.9
20	-508	82	-130	0.874	79.0	61.2	25	80.0
40	-520	85	-123	0.661	84.1	67.9	23	82.0

Electrochemical corrosion parameters such as corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_a, b_c) and corrosion current density (I_{corr}), obtained by extrapolation of Tafel lines, are collected in Table-2. The values of cathodic tafel slope (b_c) and anodic tafel slope (b_a) of [C₂Et]Br are found to change with the concentration of the inhibitor, indicates that the inhibitor controlled both anodic and cathodic reactions.

$$IE = \frac{I_0 - I_{corr}}{I_0} \times 100\% \quad (2)$$

Equation (2) was used to calculate the IE, where I₀ and I_{corr} are the corrosion current density values without and with inhibitor, respectively. The obtained results show that the inhibition efficiency increases, while the corrosion current density decreases when the concentration of the inhibitor increases. This could be explained on the basis of inhibitor adsorption on the metal surface and the adsorption process enhances with increasing inhibitor concentration. The results obtained from the polarization measurements are in good agreement with those obtained from weight-loss method.

Electrochemical impedance measurements: The corrosion behaviour of mild steel in acidic solution in the presence of [C₂Et]Br was investigated by the EIS. The impedance spectra were analyzed by fitting to the equivalent circuit model shown in Fig. 2b. It is apparent that the impedance spectra obtained yields a semi circular shape. This indicates the corrosion of the mild steel in 5 wt. % HCl is mainly controlled by a charge transfer process.

Table-2 collects various parameters such as charge-transfer resistance (R_{ct}), double layer capacitance (C_{dl}) and percentage inhibition efficiency (IE) calculated from eqn. (3), where R_{ct(inh)} and R_{ct} are the charge-transfer resistance values with and without inhibitor, respectively.

$$IE = \frac{R_{ct(inh)} - R_{ct}}{R_{ct(inh)}} \times 100 \quad (3)$$

The R_{ct} values were calculated from the difference in impedance at lower and higher frequencies as suggested by Tsuru *et al.*⁹.

The values of C_{dl} are obtained at the frequency f_{max}, at which the imaginary component of the impedance is maximal (-Z''_{max}), using the following eqn. (4)¹⁰.

$$C_{dl} = \frac{1}{2\pi f_{max} R_{ct}} \quad (4)$$

It is found that the R_{ct} values increase with increasing [C₂Et]Br concentration while the C_{dl} values tend to decrease. The decrease in C_{dl} values is due to the adsorption of [C₂Et]Br

on the metal surface. The greatest inhibition is observed at a concentration of 40 mmol/L. The inhibition efficiencies, calculated from impedance results, show the same trend as those obtained from polarization and weight loss measurements. In fact, the presence of [C₂Et]Br is accompanied by the increase of the value of R_{ct} in an acidic solution indicating a charge transfer process mainly controlling the corrosion of mild steel.

Conclusion

From the overall experimental results and discussion the following conclusions can be deduced: (1) The [C₂Et]Br is a new water soluble inhibitor for mild steel in 5 wt. % HCl. The inhibition efficiency increases with an increase of inhibitive concentration to attain a maximum value of 80.4 % at 40 mmol/L. There are good agreements between the inhibition efficiencies, obtained from gravimetric method and electrochemical measurements; (2) The potentiodynamic polarization curves indicated that the inhibitors inhibited both anodic metal dissolution and also cathodic hydrogen evolution reactions and acted as mixed type inhibitors in 5 wt. % HCl solution; (3) The electrochemical impedance study shows that the application of [C₂Et][Br] inhibitor significantly increases R_{ct} values and decreases C_{dl} values in 5 wt. % HCl, suggesting that corrosion inhibition takes place by adsorption.

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