

Adsorption effect of Methyl [5-propylthio]-1H-benzimidazol-2-yl] carbamate on the metal surface

M. Mistry

Department of Applied Chemistry, SVNIT, Surat, Gujarat, INDIA, mad.mohanmistry@gmail.com

Abstract

Electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization techniques were applied to investigate the inhibiting ability of Methyl [5-propylthio]-1H-benzimidazol-2-yl] carbamate (MPBI) on the corrosion of mild steel in 1 M HCl at 30°C. Results showed that MPBI is an effective inhibitor for mild steel corrosion in 1 M HCl solutions and inhibition efficiency is >90% at inhibitor concentration of 3.77×10^{-4} M.

Key Words: Corrosion inhibition; EIS; PDP

1. INTRODUCTION

Evaluation of corrosion inhibitors for mild steel in acidic media is important for some industrial facilities as well as is very interesting from theoretical aspects. Acid solutions are generally used for the removal of rust and scale in industrial processes. Hydrochloric acid is widely used in the pickling, cleaning and descaling of steel and ferrous alloys [1]. Most of the effective corrosion inhibitors are organic compounds containing nitrogen, oxygen, sulphur, aromatic rings and π -electrons in their structures [2, 3]. The effectiveness of these organic compounds as corrosion inhibitors has been interpreted in terms of their molecular structure, molecular size, molecular mass, presence of hetero-atoms and adsorptive tendencies [4]. The first stage in the action mechanism of these compounds in acid media is their adsorption on the metal surface [5]. The various inhibition mechanisms are considered regarding different situations created by changing various factors such as medium and inhibitor in the system metal/acid medium/inhibitor [6].

The interactions between the inhibitor molecules and the metal surfaces can be explained and understood in details by theoretical approaches. Therefore, recently a trend and an increasing attention were seen on the involvement of these theoretical approaches in corrosion studies [7-9]. Quantum chemical calculations have been used recently to explain the mechanism of corrosion inhibition [10, 11].

2. EXPERIMENTAL DETAILS

Mild steel specimens (having compositions 0.076 % C; 0.192 % Mn; 0.050 % Cr; 0.026 % Si; 0.012 % P; 0.135 % Cu; 0.023 % Al; 0.05 % Ni and remainder being iron) of size 7.5 cm \times 1.0 cm with 1.0 cm² exposed surface area (isolated with commercially available lacquer) were used for electrochemical measurements. The specimens were cleaned and prepared as per ASTM standard G1-03 [12]. This stock solution was used for all experimental purposes. We have added the same quantity of methanol to Blank to avoid the contribution of alcohol. Solutions were freshly prepared from analytical grade chemical reagents using distilled water. Measurements were carried out in aerated non-stirred

1 M HCl acid solutions at 30°C containing MPBI in the concentration range 0.38×10^{-4} to 3.77×10^{-4} M as corrosion inhibitor.

All electrochemical measurements were performed using a GAMRY PCI 4/300 electrochemical work station based on ESA 400. Gamry applications include EIS 300 (for EIS measurements) and DC 105 software (for corrosion) and Echem Analyst (5.50 V.) software for data fitting. All electrochemical experiments were performed in a Gamry three electrodes electrochemical cell under atmospheric condition with a platinum counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode mild steel (7.5 cm long stem) with the exposed surface of 1.0 cm² was immersed into aggressive solutions with and without inhibitor, and measurements were initiated about 30 min after the working electrode was immersed in solution to stabilize the steady state potential. EIS measurements were performed at corrosion potentials (E_{corr}) over a frequency range of 100 kHz to 10 mHz with an AC signal amplitude perturbation of 10 mV peak to peak. Potentiodynamic polarization studies were performed with a scan rate of 1 mV s⁻¹ in the potential range from 250 mV below the corrosion potential to 250 mV above the corrosion potential. All potentials were recorded with respect to the SCE.

3. RESULTS AND DISCUSSION

3.1. Electrochemical impedance spectroscopy (EIS) studies

Figure 1 presented impedance response, obtained from EIS measurements for mild steel corrosion in 1 M HCl solution in the presence and absence of different concentrations of MPBI at 30°C, in the form of Nyquist plots (Fig. 1a) and Bode-impedance plots (Fig. 1b). The plots show a depressed capacitive loop which arises from the time constant of the electrical double layer and charge transfer resistance. The impedance of the inhibited mild steel increases with increase in the inhibitor concentration and consequently the inhibition efficiency increases. A depressed semicircle is mostly referred to as frequency dispersion which could be attributed to different physical phenomena such as

roughness and inhomogeneities of the solid surfaces, impurities, grain boundaries and distribution of the surface active sites [13]. The impedance response of the mild steel in 1 M HCl solution in the presence of MPBI is characterized by diffusion tail (Fig. 1a). Therefore, the presence of inhibitor introduces the diffusion step in corrosion process and the reaction becomes diffusion-controlled. Hence, the corrosion process can have two steps as in any electrochemical process at the electrochemical interface, first, the oxidation of the metal (charge transfer process) and second, the diffusion of the metallic ions from the metal surface to the solution (mass transport process). Inhibitors get adsorbed on the electrode surface and thereby produce a barrier for the metal to diffuse out to the bulk and this barrier increases with increasing the inhibitor concentration [14].

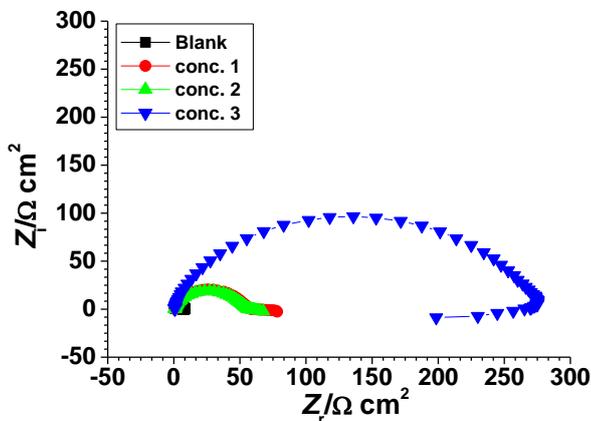


Fig. 1: (a) Nyquist plots and (b) Bode-impedance plots for mild steel in 1 M HCl containing different concentrations of MPBI.

In order to evaluate the experimental Nyquist plots an equivalent circuit model must be applied. The simplest model consists of the solution resistance (R_s) in series with the parallel combination of constant phase element (CPE) in place of double layer capacitance (C_{dl}) and charge transfer resistance (R_t) was used. Such equivalent circuit (Fig. 3) has been used previously to model the mild steel/acid interface [15]. The charge transfer resistance (R_t) must be corresponding to the resistance between the metal and OHP (outer Helmholtz plane) and can be calculated from the difference in impedance at lower and higher frequencies, as suggested by Tsuru et al. [16]. CPE in impedance is mathematically given by relation:

$$Z_{CPE} = Q^{-1} (j\omega)^{-n} \quad (1)$$

where Q is the magnitude of the CPE, j is the imaginary unit, ω is the angular frequency ($\omega = 2\pi f$, the frequency in Hz), and n is the phase shift gives details about the degree of surface inhomogeneity. When $n = 1$, this is the same equation as that for the impedance of a capacitor, where $Q = C_{dl}$. In fact, when n is close to 1.0, the CPE resembles a

capacitor, but the phase angle is not 90° . It is constant and somewhat less than 90° at all frequencies.

The term double layer capacitance is still often used in the evaluation of electrochemical impedance results to characterize the double layer which is believed to be formed at the metal/solution interface of systems displaying non-ideal capacitive behavior. For providing simple comparison between the capacitive behaviors of different corrosion systems, the values of Q were converted to C_{dl} using the relation [17]:

$$C_{dl} = Q(\omega_{max})^{n-1} \quad (2)$$

here, ω_{max} represents the frequency at which the imaginary component reaches a maximum. It is the frequency at the top of the depressed semicircle, and it is also the frequency at which the real part (Z_r) is midway between the low and high frequency x-axis intercepts. The values of η_{R_t} % inhibition were calculated as described previously [14]

The electrochemical impedance results derived by fitting the Nyquist plots were seen in Fig 1. It is clear that addition of the MPBI into the corrosive solution caused to an increase in charge transfer resistance (R_t) and a decrease in the double layer capacitance (C_{dl}) which can be given as [18].

$$C_{dl} = \frac{\epsilon\epsilon_0 A}{d} \quad (3)$$

where ϵ_0 is the vacuum dielectric constant, ϵ is the local dielectric constant, d is the thickness of the double layer, and A is the surface area of the electrode. It is obvious that a decrease in C_{dl} can happen if the inhibitor molecules (low dielectric constant) replace the adsorbed water molecules (high dielectric constant) on the mild steel surface. The capacitance is inversely proportional to the thickness of the double layer. Thus, decrease in the C_{dl} values could be attributed to the adsorption of MPBI on the metal surface. Decrease in the capacitance, which can result from a decrease in the local dielectric constant and/or an increase in the thickness of the electrical double layer, strongly suggests that the inhibitor molecules adsorbed at the metal/solution interface. In the absence and in the presence of inhibitor, phase shift value remains more or less identical; this indicates that the charge transfer process controls the dissolution mechanism [19] of mild steel in 1 M HCl solution in the absence and in the presence of MPBI.

3.2. Potentiodynamic polarization studies

Figure 3 presented typical potentiodynamic polarization curves for the mild steel in 1 M HCl in the presence and absence of MPBI at different concentrations. It could be noticed that both the cathodic and anodic reactions were suppressed the presence of MPBI, which suggested that the MPBI reduced anodic dissolution and also retarded the cathodic hydrogen evolution reaction.

Electrochemical corrosion kinetics parameters, i.e. corrosion potential (E_{corr}), cathodic and anodic Tafel slopes (b_c , b_a)

and corrosion current density (I_{corr}) obtained from the Tafel extrapolation of the polarization curves together with surface coverage (θ) can be obtained from Fig. 3. These values were calculated from the Tafel fit routine provided by Gamry Echem Analyst software, this routine uses a non-linear chi squared minimization to fit the data to the Stern-Geary equation. The percentage inhibition efficiency ($\eta_P\%$) was calculated as described previously [14]. The value of θ was calculated using the expression:

$$\theta = \eta_P\% / 100 \quad (4)$$

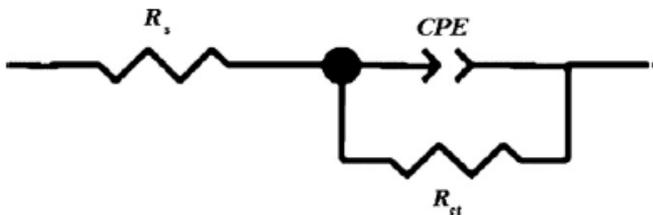


Fig. 2: The electrochemical equivalent circuit used to fit the impedance spectra

(R_s = solution resistance, R_{ct} = charge transfer resistance).

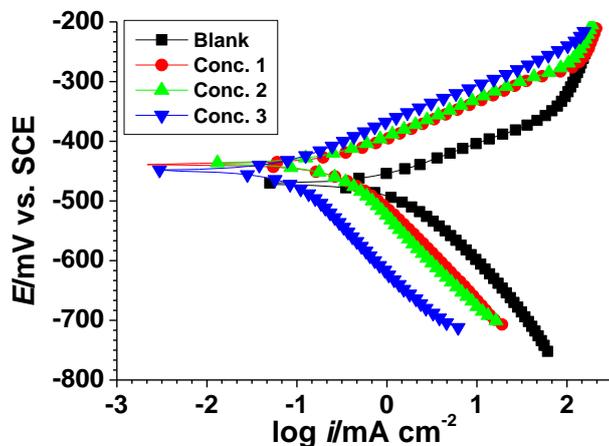


Fig. 3: Tafel polarization curves for corrosion of mild steel in 1 M HCl in the absence and presence of different concentrations of MPBI.

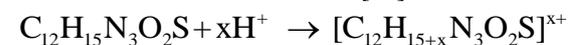
The results in Figure 2 showed that the inhibition efficiency increased, while the corrosion current density decreased with increasing concentration of MPBI. This could be explained on the basis of adsorption of MPBI on the mild steel surface and the adsorption process enhanced with increasing inhibitor concentration. The values of corrosion potential (E_{corr}) were found to be almost identical at all MPBI concentrations, indicating that it acts as mixed-type inhibitor. From Fig. 3, it is clear that the values of both anodic and cathodic Tafel slope constants increased with increasing MPBI concentration. These results suggested that

studied drug acts by affecting the mechanism of both anodic and cathodic reactions. Increase in b_c values is more pronounced than b_a values, indicating that cathode is more polarized. The increase in cathodic Tafel constant (b_c) values changes the mechanism of hydrogen evolution reaction. This is probably due to a diffusion or barrier effect [19]. According to Bockris and Srinivasan [20], this behaviour can be correlated to the decrease of the cathodic transfer coefficient which, in this case, can be ascribed to the thickening of the electric double layer due to the adsorbed inhibitor molecules. The increase in b_a values indicated a change in the mechanism of anodic dissolution of mild steel in 1 M HCl solution. This can be ascribed that adsorbed of inhibitor molecules participate in the reaction, probably in the form of complex, (iron-inhibitor)_{ads} [21]. The results obtained from the polarization measurements are in good agreement with those obtained from the EIS method.

3.3 Mechanism of corrosion inhibition

Inhibition performance of MPBI for mild steel/1 M HCl interface depends on the extent of adsorption and adsorption depends on several factors such as the number of adsorption sites, molecular size, and mode of interaction with the metal surface and extent of formation of metallic complexes. The adsorption of MPBI at the mild steel surface can take place through its active centres; unshared electron pairs of heteroatoms (N) and pi-electron of the benzimidazole ring.

In acidic solutions, it is known that inhibitor molecules can be protonated. Thus in solution both neutral molecules and cationic forms of inhibitor exist [22]:



It is assumed that Cl^- ion is first adsorbed onto the positively charged metal surface by columbic attraction and then inhibitor molecules can be adsorbed through electrostatic interactions between the positively charged molecules and the negatively charged metal surface [22]. These adsorbed molecules interact with $(FeCl^-)_{\text{ads}}$ species to form monomolecular layers (by forming a complex) on the steel surface. These layers protect mild steel surface from attack by chloride ions. Thus the oxidation of $(FeCl^-)_{\text{ads}}$ into Fe^{++} can be prevented. On the other hand, the protonated inhibitor molecules are also adsorbed at cathodic sites in competition with hydrogen ions that going to reduce hydrogen evolution.

The neutral molecules may be adsorbed on the surface of mild steel through the chemisorption mechanism, involving the displacement of water molecules from the mild steel surface and the sharing electrons between the hetero atoms and iron. The inhibitor molecules can also adsorb on the mild steel surface on the basis of donor-acceptor interactions between π -electrons of the aromatic ring and vacant d-orbitals of surface iron atoms.

4. CONCLUSION

Methyl [6-(propylthio)-1H-benzimidazol-2-yl] carbamate (MPBI) was showed excellent inhibition performance as a mixed-type inhibitor. The addition of MPBI to a corrosive

solution inhibits both anodic metal dissolution and cathodic proton reduction reactions.

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