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Quantum chemical and experimental investigations on equipotent effects of (+)R and (−)S enantiomers of racemic amisulpride as eco-friendly corrosion inhibitors for mild steel in acidic solution

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ABSTRACT

The potential of amisulpride drug as a corrosion inhibitor for mild steel in 1 M HCl has thoroughly been investigated by electrochemical methods. Polarization curves showed that this compound has high inhibiting properties for steel corrosion in acidic solution and the inhibition efficiency increased with the increase in inhibitor concentration. The adsorption of the inhibitor on the surface of steel has been found to obey a Langmuir adsorption isotherm and the influence of temperature on the adsorption of inhibitors onto a mild steel surface has been reported. Quantum chemical computations at the density functional theory have been applied to study the inhibition performance of (+)R and (−)S enantiomers of racemic amisulpride. The quantitative structure–activity relationship (QSAR) approach has also been used to correlate the quantum chemical parameters with the experimentally determined inhibition efficiencies.

1. Introduction

The study of corrosion of mild steel in acid media has become an important industrial and academic topic due to the increased industrial applications of acid solutions [1]. The corrosion rate of mild steel is very high when it forms soluble corrosion products in acid media especially in the fields of applications of acid pickling, industrial cleaning, acid descaling, oil-well acid in oil recovery and petrochemical processes [2]. Mitigation of corrosion is usually done by various engineering techniques, alloying the metal with other elements and using protective film forming thorough chemical compounds. Among them, the use of organic compounds containing the heteroatoms such as N, O, P and S, which can form protective film on the metal surface in the corrosive medium, as inhibitors is the most widely accepted technique [3–8]. Hence, the investigation and exploring of corrosion inhibitors for the corrosion control of mild steel in acid media became important not only for its academic meaning but also for its practical applications [9–13]. However, a very important problem in using organic compounds as inhibitors is that most of them are toxic and cannot be biodegraded. This leads to the emission of industrial waste waters with a large amount of toxic material to water ways [14]. Therefore, their replacement by new environment-friendly inhibitors is desirable [15]. Thus, at present, the research works on corrosion inhibitors are oriented to the development of “green corrosion inhibitors”, i.e. the compounds with good corrosion inhibition efficiency but low risk of environmental pollution [16]. Recently studies on the use of drugs as corrosion inhibitors have been reported by many researchers [17–21]. Many authors generally agree that drugs are the good corrosion inhibitors that can complete favorably with green corrosion inhibitor. Moreover, most drugs can be synthesized from natural products. The reasons for using drugs as corrosion inhibitors are as follows; (1) drug molecule contains oxygen, nitrogen and sulfur as active centers, (2) drugs are reportedly environmentally friendly and important in biological reactions and (3) drugs can be easily produced and purified [22,23]. In modern scenario, development of novel biodegradable and less toxic corrosion inhibitors is gaining importance. Biologically active molecules like sulfadimidine, sulfamethoxazole, cefatrexyl, apart from other antibacterial and antifungal drugs have been reported as good corrosion inhibitors [24–26]. The use of drugs as corrosion inhibitors for metals in different aggressive environments is not widely reported. Few reports exist in literature to date. These include the use of sulpha drugs [27,28], antimalerial drugs [29] and analgesic drugs [30] as efficient corrosion inhibitors for metals in various media. Hence the aim of this work is to gain some insight into the effect of an environmentally-friendly (+)R and (−)S enantiomers of racemic amisulpride, as corrosion inhibitor for mild steel in 1 M HCl solution utilizing; weight loss measurements, the polarization method

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and electrochemical impedance spectroscopy (EIS). Potential of charge (PZC) was also determined to establish the corrosion inhibition mechanism. Quantum chemical calculations have been performed to evaluate several quantum chemical indices and correlated with the corrosion inhibition nature of the inhibitor in 1 M HCl medium.

From the structure of the inhibitor (Fig. 1) it can be seen that it contains the hetero atoms N, O and S and therefore expected to act as corrosion inhibitor. Moreover, the study of relationship between inhibitor efficiency and molecular structure of the inhibitor became the topic of electrochemical research, soon after Hansch's discovery [31] and proven to be very useful in determining the molecular structure as well as electronic structure and reactivity which could be practical in designing novel high-efficiency inhibitors by quantitative structure–activity relationship methods [31–33]. Density functional theory has become an important tool to corrosion scientists in the quantum chemical calculations for the theoretical investigation of corrosion inhibition mechanism. DFT links the experimental results with the theoretical structural parameters of inhibitor molecule. The present work deals with the corrosion inhibition nature of (+)R and (−)S enantiomers of racemic amisulpride in the acid medium.

2. Experimental

2.1. Materials

Mild steel strips of composition 0.081% C, 0.037% Mn, 0.027% P, 0.024% S and the remainder being Fe were used for weight loss as well as electrochemical studies. The mild steel strips of dimensions 2.5 cm × 1 cm × 0.1 cm were used for weight loss studies. The amisulpride purchased from Chem Blink was used as such without further purification. The solutions of 1 M HCl with and without inhibitor were prepared from the analytical grade reagents using double distilled water.

2.2. Electrochemical measurements

Weight loss measurements were carried out according to the American Society for testing and Materials (ASTM) standard procedure [34]. The mild steel specimens in triplicate were immersed for the period of 2 h in 100 ml of 1 M HCl solutions with and without inhibitor at room temperature (300 ± 1 K). The average weight loss of these specimens was used to calculate the inhibition efficiency employing the formula:

$$IE\% = -\left(\frac{W-W'}{W}\right) \times 100 \tag{1}$$

where W and W' represent the weight losses in the uninhibited and inhibited solutions respectively. The relative difference between the replica experiments was found to be less than 2% at room temperature, which shows a good reproducibility.

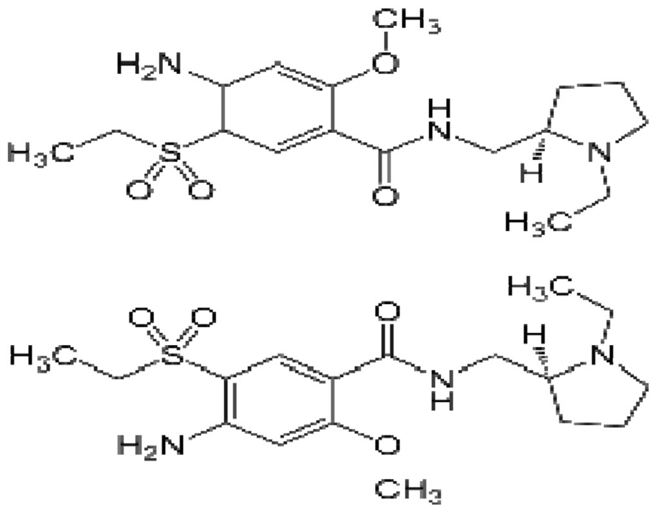

Fig. 1. Chemical structure of(+)R and (−)S enantiomers of racemic amisulpride.

The impedance measurements were performed using a computer-controlled potentiostat (model Solartron ECI-1286) and the data were analyzed using frequency response analyzer (Solartron FRA-1286). A three electrode setup was used for the electrochemical impedance measurements [35,36] with a Pt counter electrode and a saturated calomel electrode (SCE) as the reference electrode. The working electrode was a mild steel strip of above composition with exposed area of 1 cm^2 and the rest being covered by using commercially available lacquer. The measurements were carried out in the frequency range 100 kHz to 0.01 Hz at the open circuit potential by super imposing a sinusoidal AC signal of small amplitude (10 mV). A time interval of 25–30 min was given for steady state attainment of open circuit potential. The electrochemical impedance parameters such as double layer capacitance (C_{dl}) and charge transfer resistance (R_{ct}) were obtained from the Nyquist plots [37]. Since, R_{ct} is inversely proportional to the corrosion current density, the inhibition efficiency (*IE*%) is given by the relationship:

$$IE\% = -\left(\frac{R_{ct}'-R_{ct}}{R_{ct}'}\right) \times 100 \tag{2}$$

where R_{ct} and $R_{ct}'$are the charge transfer resistant values in the absence and presence of the inhibitor in 1.0 M HCl solutions respectively. The potentiodynamic polarization curves were recorded after carrying out the electrochemical impedance measurements, using the same cell setup employed in the impedance measurements, at the potential sweep rate of 1.67 mV s^{-1} from −750 mV to −300 mV vs. SCE. The inhibition efficiencies are calculated using the relationship [38].

$$IE\% = -\left(\frac{i_{corr}-i_{corr}'}{i_{corr}}\right) \times 100 \tag{3}$$

where i_{corr} and i_{corr}' are the corrosion current densities in the absence and presence of the inhibitor in 1 M HCl solutions respectively. The electrochemical impedance spectra were also recorded at the 200 Hz applied single AC frequency at different applied DC potentials and the double layer capacitance values obtained were plotted against the applied DC potentials to determine PZC. All the measurements were taken at room temperature (27 ± 1 °C).

Table 1
Inhibitor efficiency from weight loss measurement for MS in 1MHClsolutions in the presence and absence of inhibitor.

Medium	Inhibitor concentration (ppm)	Corrosion rate (mpy)	Inhibition efficiency (*IE* %)
1 MHCl	Blank	178	-
	100	79.8	55.2
	200	64.6	63.7
	300	51.2	71. 2
	400	40.1	77.5
	500	18.7	89.5
	600	15.4	91.3