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Relationship between structure and inhibition behaviour of quinolinium salts for mild steel corrosion: Experimental and theoretical approach

Punita Mourya [a], Praveen Singh [b], A.K. Tewari [b], R.B. Rastogi [a], M.M. Singh [a,*]

[a] *Department of Chemistry, Indian Institute of Technology (Banaras Hindu University), Varanasi 221005, India*
[b] *Department of Chemistry, Banaras Hindu University, Varanasi 221005, India*

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ABSTRACT

Corrosion inhibition behaviour of quinolinium salts on mild steel (MS) corrosion in 0.5 M H_2SO_4 was investigated at various concentrations and temperatures by gravimetric and electrochemical techniques. The polarization curves indicated that these salts function as mixed inhibitors. Relevant kinetic and thermodynamic parameters like C_R, E_a, ΔH_a^0, ΔS_a^0, K_{ads} and ΔG_{ads}^0 were determined and discussed. The adsorption of salts on MS leading to inhibition was found to follow the Langmuir adsorption isotherm. The existence of a protective film on MS was confirmed by SEM and AFM techniques. XPS and quantum chemical calculations were carried out to establish the mechanism of corrosion inhibition.

1. Introduction

The inhibition of MS corrosion of iron in acidic media by different organic compounds has been widely studied. The existing literature shows that most of the organic inhibitors act by getting adsorbed on the iron surface. This phenomenon is influenced by the nature and surface charge on metal, the type of aggressive electrolyte and the chemical structure of inhibitor. Most of these inhibitors are substances with at least one functional group which is considered to be the reaction centre for the adsorption process. The adsorption of inhibitor is related to the presence of hetero atoms such as nitrogen, oxygen and sulphur with or without the presence of multiple bonds or aromatic ring in their molecular structures. The relationship between the inhibitive properties and the molecular structures of organic compounds has been an area of great interest for many investigators [1–3].

The application of quaternary ammonium salts as corrosion inhibitors has been investigated earlier in different laboratories [4–7]. Noor [8] have reported that some of nitrogen containing heterocyclic compounds in the form of salts are suitable as corrosion inhibitors for mild steel in H_3PO_4. They found inhibition efficiencies of 2.5×10^{-4} M 1-methyl-4[4(-N$(CH_3)_2$)-styryl] pyridinium iodide, 1-methyl-4[4(-N$(CH_3)_2$)-styryl] quinolinium iodide and 1-methyl-4[4(-OCH_3)-styryl] quinolinium iodide at 30 °C to be 56.1%, 75.6% and 98.9%, respectively. Popova et al. [4] investigated the corrosion inhibition of mild steel in 1 M HCl and 1 M H_2SO_4 using some quaternary ammonium bromides of benzothiazole. Their results showed that the protection efficiency of all seven compounds reached around 90% at 1×10^{-4} M concentration in both the acids. A benzimidazole derivative, 1-butyl-3-methyl-1H-benzimidazolium iodide [BMBIMI] was tested by Zheng et al. [9] as inhibitor for mild steel in sulphuric acid and inhibition efficiency was observed as 97.8% at 5 mM. In another investigation on corrosion inhibition of carbon steel in alkaline – chloride solution employing 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIM]BF_4) nearly 86% inhibition has been reported [10]. The foregoing literature survey reveals that N-alkyl-quaternary ammonium salts are promising inhibitors. In view of this, during the present investigation, some new derivatives of quaternary ammonium salts having quinoline ring have been synthesized and tested for their inhibitive properties towards mild steel corrosion in 0.5 M H_2SO_4.

Some of the reports in literature mention that halide ions improve the inhibition performance of organic compounds through synergistic effect [11,12]. The synergism by halides has been attributed to the improved surface coverage as a result of ion-pair interactions between organic cation and halide anion. The effect of halide ions in improving inhibition efficiency has been found to increase from chloride to iodide [13]. Therefore, in this

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* Corresponding author. Tel./fax: +91 542 6702859.
E-mail address: mmsingh.apc@iitbhu.ac.in (M.M. Singh).

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study quinolinium salts having positively charged —N$^+$ centre on quinoline ring with I$^-$/Br$^-$ have been synthesized and tested as corrosion inhibitors for MS corrosion in sulphuric acid.

The investigation on the inhibition effect of synthesized 1-methylquinolinium iodide (QUMEI), 1-propylquinolinium iodide (QUPRI), 1-(2-(1,3-dioxoisoindolin-2-yl)ethyl)quinolinium bromide (QUETBR), 1-(3-(1,3-dioxoisoindolin-2-yl)propyl)quinolinium bromide (QUPRBR) on the corrosion of MS in 0.5 M H_2SO_4 was performed by gravimetry, potentiodynamic polarization, linear polarization (LPR) and electrochemical impedance spectroscopic (EIS) measurements. The effect of concentration and temperature on the inhibition efficiencies of these quinolinium salts has been systematically studied. Surface morphology of corroded/inhibited MS has been studied by scanning electron microscopy (SEM) and atomic force microscopy (AFM). X-ray photoelectron spectroscopy (XPS) of the inhibited MS surface has been carried out to determine the composition of the surface film. In addition to this, quantum chemical calculations were performed to add theoretical support to the experimental results.

2. Experimental

2.1. Materials and sample preparation

The composition (wt.%) of mild steel samples used for all the experiments was as follows: C = 0.253; Si = 0.12; P = 0.013; S = 0.024; Cr = 0.012; Mn = 0.03 and balance Fe. Coupons cut into 3 × 4 × 0.1 cm size were used for gravimetric measurements whereas specimens of size 3 × 1 × 0.1 cm with 1 cm^2 exposed surface areas were used as working electrode for polarization and EIS measurements. Before starting the experiments, the specimens were mechanically abraded with 320, 400, 600, 800, 1000, 1500 and 2000 grade of emery papers. These were then degreased with acetone, washed with double distilled water and dried in air before immersing in the corrosive medium.

The corrosive solution, 0.5 M H_2SO_4 was prepared by dilution of analytical grade H_2SO_4 of predetermined normality with triple distilled water. The concentration range of quinolinium salts used was 10–100 ppm for QUETBR and QUPRBR while for QUMEI and QUPRI 10–200 ppm was preferred. The volume of electrolyte used in each experiment was 150 mL.

2.2. Synthesis of quinolinium salts

All these quinolinium salts were synthesized by the standard method [14,15] depicted in Scheme 1. In a 100 mL round bottom flask, quinoline (5.0 g, 0.039 mol) and corresponding alkyl halide (0.039 mol) were taken in 10 mL acetonitrile solvent. The reaction mixture was kept at 80–85 °C for 24–48 h till the completion of reaction. The completion of reaction was checked by TLC (40% ethyl acetate and 60% hexane). After the completion of reaction, acetonitrile was evaporated by rotary evaporator. A dark greenish brown coloured solid compound appeared after evaporation. It was recrystallized from methanol. It has not been possible to prepare the iodides and bromides all four quinolinium cations. Only those quinolinium salts which could be prepared in the laboratory were tested for their inhibition efficiency. The synthesized quinolinium salts were characterized by spectral analysis. The molecular structure, IUPAC name, abbreviation and characterization data of all the synthesized quinolinium salts are given in Table 1. NMR data is attached in Supplementary Materials (S2–S7).

2.3. Experimental techniques

2.3.1. Gravimetric measurements

Finely abraded and dried MS specimens of dimension 3 × 4 × 0.1 cm were weighed on a digital balance with 1 mg sensitivity and immersed for 24 h in 0.5 M H_2SO_4 at 298 K in the absence and presence of 10, 20, 40, 60, 80, 100 ppm (weight/volume) of QUETBR and QUPRBR. The immersion time of 24 h was selected because the corrosion rate attends its limiting value. On the other hand, in case of QUMEI and QUPRI the test was conducted at two additional concentrations of 150 and 200 ppm. The temperature dependence of inhibition efficiency in the range 298–338 K was studied at three selective concentrations i.e., 10, 40 and 80 ppm, only. The corroded/inhibited specimens were washed thoroughly with soap, rinsed with distilled water, cleaned with acetone, dried and weighed. The weight loss was calculated as the difference in weight of the specimen before and after immersion in corrosive medium.

In all the above measurements, at least three closer results were considered for taking the average values. The corrosion rate (C_R) in mg cm^{-2} h^{-1} was calculated from the following equation

$$C_R = \frac{\Delta W}{s \times t} \tag{1}$$

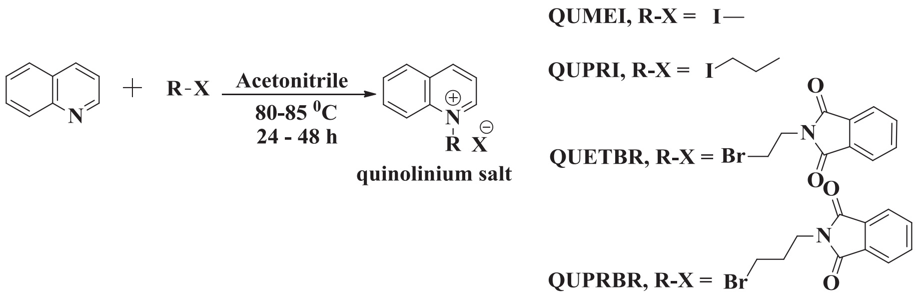
where ΔW is average weight loss, s the total area of the specimen, and t is the immersion time. The corrosion rate values were further used for evaluating the inhibition efficiency (η), as follows

$$\eta\ \% = \frac{C_R^0 - C_R}{C_R^0} \times 100 \tag{2}$$

where C_R^0 and C_R are the corrosion rates of mild steel specimens in the absence and presence of an inhibitor, respectively.

2.3.2. Electrochemical measurements

Electrochemical measurements were carried out in a conventional three electrode cell assembly. This assembly consisted of a flat bottom Pyrex glass flask with three openings one each for working, reference and counter electrodes. A rectangular working electrode of MS with an exposed surface area of 1 cm^2 was attached to a self-designed holder and the rest of the surface was covered with lacquer. Platinum wire and a silver–silver chloride



Scheme 1. Synthesis of quinolinium salts.