



Inhibition of acid corrosion of carbon steel using four imidazolium tetrafluoroborates ionic liquids



M.A. Deyab ^{*}, M.T. Zaky, M.I. Nessim

Egyptian Petroleum Research Institute (EPRI), Nasr City, P. O. Box: 11727, Cairo, Egypt

ARTICLE INFO

Article history:

Received 19 October 2016

Received in revised form 19 December 2016

Accepted 27 December 2016

Available online 28 December 2016

Keywords:

Corrosion inhibitor

Carbon steel

Ionic liquids

Electrochemistry

ABSTRACT

In the present paper, four ionic liquids namely: 3-Decyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL1), 3-Dodecyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL2), 3-Decyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL3) and 3-Dodecyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL4), were synthesized, characterized and tested as corrosion inhibitors for carbon steel in 1.0 M HCl solution. The molecular structure and characterizations of these ionic liquids were confirmed by elemental analysis, FTIR, X-Ray Diffraction (XRD), thermo gravimetric analysis (TGA) and ¹H NMR spectroscopy. The corrosion performance of the ionic liquids was evaluated by using polarization and electrochemical impedance spectroscopy (EIS) measurements. The compounds presented relatively good inhibition efficiencies at 200 ppm. The order of the inhibition efficiency is as follows: IL4 > IL3 > IL2 > IL1. The adsorption of the studied ionic liquids obeyed the Temkin adsorption isotherm.

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1. Introduction

Carbon steel is a material commonly used for the production and transportation of crude oil in the oil industry and natural gas due to its excellent mechanical properties [1–4]. Several problems occur during transportation of crude oil in the pipelines, where the migrating ions come into contact with metal due to the breakdown of the oil-aqueous emulsion, which stimulates the corrosion process [5]. Furthermore, the corrosion is enhanced by the presence of trace water and salts in the oil and the acidic media which are used in descaling and oil well acidification [6,7]. In a strong acid medium, the corrosion processes produce structural damage to the steel. There are several types of corrosion inhibitors which are widely used to control the corrosion problem of low carbon steel upon exposure to acidic solutions, which vary from organic macromolecules to nano-composites [8–15].

Organic compounds act through adsorption on the metal surface and blocking the active corrosion sites. The applicability of these materials as corrosion inhibitors for metals in acidic media has been recognized for a long time. However, most of these materials are heavily toxic and environmentally hazardous [16], therefore, attempts have been carried out to search for eco-friendly treatment materials for metals in acid solutions. Recently, ionic liquid (IL) based products have been developed to solve this problem [17]. Ionic liquids are organic salts (containing both organic cations and inorganic anions with various functional groups) having negligible vapor pressure and a melting point below

373 K, which makes them less hazardous inhibitors and eco-friendlier metal corrosion inhibitors [17]. Moreover, they have a large number of advantageous physicochemical properties such as non-flammability and high ionic conductivity, as well as excellent thermal and chemical stability [18–20].

Most of ionic liquids are based on imidazolium and pyridinium species as cations, while typical anions are sulfonium, phosphonium, Al₂Cl₇, tetrafluoroborate, and bis(trifluoromethane-sulfonyl) imide [17].

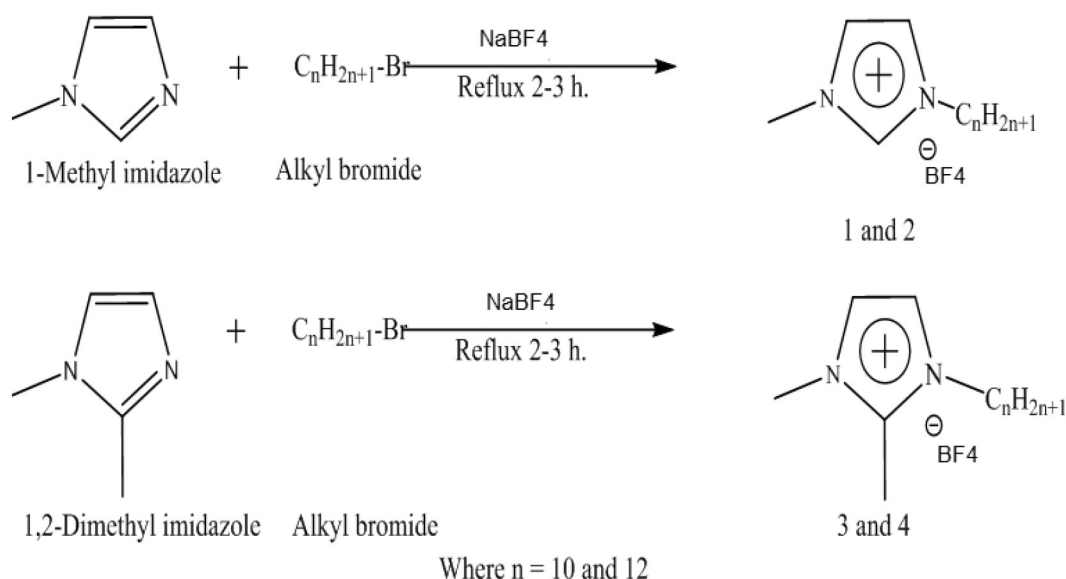
Ionic liquids are generally considered to be efficient corrosion inhibitors for various metals and alloys due to their high activity in acid media [21–25].

Y. Sasikumar et al. [26] have investigated the behavior of 1-decyl-3-methylimidazolium tetrafluoroborate for steel in acidic medium. It was found that this compound exhibited good inhibition performance for mild steel in 1 M HCl solution. 1-decyl-3-methylimidazolium tetrafluoroborate compound was also reported to show corrosion resistant behavior of zinc in acid solution by K. M. Manamela et al. [27].

In the present study, we modify the chemical structure of 1-decyl-3-methylimidazolium tetrafluoroborate by increase the alky chain length from C10 to C12 and also the hydrogen in carbon 2 of the imidazole ring (between the two nitrogen atoms) was replaced by methyl group. Finally we obtained three new ionic liquids i.e. namely: 3-Dodecyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL2), 3-Decyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL3) and 3-Dodecyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate (IL4). The aim of this work is to evaluate the corrosion inhibitions performance of these new compounds. For comparison, the effect of IL1 was examined.

^{*} Corresponding author.

E-mail address: hamadadeiab@yahoo.com (M.A. Deyab).



Scheme 1. The synthetic procedure of ionic liquids (IL1, IL2, IL3 and IL4).

Table 1

The chemical names and molecular structures of prepared ionic liquids.

| Compound | Chemical names | Molecular structures |
|----------|--|----------------------|
| IL1 | 3-Decyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate | |
| IL2 | 3-Dodecyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate | |
| IL3 | 3-Decyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate | |
| IL4 | 3-Dodecyl-1,2-dimethyl-1H-imidazol-3-ium tetrafluoroborate | |

The polarization and electrochemical impedance spectroscopy (EIS) measurements were used to investigate the inhibition efficiency of such materials in 1.0 M HCl solution.

2. Experimental details

2.1. Materials and chemicals

Electrochemical experiments were carried out using carbon steel cylindrical disk with following composition (wt.%): 0.064 C, 0.029 Cu, 1.24 Mn, 0.27 Si, 0.004 N, 0.024 Al, 0.028 Ni, 0.018 Cr, 0.002 S, 0.14 Mo, 0.018P, 0.06 Nb, 0.02 Ti, 0.002 V, and balance Fe. The cylindrical disk (surface area of 0.645 cm²) formed the working electrode. The working surfaces of the electrode were abraded with 1200 grit silicon carbide paper and rinsed with distilled water and ethanol before using.

All reagents used were analytical fine grade. They were used as received without further purification. An aqueous solution of 1.0 M HCl was used as a corrosive solution (blank solution). n-Decyl bromide 98%, n-dodecyl bromide 97%, 1-methyl imidazole 99%, 1,2-dimethyl imidazole 98% and sodium tetrafluoroborate 98% (NaBF₄) were purchased from

Aldrich. Acetonitrile 99.7% and silver nitrate 99.85% (AgNO₃) were supplied by Romil and Acros Chemical Companies, respectively.

2.2. Preparation of ionic liquids

3-Decyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL1) and 3-dodecyl-1-methyl-1H-imidazol-3-ium tetrafluoroborate (IL2) was prepared as the following procedure: 1-methylimidazole (0.05 mol), decyl bromide (0.05 mol) or dodecyl bromide (0.05 mol) and sodium salt of

Table 2
Elemental analysis of ionic liquids.

| Compound | Element | | | | | |
|----------|---------|-------|-------|------|-------|------|
| | C% | | H% | | N% | |
| | Calc. | Obs. | Calc. | Obs. | Calc. | Obs. |
| IL1 | 54.21 | 54.37 | 8.77 | 8.52 | 9.03 | 8.89 |
| IL2 | 56.82 | 56.34 | 9.24 | 9.01 | 8.28 | 8.52 |
| IL3 | 55.57 | 55.67 | 9.02 | 9.12 | 8.64 | 8.45 |
| IL4 | 57.96 | 57.56 | 9.44 | 9.57 | 7.95 | 8.05 |

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