Journal of Molecular Liquids 211 (2015) 363–369

Contents lists available at ScienceDirect

Journal of Molecular Liquids

journal homepage: www.elsevier.com/locate/molliq

Anti-bacterial and anti-corrosion effects of the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate

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ARTICLE INFO

Article history:
Received 18 February 2015
Received in revised form 28 April 2015
Accepted 10 July 2015
Available online xxxx

Keywords:
Ionic liquids
Corrosion
Inhibition
Biocide
Microbial corrosion

ABSTRACT

In this paper we report on the antibacterial and anticorrosion impacts of the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([$Py_{1,4}$]TfO). The results reveal that the employed ionic liquid can effectively inhibit the planktonic and sessile bacterial growth, and the inhibition efficiency is dependent on the ionic liquid concentration. Compared with planktonic bacteria, higher concentrations of [$Py_{1,4}$]TfO are needed, about 2–3 times, for sessile bacteria to get the same inhibition efficiency. The inhibition effect of [$Py_{1,4}$]TfO on the corrosion of mild steel in 3.5% NaCl solutions was also explored. The potentiodynamic polarization and impedance spectroscopy results indicate the anticorrosion influence of the employed ionic liquid. A concentration of about 100 ppm [$Py_{1,4}$]TfO can effectively inhibit the corrosion of mild steel with efficiency of more than 80%. The corrosion inhibition influence of [$Py_{1,4}$]TfO is ascribed to the adsorptive interaction of the ionic liquid species with the surface of mild steel and formation of a protective layer against the corrosion attack.

1. Introduction

Microbially influenced corrosion (MIC) of metals and alloys is a serious industrial problem as it represents about one fifth of the total damage caused by corrosion [1,2]. In general MIC is a process in which the corrosion attack is initiated by microbes in non-sterile aqueous media. The presence of microorganisms in solutions can considerably influence the interfacial structure at the metal/solution interface, resulting in the formation of biofilms. The microbial colonization on a metal surface and the subsequent accumulation of biofilms can cause localized gradients of pH, dissolved oxygen and corrosive anions, leading to accelerated corrosion [3]. Therefore, it is essential to kill the microorganisms present in the solutions or at least inhibit their growth rate in order to mitigate the MIC. For this purpose biocides, which can exert either biostatic or biocidal effects, are usually employed. The conventional biocides can be classified into two main types, oxidizing (such as chlorine, bromine and ozone) and non-oxidizing (such as quaternary ammonium compounds, organic acids, aliphatic alcohols, phenols, aldehydes, esters) [4–6]. Non-oxidizing biocides were reported to be more effective against a broad range of microorganisms such as, algae, fungi, and bacteria [7].

However, due to increased restrictions of environmental regulations and safety concerns the use of conventional toxic biocides, especially with high concentrations, is not recommended. Furthermore, some biocides may contribute to corrosion acceleration if high concentrations were used [8]. Therefore, there is a strong need for the development of new environmentally friendlier and less hazardous biocides.

Ionic liquids (ILs) were shown to have pronounced antimicrobial activities and they can be employed for biocide applications [9–13]. The surface activity and antimicrobial impact of ionic liquids may enhance their application as surface biocides. Generally, ionic liquids are fluids composed entirely of ions, and their extraordinary physical properties made them attractive materials for a wide variety of applications including electrodeposition, electrocatalysis, electrochemical capacitors, batteries, fuel cells, sensors and organic synthesis [14–20]. They are usually nonvolatile, nonflammable, and less toxic than conventional organic solvents. Most of ionic liquids have very low vapor pressure (for example at or near room temperature around 10^{-11}–10^{-10} mbar) which eliminates releasing of harmful vapors into the atmosphere. They also have high thermal stability, up to 300–400 °C and extremely large electrochemical windows, up to 7 V, that make them very attractive as electrochemical solvents. Moreover, the ionic liquids are "designable" as it is possible to design ILs with the required chemical, physical or biological properties for specific applications by a proper choice of cations and anions [21]. It was estimated that more than one million of simple ionic liquids can be prepared and about one billion of binary and one trillion of ternary systems can be obtained [19].

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http://dx.doi.org/10.1016/j.molliq.2015.07.028
0167-7322/

Therefore, a broad range of ionic liquids with anti-microbial activity can be used as biocides. Forsyth et al. [22,23] synthesized and evaluated a number of novel ionic liquids as antimicrobial agents to combat biofilm formation and microbially influenced corrosion of steel in the marine environment. Seddon et al. [11] showed the antibiofilm activities of a series of 1-alkyl-3methylimidazolium chloride ionic liquids, and the activity intensifies as the alkyl chain length increases. The antimicrobial characteristics of a number of hydroxyl-functionalized imidazolium chloride ionic liquids were reported [13].

Presently, there is also a growing interest in the use of ionic liquids as corrosion inhibitors [24–30]. A number of ionic liquids were reported to be efficient inhibitors for the corrosion of mild steel [24–30], aluminium [31,32] and copper [33] in acidic solutions.

In the present study we have investigated the influence of the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate on the bacterial growth inhibition and on the corrosion inhibition of mild steel in 3.5% NaCl solutions. To our knowledge, the antimicrobial and anticorrosion impacts of $[Py_{1,4}]TfO$ have not yet been investigated. The employed ionic liquid has been extensively investigated as a potential solvent for electrodeposition of many metals and semiconductors such as Sn, Fe, Cu, Al, Si and Ge (see, e.g. [34–36]). The ionic liquid $[Py_{1,4}]TfO$ has good miscibility with water and compared with imidazolium based ionic liquids the adsorptive interaction of pyrrolidinium ones with surfaces is much stronger [37]. $[Py_{1,4}]^+$ cation is strongly adsorbed onto metal surfaces as the charge on the cation is localized. Furthermore, the TfO^- anion has a strong structure dissociation tendency due to its bulky size and hence, more $[Py_{1,4}]^+$ cations can easily be detached from the transient bonding with anions. The ease of ion dissociation in the employed ionic liquid can lead to enhanced adsorption on the steel surface [38]. The capability of the employed ionic liquid to be adsorbed on the steel surface and assembling a protective film can enhance the inhibition of the corrosion attack. Furthermore, the antimicrobial activity of the ionic liquid would inhibit the bacterial growth and prevent the formation of biofilms.

2. Experimental

2.1. Enumeration of bacteria

The ionic liquid $[Py_{1,4}]TfO$ (Io.Li.Tec., Germany) with purity of 99% was used as received without further purification or drying. Enumeration of bacteria was made by using the most probable number (MPN) method, [39,40]. First, the water sample was subjected to circulation in open air for 24 h to enrich the planktonic bacterial growth then, 1 ml was used to detect the bacterial counts before injection of the ionic liquid dose. Synthetic postgate media were used and distributed in test tubes, each tube contained 9 ml, and 6 sterilized tubes were used for each MPN experiment. The circulated water was used to determine the biocidal efficiency of the employed ionic liquid through injection of the IL with different doses and then 1 ml from each treatment was used to inoculate in the first sterilized tube. Afterward, the tube was shook well and then 1 ml was withdrawn and injected in the second tube and the same was done with the other tubes. The tubes used for the MPN analysis were incubated at 30 °C.

For sessile bacteria, the water was circulated for 3 days. After the first day the population of planktonic bacteria was more than 100,000 colony/ml. A mild steel coupon of area 1×1 cm^2 was then immersed in the medium and the bacteria started to settle on the surface in the second and third days, forming a biofilm. The obtained biofilm was removed by sonication of the steel sample in a sonicator for 10 s in sterile water, then samples from water were used to detect the bacterial counts by using the serial dilution method as mentioned above for planktonic bacteria. All steps were repeated with different concentrations of the employed ionic liquid to show its effect on the sessile bacteria.

2.2. Electrochemical measurements

The corrosion experiments were carried out in 3.5% NaCl solutions free and containing different concentrations of $[Py_{1,4}]TfO$ using a three-electrode cell assembly at room temperature. The working electrode was a mild steel sheet with an active area of 1 cm^2 and the rest being covered by using commercially available lacquer. Prior to experiments, the working electrode was successively polished with different grades of emery paper, degreased with acetone and washed with distilled water. A Platinum sheet and a saturated calomel electrode (SCE) were used as counter and reference electrodes, respectively. The potentiodynamic polarization and impedance measurements were carried out using a Radiometer Voltalab master (Model PGZ 301), controlled by Voltamaster 4 software, after a 30 minute immersion time to stabilize the system. For polarization experiments, the potential was scanned from a potential that is 300 mV more negative than the open circuit potential up to a potential that is 300 mV more positive than the open circuit potential at a scan rate of 2 mV s^{-1}. The linear Tafel segments of anodic and cathodic curves were extrapolated to corrosion potential to obtain the corrosion current densities (I_{corr}). The corrosion current was obtained from the intersection of the extrapolation of anodic and cathodic Tafel lines. The polarization resistance (R_p) was estimated using the following equation [41]:

$$R_p = 2.303 \frac{\beta_a \ \beta_c}{\beta_a + \beta_c} \left(\frac{1}{I_{corr}} \right) \quad (1)$$

where, β_a and β_c are the anodic and cathodic Tafel slopes, respectively, and I_{corr} is the corrosion current. The Tafel plots were quantitatively analyzed using the Voltamaster 4 software to obtain the corrosion parameters. The impedance studies were carried out under open circuit conditions in the frequency range from 100 kHz to 50 mHz with an amplitude of 10 mV. A scanning electron microscope (Jeol 5300 GSM, Japan) was used to examine the electrode surface.

3. Results and discussion

3.1. Antibacterial effect of $[Py_{1,4}]TfO$

The influence of the ionic liquid $[Py_{1,4}]TfO$ on the planktonic bacterial growth was investigated. Fig. 1 shows the decay of the bacterial counts with time at different concentrations of $[Py_{1,4}]TfO$. As seen, at a concentration of 50 ppm the bacterial counts obviously decrease with time and a complete inhibition is achieved after 6 h. As the ionic liquid concentration increases the rate of bacterial growth inhibition increases and after 1 h of the treatment, the bacterial counts are reduced from about 10^6 cells/ml to less than 10^5, 10^4, 10^3, 10^2 and 10 cells/ml at IL concentrations of 50, 100, 150, 200 and 300 ppm, respectively.

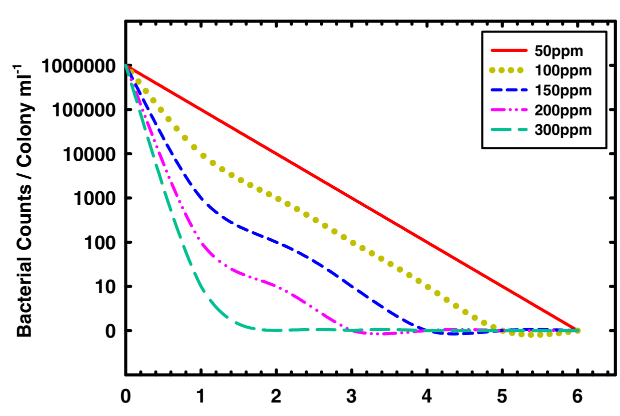

Fig. 1. The decay of bacterial counts with time at different concentrations of $[Py_{1,4}]TfO$.