Research on synthesis of imidazole-based ionic liquids as metal corrosion inhibitors

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Received 15 Feb. 2024; Revised 4 Apr. 2024; Accepted 8 Apr. 2024 ; Published 22 Apr. 2024.
DOI: https://doi.org/10.54939/1859-1043.j.mst.94.2024.102-108

ABSTRACT

Ionic liquids (ILs) have gained significant attention in recent years as potential corrosion inhibitors to various applications. Traditional corrosion inhibitors, such as organic compounds and inorganic salts, have limitations in terms of toxicity, volatility, and environmental impact. However, ionic liquids offer a promising alternative. Ionic liquids are salts that exist in a liquid state at or below 100 degrees Celsius. They typically comprise an organic cation and an inorganic or organic anion. The unique combination of a liquid state and ionic nature gives them several advantageous properties, such as high thermal stability, low vapor pressure, and tunable physicochemical properties. Additionally, the charged nature of the ionic liquid allows for electrochemical interactions with the metal surface, further enhancing corrosion inhibition. In this paper, imidazole-based ionic liquids were synthesized by alkylation of imidazole derivatives using 1-bromohexadecane. The anti-corrosion properties of the material were evaluated using the weight method and potentiodynamic polarization method. Results showed that the synthesized ILs are good corrosion inhibitor for CT3 steel.

Keywords: Ionic liquids; Corrosion inhibitor; Imidazole; 1-hexadecylbromide.

1. INTRODUCTION

Corrosion, the degradation of materials because of chemical reactions with their environment, is a major concern in industries such as oil and gas, chemical processing, and metal manufacturing. Corrosion inhibitors are among the best methods for preventing corrosion because of their low cost and effectiveness [1]. Traditional inhibitors often contain harmful elements for human health and environment, among them, chromate inhibitors are the most common. In order to address this matter, greener corrosion inhibitor have been studied, and ionic liquids are one of the most promising candidates [2, 3]. Ionic liquids have low volatility, reducing the risk of release into the environment. They also exhibit low toxicity compared to traditional inhibitors, making them more environmentally friendly. This is particularly important in industries where worker safety and environmental impact are paramount concerns. They are organic salts in liquid form because of their low melting temperature. When used as corrosion inhibitors, ionic liquids form a protective film on the metal surface, preventing further corrosion reactions. The film acts as a physical barrier, shielding the metal from corrosive agents [4, 5].

One of the key advantages of ionic liquids, as corrosion inhibitors, is their ability to be tailored for specific applications [6]. By modifying the cation or anion structure, the properties of the ionic liquid can be adjusted to suit different metal substrates and corrosive environments. This allows for the development of highly efficient and selective corrosion inhibitors [7].

Ionic liquids are composed of positively charged organic cations and negatively charged inorganic or organic anions. The combination of these ions creates a unique, non-volatile, and often non-flammable liquid with a wide liquid range. The choice of cation and anion significantly influence the properties of the ionic liquid, such as viscosity, conductivity, and solvation ability. Common cations include imidazolium, pyridinium, and phosphonium, while anions can range from halides to

organic salts. Among several approaches to synthesize ionic liquids, alkylation is frequently used because of its high yield and simplicity [8, 9]. In this work, two ionic liquids were synthesized by alkylation of 1-methylimidazole and 1,2-dimethylimidazole using 1-bromohexadecane. The CT3 steel treated with synthesized ILs showed great corrosion resistance behavior.

2. EXPERIMENTAL

2.1. Materials

1-bromohexadecane $C_{16}H_{33}Br$ 97%, 1-methylimidazole $C_4H_6N_2$ 99%, 1,2-dimethylimidazole $C_5H_8N_2$ 99% were purchased from Macklin, China; sodium chloride NaCl 99%, acetonitrile CH_3CN 99% were obtained from Xilong.

2.2. Experiment preparation

2.2.1. Instrumentation

The synthesized ionic liquids were characterized by Fourier transform infrared (FT-IR) using Tensor II with a scan range of 400-4000 cm^{-1} to identify the functional groups. Proton nuclear magnetic resonance ^{1}H-NMR was measured by AVANCE III HD 500 MHz to learn the structure of the ionic liquids. Thermogravimetric analysis was measured by NETZSCH STA 409PC/PG up to 900 °C at a heating rate of 10 °C/minute.

2.2.2. Synthesis imidazole based ionic liquids

a. 1-hexadecyl-3-methylimidazolium bromide

In the first step, 30.5 g 1-bromohexadecane was dissolved in 30 mL acetonitrile solvent in a round bottom flask and then the mixture was heated to 80 °C. After that, 8.2 g of 1-methylimidazole was gradually added to the above solution. The reaction mixture was performed for 3 hours while stirred continuously and the temperature was set to 80 °C for the whole procedure. Then, the product was filtered out, washed three times with CH_3CN. The product was left to dry in air and then weighted. Finally, 34 g of product was obtained.

b. 1-hexadecyl-2,3-dimethylimidazolium bromide

The synthesis procedure was performed similar to the above process, using 30.5 g 1-bromohexadecane and 9.6 g of 1,2-dimethylimidazole. Acetonitrile was the solvent of choice, and the reaction mixture was performed for 3 hours at 80 °C. Finally, the product was filtered out, dried and then weighted. Finally, 31.3 g of product was obtained.

2.2.3. Corrosion inhibiting performance

The weight method was used to determine the rate of metal corrosion caused by +saline environment: the difference in mass of metal sample before and after experiments during a period of test time. Test procedure and corrosion rate evaluation were executed according to ASTM G1-03. The polarization curve of electrodes was determined by the potentiodynamic method on the Autolab PGSTAT30 device at the scanning speed of 10 mV/s, using CT3 steel. The test solution was 3.5% aqueous NaCl solution, in which the synthesized ionic liquids were dissolved. The corrosion inhibitor performances of ionic liquids were tested by ranging the concentration from 0 to 300 ppm. The average corrosion rate of the sample can be calculated as follows:

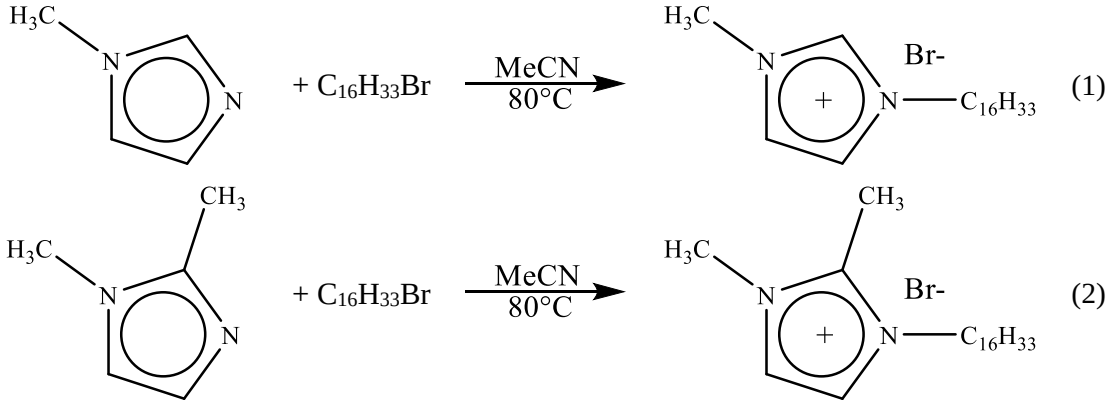
$$\text{Corrosion rate} = \frac{K \times W}{A \times T \times D}$$

Where K is corrosion rate constant, 8.76×10^4 for mm/year unit; T is time of exposure in hours; A is the area in cm^2; W is the weight loss in grams, and D is the density of the materials, in this case, density of CT3 steel is 7.85 g/cm^3.

3. RESULTS AND DISCUSSION

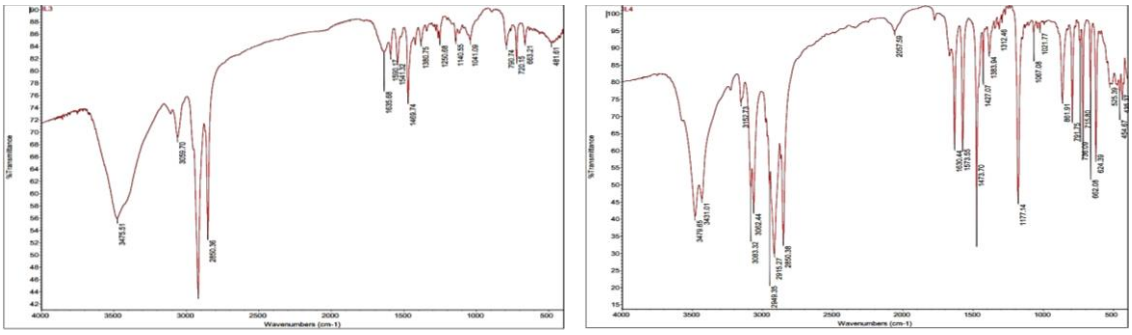
3.1. Synthesis of imidazoline based ionic liquids

Both ionic liquids were synthesized via alkylation reaction using 1-bromohexadecane as alkylated agents. The chemical reactions occur as follows:



Under the same reaction conditions, 1-methylimidazole is more susceptible to alkylation than the dimethyl derivative. The extra methyl group on carbon atom 2 makes the bulky alkylated agent 1-bromohexacane harder to access. As the result, the productivity of 1-hexadecyl-3-methylimidazolium bromide HdmImBr (87.9%) was slightly higher than of 1-hexadecyl-2,3-dimethylimidazolium bromide HddmImBr (78.1%).

The IR spectra of HdmImBr and HddmImBr are presented in figure 1 a,b, respectively. In both cases, they show characteristic IR transmittance of imidazole ring. For HdmImBr (Fig. 1a), the peaks at 3060 and 3150 cm^{-1} are correspond to the stretching of the C-H bond of imidazole ring, and the bending of the same bond is at 1380 cm^{-1}. The imidazole ring also has characteristic peaks at 1635 and 1590 cm^{-1}, attributed to the C=C stretching. The stretching of C-N is confirmed as the existence of a peak at 1250 cm^{-1}. The bending of H-C-C and H-C-N in the ring also results in a peak at 1140 cm^{-1}, while of C-N-C bending is showed at 660 cm^{-1}.



(a) *(b)*

Figure 1. *IR spectrum of (a) 1-hexadecyl-3-methylimidazolium bromide and (b) 1-hexadecyl-2,3-dimethylimidazolium bromide.*

Alkyl groups on the imidazole ring show characteristic transmittance of aliphatic bonding. The presence of methylene groups (-CH_2-) can be seen at 2950 cm^{-1} (strongest peak, correspond to the stretching of C-H bond), and 1470 cm^{-1} corresponds to the bending of the C-H bond. Methyl groups (-CH_3) show the same C-H bond stretching and bending at 2850 and 1430 cm^{-1}, respectively. Owing to the long chain of hexadecyl group, the intensity of peaks caused by (-CH_2-) groups is stronger than that of (-CH_3) groups, as the number of methylene groups is greater than the number of methyl groups. This results show similarity with previous publication [10].

FTIR spectrum of HddmImBr (Fig. 1b) show similar characteristics as of HdmImBr. The bending and stretching of corresponding bonds in imidazoline and alkyl groups only show minor deviation between the two IR spectra. The presence of methyl group on carbon atom 2 makes a small difference as corresponding to an extra C-H stretching at 2915 cm^{-1}. The increase in methyl groups compared to HdmImBr also makes the intensity of peaks cause by bending and stretching of (-CH_3) groups stronger.

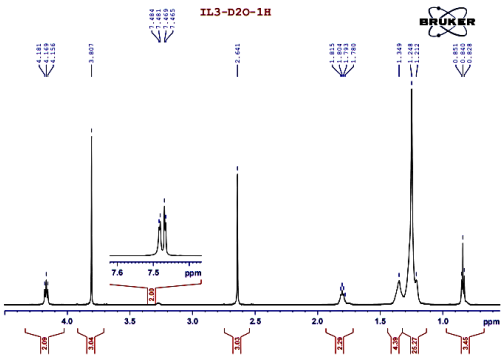


Figure 2. *^{1}H-NMR magnetic resonance spectrum of 1-hexadecyl-2,3-dimethylimidazolium bromide (D_2O).*

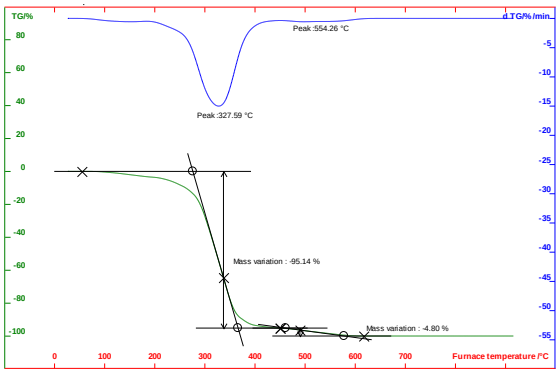


Figure 3. *Thermogravimetric analysis of 1-hexadecyl-2,3-dimethylimidazolium bromide.*

The synthesized ILs were characterized by ^{1}H-NMR magnetic resonance spectroscopy (figure 2). It can clearly be seen that in the NMR spectrum, two doublet very close to each other at chemical shift 7.482 and 7.467 ppm are belong to the two adjacent hydrogen atoms on the carbon atom 4 and 5, each contributes to the integration value of 2. A triplet at 4.169 ppm with an integration value of 2 indicate two hydrogen atoms of the alpha methylene group (-CH_2-) in hexadecyl chain that directly bond with the nitrogen atom 3. Meanwhile, 3 hydrogen atoms of methyl group (-CH_3) that bond with nitrogen atom 1 show a singlet at 3.807 ppm. The existence of the methyl group on carbon number 2 of the imidazole ring was confirmed by a singlet at 2.641 ppm with integration value of 3. Two hydrogen on a beta methylene group of hexadecyl show peaks at 1.8 ppm because they still affected by the shielding effect of the nitrogen atom 3 and the aromatic ring. The rest of the methylene groups of the long chain have a regular chemical shift and form a multiplet at 1.2 ppm. The methyl group at the end of the chain shows a triplet at 0.84 ppm.

The thermogravimetric analysis show that 1-hexadecyl-2,3-dimethylimidazolium bromide is thermal stable up to 200 °C. At higher temperature, the ionic liquid shows degradation. The weight loss rate reaches a maximum at about 327 °C, and nearly all sample was thermolysis at 400 °C. This result shows that the synthesized ionic liquid is thermally stable at high temperature.

3.2. Corrosion inhibition characteristics

3.2.1. Corrosion inhibition mechanism

The mechanism of ionic liquids adsorption and corrosion inhibition was illustrated in figure 4.

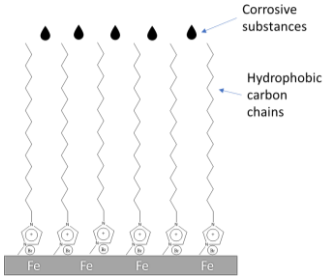


Figure 4. *Illustration of ILs corrosion inhibition mechanism .*

In corrosive environment, metallic iron was oxidized to become ferrous (Fe^{2+})/ferric (Fe^{3+}) cations. The bromine anions from the ILs will then be adsorbed on the steel surface by electrostatic attraction, serving as a bridge connecting imidazolium ions and the substrate. As a results, a self-assembled hydrophobic layer made of long-chain hydrocarbon was formed, acting as a barrier that prevents the steel surface from corrosive substances. The interaction between ferrous cations and π system of aromatic rings also contribute to the adsorption of ILs on the steel surface.

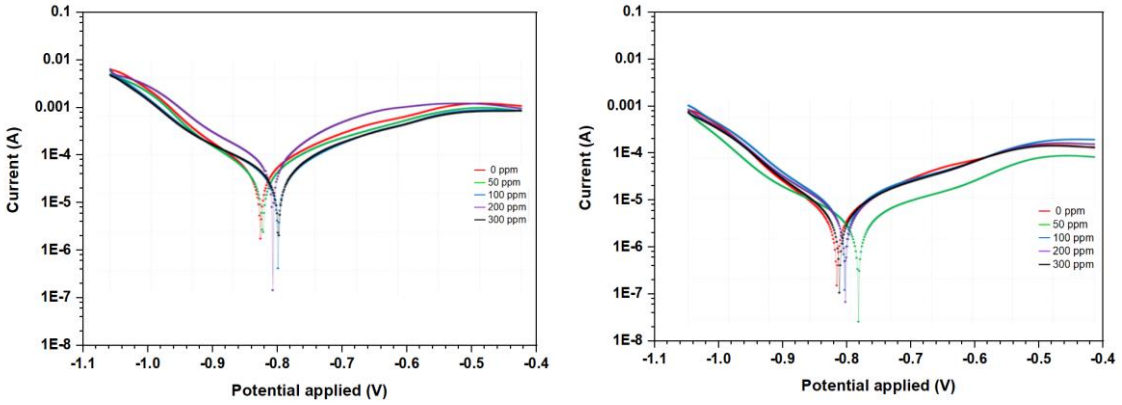
3.2.2. Corrosion inhibition measurement

Three CT3 samples were submerged in saline solution of NaCl 3.5%, one added 300 ppm 1-hexadecyl-3-methylimidazolium bromide and one added 300 ppm 1-hexadecyl-2,3-dimethylimidazolium bromide. The test was performed at 42 hours. After that, the samples were taken out, weighted again and the corrosion rate was calculated using formula in section 2.

Table 1. *Assessment of corrosion by weight method.*

Samples	Weight loss (g)	Exposure Area (cm^2)	Time (h)	Corrosion rate (mm/y)	Protection effect (%)
Control	0.017	10	42	**0.451**	-
HdmImBr	0.007	10	42	**0.186**	**58.76**
HddmImBr	0.008	10	42	**0.213**	**52.77**

The results show that ionic liquids have anti-corrosion property, by forming a layer of hydrophobic film on the surface of the metal, prevent the direct exposure to the corrosive environment.



a) *b)*

Figure 5. *Tafel diagrams of CT3 steel at different concentrations of 1-hexadecyl-3-methylimidazolium bromide (a) and 1-hexadecyl-2,3-dimethylimidazolium bromide (b).*

Table 2. *Tafel parameters and corrosion inhibition efficiency of ILs at different concentration.*

Inhibitor	Conc. (ppm)	I_{corr} (mA/cm^2)	E_{corr} (V/SCE)	β_a (V/dec)	$-\beta_c$ (V/dec)	IE (%)	Corr. rate (mm/y)
Control	-	4.441	-0.548	0.069	0.102	-	0.516
1-hexadecyl-3-methylimidazolium bromide	50	3.224	-0.574	0.065	0.071	43.2	0.394
	100	4.550	-0.590	0.055	0.053	60.9	0.529
	200	2.649	-0.580	0.071	0.071	35.5	0.324
	300	6.851	-0.668	0.077	0.711	91.8	0.238
1-hexadecyl-2,3-dimethylimidazolium bromide	50	3.128	-0.595	0.051	0.047	41.9	0.387
	100	4.962	-0.579	0.054	0.534	66.5	0.607
	200	4.201	-0.654	0.070	0.075	56.3	0.514
	300	2.892	-0.622	0.072	0.066	38.7	0.354

The potentiodynamic method show the similar results at the same ionic liquid concentration (table 2 and figure 5). At lower content, however, the added ionic liquid have adverse effect, especially at 100 ppm. The increase in corrosion rate can be attributed to the ionic nature of the inhibitor. At low concentration, the inhibitor amount is not enough to cover the whole metal surface, meanwhile, the extra bromide ion contributes to the accelerated corrosion rate. At higher content, ILs show good corrosion protection property. HdmImBr displays a better performance overall in both weight and electrochemical method. Although the extra methyl group of HddmImBr make it potentially more hydrophobic, the bulkier imidazolium head of HddmImBr make a bond between the IL and metal surface weaker.

4. CONCLUSIONS

Two imidazole-based ionic liquids were successfully synthesized by alkylation reaction using 1-hexadecylbromide at high productivity. The FTIR and ^{1}H-NMR magnetic resonance spectrum prove the structure of the products. The thermogravimetric analysis reveal the synthesized ILs have high thermal stability, up to 200 °C. The corrosion tests by weight method and potentiodynamic method show unanimous results. Although at low concentration, synthesized ILs are not good at protecting metal; at higher content, ILs show promising corrosion inhibiting properties. Between two products, 1-hexadecyl-3-methylimidazolium bromide shows better performance, decrease corrosion rate from 5 mm/year to about 2 mm/year at 300 ppm concentration.

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TÓM TẮT

Nghiên cứu tổng hợp chất lỏng ion trên cơ sở imidazole ứng dụng làm chất ức chế ăn mòn kim loại

Chất lỏng ion đã thu hút được sự chú ý đáng kể trong những năm gần đây vì có tiềm năng sử dụng làm chất ức chế ăn mòn. Các chất ức chế ăn mòn truyền thống, chẳng hạn như các hợp chất hữu cơ và muối vô cơ, có những hạn chế là độc tính cao, tính dễ bay hơi và tác động xấu tới môi trường. Tuy nhiên, chất lỏng ion mang lại một giải pháp thay thế đầy hứa hẹn. Chất lỏng ion là muối tồn tại ở trạng thái lỏng ở nhiệt độ bằng hoặc dưới 100 độ C. Chúng thường bao gồm một cation hữu cơ và một anion vô cơ hoặc hữu cơ. Sự kết hợp độc đáo giữa trạng thái lỏng và bản chất ion mang lại cho chúng một số đặc ưu việt, chẳng hạn như độ ổn định nhiệt cao, áp suất hơi thấp và các đặc tính hóa lý có thể điều chỉnh. Ngoài ra, bản chất tích điện của chất lỏng ion cho phép tương tác điện hóa với bề mặt kim loại, tăng cường hơn nữa khả năng ức chế ăn mòn. Trong bài báo này, chất lỏng ion trên cơ sở imidazole được tổng hợp bằng cách alkyl hóa dẫn xuất imidazole sử dụng 1-bromohexadecane. Đặc tính chống ăn mòn của vật liệu được đánh giá bằng phương pháp trọng lượng và phương pháp phân cực thế động. Kết quả cho thấy chất lỏng ion tổng hợp được có khả năng ức chế ăn mòn tốt cho thép CT3.

Từ khoá: Chất lỏng ion; Chất ức chế ăn mòn; Imidazole; 1-hexadecylbromide.