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A NEW APPLICATION OF *N, N'*-BIS[(BENZIMIDAZOL-1-YL)ETHYL]-4-METHYLBENZENESULFONAMIDE AS A CORROSION INHIBITOR FOR MILD STEEL

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Abstract

Corrosion is the deterioration of material typically metal alloys that cause the main problems in the industry that is associated with significant economic losses, such as loss of their surface function and strength, reduction in efficiency, and increase in maintenance. Hence, procedures for the protection of the materials must be developed to minimise the damage effects of the metals. Organic ligands as corrosion inhibitors are known as one of the most effective, profitable, and easy techniques. This study discussed the synthesise and characterization of the compound from *N*-heterocyclic carbene (NHC) groups, namely *N, N'*-Bis[(benzimidazol-1-yl) ethyl] -4-methylbenzene sulfonamide (bis-benzimidazole). Its application as a corrosion inhibitor of mild steel in acidic media (1 M HCl and 1 M H_2SO_4) was investigated at different temperatures, times, inhibitor concentration, and salinity of the water. The structure of bis-benzimidazole was confirmed using Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR), Ultraviolet-Visible (UV-Vis), and Nuclear Magnetic Resonance (NMR) spectroscopies. The bis-benzimidazole (0.01 M) was successfully used as the corrosion inhibitor in 8 h immersion time at room temperature with 100% and 92.51% inhibition efficiency in 1 M HCl and 1 M H_2SO_4, respectively. This showed that the bis-benzimidazole would adsorb chemically on a mild steel surface, which lead to the formation of a protective thin film with an inhibiting effect, thus inhibiting the corrosion activity.

Keywords: Acidic medium, corrosion inhibitor, mild steel, *N*-heterocyclic carbene

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Introduction

Mild steel is one of the important raw materials in the industries for a variety of purposes. This is because mild steel has excellent mechanical properties and availability for fabrication in many reactions' vessels, such as cooling power tanks, pipelines, and power generation. Meanwhile, acid solutions have been used in the chemical cleaning process, acid pickling, and descaling of steel and iron, oil well acidification, and petrochemical processes (Muralisankar et al., 2017).

The presence of acid causes corrosion and becomes a primary source of many losses in the industry. There are many methods to prevent corrosion, and the corrosion inhibitor is well known as a chemical compound used for corrosion protection thus it is very useful in the industry. This method is significant due to its low cost and practical ability (Galio and Dariva, 2014).

There are various types of corrosion inhibitors, such as natural products, and inorganic and organic compounds. The *N*-heterocyclic carbene (NHC) is classified as an organic inhibitor and has been proven to be an effective inhibitor for the corrosion of steel in acid media due to the presence of heteroatoms, such as N, O, and S in the organic compounds (Elouadi et al., 2015; Muralisankar et al., 2017). The lone pair electrons of the heteroatom and conjugated bonds can form a chemisorptive film on the metal surface through chemical interaction. The adsorption of the inhibitors' molecules onto the mild steel can block the active site on the surface, thereby reducing the corrosion rate (Wang et al., 2012). NHC has unique properties, such as good stability and compatibility with metal in low and high oxidation states, and ease of handling (Haque et al., 2011). This study focuses on the synthesis, characterisation, and application of NHC type of compound, namely *N, N*'-Bis[(benzimidazol-1-yl)ethyl]-4-methylbenzenesulfonamide (bis-benzimidazole) as a corrosion inhibitor for mild steel in acidic media and different parameters.

Methods

Materials

The material and chemicals used are mild steel, hydrochloric acid (R&M Chemicals, U.K), sulfuric acid (R&M Chemicals, U.K), benzimidazole (MERCK, USA), potassium hydroxide (R&M Chemicals, U.K), dimethylsulfoxide (DMSO) (BENDOSEN, Norway), chloroform (R&M Chemicals, U.K), and tri-sulfonamides used as synthesized by Said (2016).

Instrumentation

The instruments used are a melting point analyser (Stuart SMP10), CHNS elemental analyser (Flash 2000, Thermo Scientific), Ultraviolet-Visible (UV-Vis) spectroscopy (T80+, PG Instruments Ltd), Attenuated Total Reflection-Fourier Transform Infrared (ATR-FTIR) (PerkinElmer Spectrum 100) and Nuclear Magnetic Resonance (NMR) spectroscopies (Bruker Avance III HD 400 MHz).

Synthesis of corrosion inhibitor

The synthesis route of bis-benzimidazole is shown in Figure 1. The reaction started with benzimidazole (2.36 g, 0.02 mol) was dissolved in 20 mL of DMSO and followed by the addition of potassium hydroxide (1.68 g, 0.03 mol). The reaction mixture was stirred for 30 min at a temperature of 20 °C in a water bath. After that, tri-sulfonamide (5.67 g, 0.01 mol) was added portion-wise under vigorous stirring. The stirring process was continued for 2 h and white milky mixture was obtained. A 200 mL of distilled water was added to the reaction mixture and the mixture combination was extracted with chloroform (6 x 30 mL). The combination of extracts was dried over anhydrous magnesium sulphate and the solvent was removed under vacuum. The product was recrystallised from methanol to obtain white solid (Al-Mohammed et al., 2013). The product was characterised using a CHNS analyser, UV-Vis, FTIR, and NMR spectroscopies.

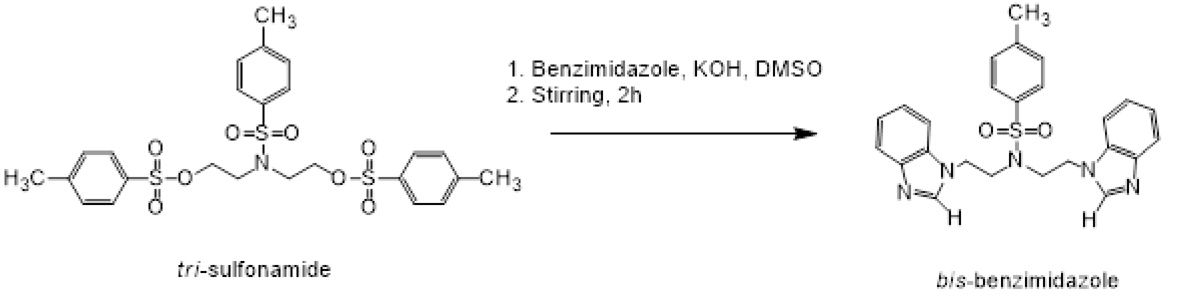

Figure 1. Synthesis route of bis-benzimidazole

Corrosion Inhibition Study

The study on corrosion inhibition was conducted using weight-loss method. The mild steel with the size of 2 × 2 cm was cleaned, washed with water, and dried. The initial weight of mild steel was measured (W_1) before each experiment. The corrosion inhibition study was conducted in varying conditions, such as different acid environments, inhibitor concentration, immersion time, temperature, and the mass of salt. At the end of the experiment, the final weight of mild steel was measured (W_2). The weight loss ΔW (g) was calculated using equation 1.

$$\Delta W = W_1 - W_2. \qquad .....1$$

The corrosion rate was measured by using the equation 2.

$C_{RW} = \Delta W / S \times t$ …..2

Where;
C_{RW} = corrosion rate with the present of inhibitor (g cm^{-2} h^{-1})
S = the surface area of mild steel (cm^2)
t = the immersion time (hour)

The values of inhibition efficiency η_w (%) was calculated by using the equation 3 and 4.

$\theta = (C^o_{RW} - C_{RW}) / C^o_{RW}$ …..3
$\eta w (\%) = \theta / 100$ …..4

Where;
ηw = inhibition efficiency (%)
C^o_{RW} = the corrosion rate in the absence of inhibitor (g cm^{-2} h^{-1})
θ = the surface coverage

Result and Discussion

Characterisation of Corrosion Inhibitor

Physico-Chemical Analysis

The bis-benzimidazole was successfully synthesised as a white solid powder (Figure 2) with a 63% yield and 190-194°C melting point. The data on CHNS analysis of bis-benzimidazole was recorded and the percentage of the experimental values found was compared with the calculated values. The CHNS elemental analysis (%) found that the calculated values showed C, 65.36; H, 5.45; N, 15.25; S, 6.97, while the experimental values showed C, 63.23; H, 5.65; N, 11.87; S, 6.53.

Figure 2. The white solid powder of bis-benzimidazole

UV-Vis Spectroscopy

The UV-Vis spectrum of synthesised bis-benzimidazole was measured in dimethyl sulfoxide (DMSO) between 200–600 nm at room temperature. The UV-Vis spectrum in Figure 3 shows the λ_{max} at 265 nm which is attributed for the π- π^* transition (benzene) in the structure of bis-benzimidazole (Pavia et al., 2015).

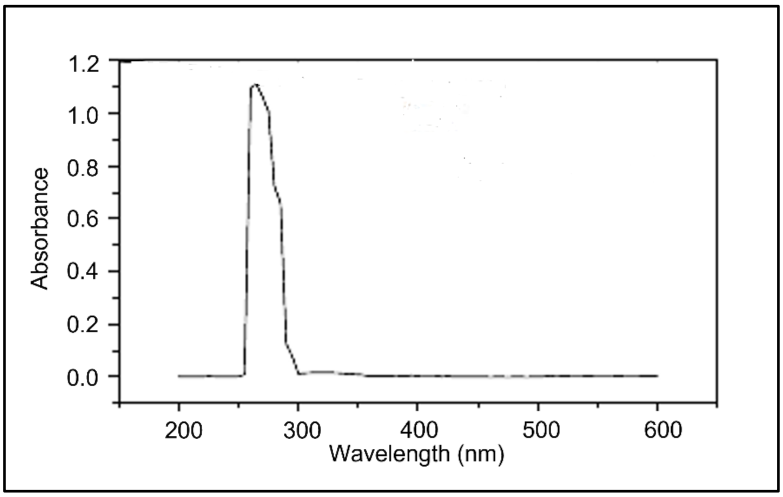

Figure 3. UV-Vis spectra of bis-benzimidazole

ATR-FTIR Spectroscopy

The significant changes of the FTIR absorption band from tri-sulfonamide to bis-benzimidazole were summarised in Table 1. The structure of the synthesised compound was confirmed by the presence of main functional groups, ʋ(S=O) at 1159 cm^{-1} and 1326 cm^{-1}, ʋ(C=C) for the aromatic ring at 1461 cm^{-1} and 1597 cm^{-1}, and ʋ(C-N) at 1091 cm^{-1}. Meanwhile, the appearance of a new stretching band, ʋ(C=N) which is referred to the benzimidazole ring at 1618 cm^{-1} confirmed the transformation from tri-sulfonamide (Said et al., 2016).

Table 1. The significant FTIR absorption band

Functional group	**Tri-sulfonamide absorption band (cm^{-1})**	***Bis*-benzimidazole absorption band (cm^{-1})**
C=C (aromatic)	1598 (m)	1498 (m)
S=O	1090 (s)	1090 (s)
C-N	1355 (m)	1364 (m)
C=N	-	1618 (w)

NMR Spectroscopy

Figure 4 illustrates the bis-benzimidazole structure with a numbering position of C for NMR result discussion. The ^{1}HNMR spectrum of bis-benzimidazole exhibited a singlet at δ 2.342 which referred to the $-CH_3$ (H_1) and two triplets at δ 3.521 and δ 4.297 which were assigned to $-CH_2$ protons (H_6 and H_7) in between N-carbene and N-SO_2. The $-CH_2$ (H_7) protons near *N*-carbene showed a downfield position due to the presence of more electronegative nitrogen atom. The aromatic proton was detected at δ 7.251 to δ 7.644 as multiplets. The carbene proton (H_8) in the benzimidazole ring was observed as a singlet at δ 8.316. The proton was observed in the downfield region due to the deshielding effect of the nitrogen atoms electronegativity (Pavia et al., 2015). Table 2 shows the summary of the ^{1}HNMR chemical shift.

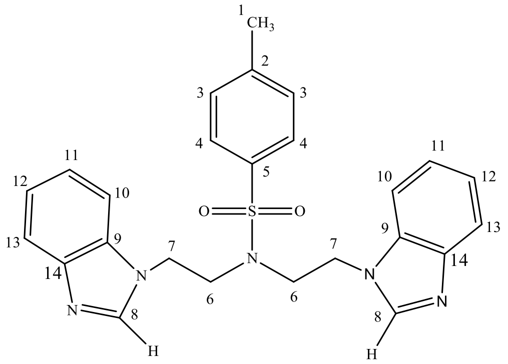

Figure 4. Bis-benzimidazole structure

Table 2. The significant ^{1}HNMR chemical shift for bis-benzimidazole

position	Chemical shift, δ ppm	multiplicity
$-CH_3$ (H_1)	2.342	Singlet
$-CH_2$ (H_6)	3.521	Triplet
$-CH_2$ (H_7)	4.297	Triplet
-CH (aromatic)	7.251 to 7.644	Multiplet
-CH carbene (H_8)	8.316	Singlet

On the other hand, the ^{13}CNMR spectrum shows a similarity with the compound synthesised in the previous literature (Al-Mohammed et al., 2013) and the chemical shifts were summarised in Table 3. The replacement of sulfonyl groups with benzimidazole at both arms of tri-sulfonamide was confirmed by the presence of three new peaks at a downfield region which is referred as quaternary carbon. It included two quaternary carbons at benzimidazole benzene rings (δ 133.95 and δ 143.49) and carbon carbene (δ 130.36). The large downfield shift was observed due to hybridisation, anisotropy, and electronegativity atoms that were directly attached to the carbons, respectively (Pavia et al., 2015).

Table 3. The significant ^{13}CNMR chemical shift for bis-benzimidazole

C-position	Chemical shift, δ ppm
$-CH_3$ (C_1)	21.44
$-CH_2$ (C_6)	43.70
$-CH_2$ (C_7)	48.57
-CH (aromatic $C_{10\text{-}13}$)	110.62-123.09
-CH (aromatic $C_{3,4}$)	125.97, 127.40
-CH carbene (C_8)	130.36
-C quaternary (C_{14})	133.95
-C quaternary (C_2)	135.55
-C quaternary (C_9)	143.49
-C quaternary (C_5)	144.15

Corrosion Inhibition Study

The synthesised compound was applied as a corrosion inhibitor of mild steel coupon in 1 M HCl and 1 M H_2SO_4 solution. This study was conducted in varying conditions, which are inhibitor concentration, immersion time, temperature, and mass of NaCl (salinity). The results are summarised in Table 4 and the proposed inhibition mechanism of bis-benzimidazole on the surface of mild steel is illustrated in Figure 5.

In table 4, blank sample (without the presence of inhibitor) which refer to experiment number 1, 11 and 15 no corrosion inhibition activity will be observed. Meanwhile, in the presence of inhibitor at the difference of immersion time and inhibitor concentration, both acidic medium shows the percentage of inhibition efficiency decreased from 8 h to 24 h and from 0.01 M to 0.0001 M, respectively. The results can be observed in experiment number 8 to 10 (8 h), 12 to 14 (16 h) and 16 to18 (24 h). This was due to the increase in the exposure time of mild steel towards the acidic environment that gave ample time for the corrosion process to occur (Ahamad et al., 2010). In addition, during the longest immersion time course the inhibitor desorbed from the surface of mild steel and becomes inactive that consequently reduce its inhibition efficiency (Mohammed et al., 2021).

The effect of the inhibitor concentration study (experiment number 8 to 10) for 1M HCl condition shows the inhibition efficiency was 100% at all concentration levels. This shows that the inhibitor has excellent inhibition properties that could prevent 100% corrosion yet at low concentration and at a shorter immersion time (8 h). However, for other reaction conditions, the highest concentration of inhibitor (0.01 M) showed the best inhibition efficiency at different immersion times, followed by 0.001 M and 0.0001 M. The results showed a similarity with the study conducted by Şafak et al. (2012), which discovered that the inhibition efficiencies increased when the mild steel surface was treated with increasing inhibitor concentration. This was attributed to the larger coverage of metal with inhibitor molecules being chemically adsorbed on the mild steel surface, thus it could form a layer on the steel surface that can inhibit the corrosion (Ashassi-sorkhabi et al., 2005; Vinutha and Venkatesha, 2016). The presence of the nitrogen atom with its lonely sp^2 electron pair and the aromatic rings on the NHC structure provided two anchoring sites that were suitable for bonding mild steel surfaces. Moreover, the increase in the resonance capability of molecules towards conjugations owed to the presence of unshared electron pairs on the nitrogen, sulphur, and oxygen atoms and thus increased the inhibition performance (Jamil et al., 2018; Al-Baghdadi, 2018).

The percentage of corrosion inhibition of mild steel in H_2SO_4 is observed lower than in HCl. It can be deduced that the H_2SO_4 is a more concentrated acid than HCl since it has more hydrogen ions in the solution environment (Saeid, and Chojnacka, 2014). Since the 0.01 M concentration of the inhibitor showed the best inhibitor efficiency as compared to the other two concentrations. Therefore, this concentration was chosen as the indicator for further study on the effect of temperature and salinity (mass of NaCl).

The temperature played an important role in accelerating the corrosion rate of metals. Experiment number 5 to 8 show the comparison of decrease in inhibition efficiency at different temperature from 25 °C to 50 °C at 8 h using 0.01 M concentration of inhibitor. Higher temperature increases the hydrogen generation which leads to an increase in corrosion activities, thus reducing inhibitors efficiency (Nassar and Nassar, 2016).

Environment salinity is another factor that will affect the rate of corrosion in which the chloride concentration will increase the corrosion rate. Experiment number 2 to 4 show that the percentage dropped in the inhibition efficiency with an increase in the mass of NaCl. This is because the presence of NaCl salt increases the conductivity of water which subsequently increases the concentration of ions with the time that would lead to the increase of metal corrosion (Ibrahim, 2013). The presence of chloride ions slowly penetrates the surface of mild steel and destroys the protective film causing the tendency of the corrosion to evenly space the entire surface area of the specimens with shallow, flat-bottomed, and irregular-shaped pits (Prawoto et al., 2009).

Table 4. The results of corrosion inhibition study at various reaction condition

No. of experiment	Immersion time (h)	Concentration of inhibitor (M)	Mass of NaCl (g)	Temperature (°C)	Inhibition efficiency (%)	
					1M HCl	1M H_2SO_4
1	8	Blank	-	25	-	-
2		0.01	0.5	25	99.91	92.15
3		0.01	1.0	25	99.82	91.40
4		0.01	1.5	25	98.59	90.76
5		0.01	-	30	99.09	87.22
6		0.01	-	40	98.67	85.15
7		0.01	-	50	98.10	80.63
8		0.01	-	25	100.00	92.51
9		0.001	-	25	100.00	80.99
10		0.0001	-	25	100.00	55.01
11	16	Blank	-	25	-	-
12		0.01	-	25	81.20	85.70
13		0.001	-	25	81.20	78.42
14		0.0001	-	25	59.09	53.18
15	24	Blank	-	25	-	-
16		0.01	-	25	76.92	83.14
17		0.001	-	25	65.38	72.95
18		0.0001	-	25	46.15	47.90

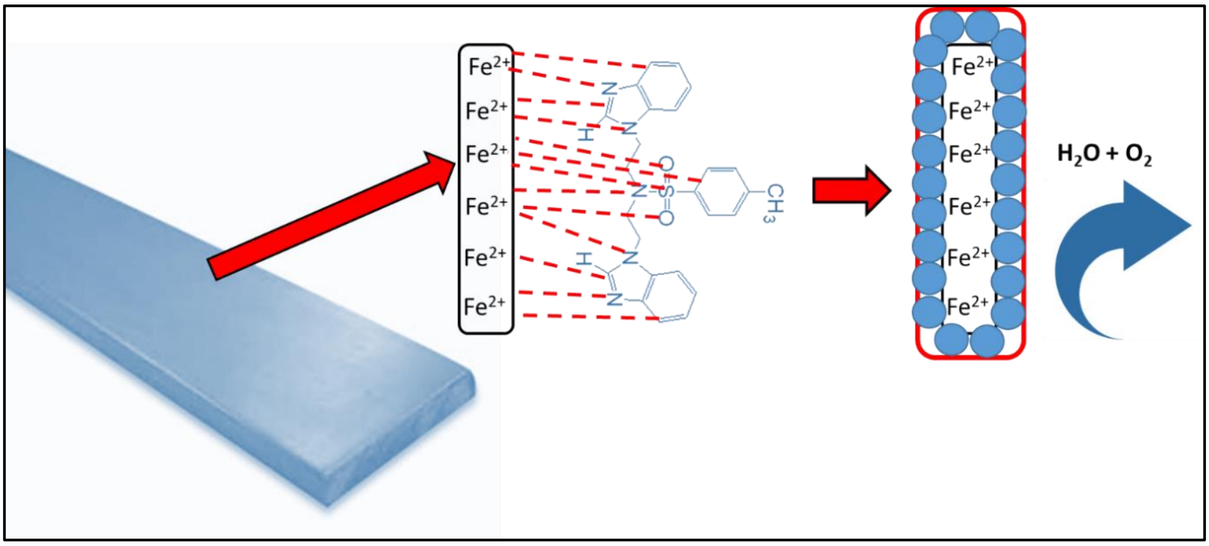

Figure 5. The inhibition mechanism of bis-benzimidazole on the surface of mild steel

Conclusion

In conclusion, the bis-benzimidazole was successfully synthesised and applied as an inhibitor for mild steel corrosion in different acid environments. The CHNS elemental analysis, ATR-FTIR, UV-Vis, and NMR spectroscopies data supported the formation of the bis-benzimidazole. Meanwhile, for the corrosion inhibition study, the optimum inhibition efficiency was achieved using 0.01 M of bis-benzimidazole in 8 h immersion time at room temperature with 100% and 92.51% in 1 M HCl and 1 M H_2SO_4, respectively.

Acknowledgement

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