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Morpholine and piperazine based carboxamide derivatives as corrosion inhibitors of mild steel in HCl medium

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ABSTRACT

N-(2-chloroethyl)morpholine-4-carboxamide (NCMC), *N*-(2-chloroethyl)tiomorpholine-4-carboxamide (NCTC) and *N*,*N*-bis(2-chloroethyl)piperazine-1,4-dicarboxamide (NCPD) were studied as corrosion inhibitors for mild steel using atomic absorption spectroscopy (AAS) and gravimetry and thermometry. Results obtained from the three techniques are similar and reveal that the compounds inhibit mild steel corrosion. The inhibition efficiencies increased from 35.6% to 74.9% (NCMC), 44.5% to 82.4% (NCPD) and 52.6% to 90.1% (NCTC) at 30 °C when the inhibitor concentrations increased from 10 μM to 50 μM. The maximum inhibition efficiency values (at 50 μM) decreased to 46.6%, 58.1% and 61.2% for NCMC, NCPD and NCTC respectively, when the temperature was raised to 50 °C. The decrease in inhibition efficiency with increase in temperature suggested predominant physisorption mechanism in metal/inhibitor interactions. The formation of protective films of NCMC, NCPD and NCTC molecules on mild steel surface were confirmed by FTIR and XRD. The order of inhibitive strengths of the molecules is NCTC > NCPD > NCMC. Quantum chemical calculations revealed the prospective sites through which the molecules can interact with mild steel surface and some quantum chemically derived parameters were used to corroborate experimental.

1. Introduction

Many facilities used at the oil and gas refinery plants are made of mild steel. Steel is a major construction material extensively used in chemical and allied industries for material constructions [1]. It has therefore become the most useful metal in human development. The utilization of mild steel in construction and fabrication of industrial facilities is not only due to its optimum strength to mass ratio that fits the strength requirement of many industrial equipment, but also as a result of its ready availability at moderately low cost. Unfortunately, mild steel being an active alloy of iron undergoes corrosion in nearly all environments, most especially acidic environment. Corrosion of metals has both economic and environmental effects that are of great concern to corrosion and corrosion prevention experts. Corrosion products can be hazardous to man, animal and vegetation. El-Melgi [2] believes that corrosion products from various sources including car constructions, bridges and buildings, water pipeline systems and petroleum industries are notable environmental pollutants.

Steel made materials are often used to hold acid, alkali and salt solutions in chemical and allied industries [2]. Acid induced steel corrosion is by far the most common in industries. Industrial processes that lead to steel corrosion by acids include acid pickling, acid cleaning and oil well acidizing [3]. Safety and cost-effective maintenance of steel materials used for these industrial activities are of paramount consideration [4]. Increased metal corrosion resistance can be achieved in various ways, but often at elevated cost. The use of corrosion inhibitors is therefore a more practical and economic alternative [5]. The use of corrosion inhibitors in industries is extensive and broad based [6].

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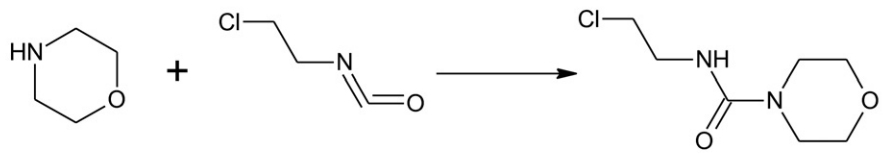


Scheme 1. Synthesis of *N*-(2-chloroethyl)morpholine-4-carboxamide [NCMC].

Though excellent corrosion resistance has been reported for inorganic inhibitors such as chromates, unfortunately, their uses are discouraged due to health and environmental reasons. Notable are the heavy metal based inhibitors which are not favored because of their associated environmental issues. Lanthanide salts, though have low toxicity and good inhibitive properties, are very expensive and their uses are therefore discouraged [7]. Owing to stringent environmental regulations caused by environmental limitations of inorganic inhibitors, and the high cost of less toxic ones, organic compounds are fast replacing inorganic corrosion inhibitors especially the heavy metal derivatives [8].

Carboxamide derivatives are among organic compounds that have been reported in some previous studies as efficient corrosion inhibitors for metals [9–13]. The inhibitive effect of 2-(1-(2-oxo-2h-chromen-3-yl)ethylidene)hydrazinecarboxamide on zinc-aluminium alloy in 1.8 M hydrochloric acid has been reported by Aladesuyi et al. [9]. Paramasivam et al. [10] had reported 4-(pyridin-2yl)-*N*-p-tolylpiperazine-1-carboxamide as effective inhibitor of mild steel corrosion in hydrochloric acid. Zulfareen et al. [11] investigated the inhibitive effect of newly synthesized *N*-(4-morpholinomethylcarbamoylphenyl)-furan-2-carboxamide on corrosion of brass in HCl medium. Shahabi et al. [12] also reported the corrosion inhibition performances of two carboxamide compounds, *N*-{3-methyl-2-[(2-thienylcarbonyl)amino]phenyl}-2-thiophenecarboxamide and *N*-(3-methyl-2-(picolinamido)phenyl)picolinamide for carbon steel corrosion in HCl solution [12].

However, many of these compounds only exhibited high corrosion inhibition performances at relatively high concentrations [10–13] of about 1000 folds higher than what was obtained in the present study. For instance, 4-(pyridin-2yl)-*N*-p-tolylpiperazine-1-carboxamide was used up to 3 mM to obtain inhibition efficiency of about 92% [10]; *N*-(4-morpholinomethylcarbamoylphenyl)-furan-2-carboxamide was used at a concentration as high as 2 mM to get 62% protection performance [11], while *N*-{3-methyl-2-[(2-thienylcarbonyl)amino]phenyl}-2-thiophenecarboxamide and *N*-(3-methyl-2-(picolinamido)phenyl)picolinamide were used at 1 mM to amass 88–91% inhibition efficiency.

In view of the aforementioned, the present work was designed towards the investigation of carboxamides with potentially high inhibition efficiencies at relatively low concentrations. The protection performances of some novel morpholine and piperazine based carboxamide derivatives namely, *N*-(2-chloroethyl)morpholine-4-carboxamide (NCMC), *N*-(2-chloroethyl)thiomorpholine-4-carboxamide (NCTC), and *N*,*N*″”-bis(2-chloroethyl)piperazine-1,4-dicarboxamide (NCPD) for mild steel in HCl medium are hereby reported. Experimental studies were carried out using atomic absorption spectrometry (AAS), gravimetric and thermometric techniques. Density functional theory calculations were also carried out to corroborate experimental findings.

2. Experimental

2.1. Composition of mild steel coupon

Percentages by weight (%) of elemental constituents of mild steel coupon used in corrosion tests are carbon (0.10), manganese (0.54), phosphorus (0.34), sulphur (0.02), silicon (0.26), and iron (98.74).

2.2. Synthesis of the inhibitors (NCMC, NCTC and NCPD)

The synthesis of *N*-(2-chloroethyl)morpholine-4-carboxamide (NCMC) involves the addition of morpholine ($HN(CH_2CH_2)_2O$, 0.174 g, 0.002 mol) to a solution of 2-chloroethylisocyanate ($ClCH_2CH_2NCO$, 0.211 g, 0.002 mol) in dimethylether (30 mL) in a 100 mL round bottom flask. Afterwards, the reaction mixture was stirred for 5 min and a quantitative precipitate of the product, *N*-(2-chloroethyl)morpholine-4-carboxamide, formed immediately. Thereafter, the product was filtered, washed with ether (20 mL), dried under vacuum and characterized using infrared spectroscopic technique. Synthetic technique for NCMC synthesis has been reported elsewhere [14]. NCPD was prepared using piperazine and NCTC using thiomorpholine following similar steps involved in NCMC synthesis. Spectroscopic characterization data of NCMC, NCPD and NCTC have been reported somewhere else [14–16].

The synthetic schemes for the three compounds are summarized in Schemes 1–3.

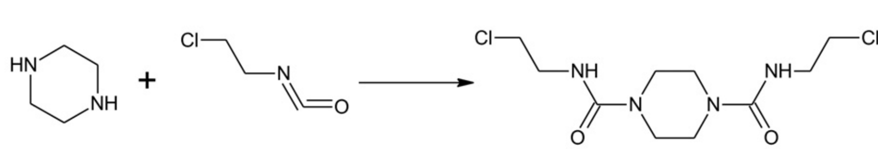
2.3. Materials

Mild steel sheet was obtained commercially and was mechanically press cut into 5 cm × 4 cm × 0.11 cm coupons for the AAS and gravimetric measurements. Prior to all measurements, the mild steel coupons were successively abraded with emery papers of 240, 400 and 800 grit sizes respectively, degreased in acetone, washed in distilled water and dried. Afterwards, the specimens were put in a desiccator and then used for the respective experiments. Acetone and concentrated hydrochloric acid were of BDH-Analar grades purchased from BDH, Poole, England.

NCMC was dissolved in 10 mL methanol and made up to mark in a 2 L standard flask using hydrochloric acid solution. In 2 L standard flasks, NCTC and NCPD were dissolved in 10 mL of hydrochloric acid solution and made up to mark using same solution. From the stock solutions in the 2 L standard flasks, different concentrations (10–50 μM) of NCMC, NCTC and NCPD were prepared from the stock solutions.

2.4. Weight loss/gravimetric technique

The gravimetric technique used here has been reported earlier [15–18]. Briefly stated, gravimetric measurements were taken by suspending mild steel coupons stored in a desiccator. These coupons were weighed



Scheme 2. Synthesis of *N*,*N*″”-bis(2-chloroethyl)piperazine-1,4-dicarboxamide [NCPD].