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Review

Benzimidazole: Small planar molecule with diverse anti-corrosion potentials

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ABSTRACT

The cost of corrosion greatly impacts the economics of industrialized nations that a significant percentage could be equated in some way to a fraction of their GDP. The use of organic inhibitor compounds has proven to be one of the most practically effective methods for mitigating metal corrosion in various aggressive media. Most inhibitors play important roles in retarding corrosion due to the presence of sites of adsorption for metal surface bonding. Benzimidazoles being a unique stock of bicyclic compounds with a fused benzene/imidazole structure belong to this class of inhibitors. With their numerous therapeutic properties, their biological activities are also accompanied by safe and efficient corrosion protection abilities with negligible negative effects on man and his environment. Their superior inhibiting potency for metal corrosion over some other compounds is attributed to their rate of molecular adsorption at the metal/solution interface due to the presence of the nitrogen atom bearing the sp^2 electron pair known to act as metal surface anchoring sites. This review covers older and most recent investigations related to the application of a number of benzimidazole derivatives as corrosion inhibitors for industrial metals in many simulated and real aqueous media. The mechanisms of corrosion protection for each inhibition system have also been highlighted via experimental and theoretical based approaches in acid, alkaline and near neutral media. The use of this class of compounds for microbial corrosion inhibition and sweet corrosion have also been proposed for future studies since reported research in this aspect are relatively scanty.

Contents

1. Introduction: corrosion inhibitors

Corrosion of metals deployed for household water pipeline systems and other metal-based household appliances has resulted in water contamination and environmental pollution with immeasurable losses and

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Nomenclature

Abbreviations

USA	United States of America
GDP	Gross Domestic Product
FHWA	Federal Highway Administration (US based)
NACE	National Association of Corrosion Engineers
MIC	Microbial induced corrosion
MICC	Microbial induced concrete corrosion
MICI	Microbial induced corrosion inhibition
ANN	Artificial neural network model
B3LYP	Becke, three-parameter, Lee-Yang-Parr
DFT	Density Functional Theory
SQM	Scaled Quantum Mechanical *methodology*
FMO	Frontier molecular orbitals
FTIRS	Fourier transform infrared spectroscopy
NMRS	Nuclear magnetic resonance spectroscopy
UV–vis	UV–visible spectroscopy
TGA	Thermogravimetric analysis
GPC	Gel permeation chromatography
PCM	Polarizable continuum model
rds	Rate determining step
XRD	X-ray diffraction
DFT	Density functional theory
QSIR	Quantitative structure inhibition (activity) relationship
EIS	Electrochemical impedance spectroscopy
R_{ct}	Charge transfer resistance
c_{dl}	Double layer capacitance
SEM	Scanning electron microscopy
AFM	Atomic force microscopy
EDX/S	Energy dispersive X-ray/spectroscopy
XPS	X-ray photoelectron spectroscopy
MDS	Molecular dynamics simulations
LUMO	Lowest unoccupied molecular orbital
HOMO	Highest occupied molecular orbital
SERS	Surface-enhanced Raman scattering
SCE	Standard calomel electrode
EQCM	Electrochemical quartz crystal microbalance
EQCN	Electrochemical quartz crystal nanobalance
SRB	sulphate-reducing bacteria

disease. In a large scale, mishaps associated with failures of engineering structures due to corrosion could result in loss of life and properties, and with negative social impacts. Oilfield industries including servicing companies experience corrosion episodes everywhere, from the facilities deployed in processing and maintenance to surface and downhole equipment (e.g., pumps, valves, pipes, etc.). Left unchecked, simple leakages in storage tanks and casings could amount to huge economic losses for the company, and those from tubings and pipelines may release toxic chemicals to the adjoining environments thereby causing disease in an epidemic proportion. Some spillages in oil and gas producing companies have resulted in recurrent partial and even total shutdown of operations for complete overall maintenance and structural changes, hence economic loss [1]. Between 10 and 30% of annual profit of most oil processing is allocated for the general maintenance of corrosion related damages, particularly those linked with natural gas sweetening and oil refining plants [2]. Garcia-Arriaga et al. [2] have reported that pipeline corrosion could be linked with the corrosive agents (H_2S, CO_2, O_2, Cl and H_2O) evolved during the drilling operation as well as the sweetening processes (e.g. pre-processing step for hydrocarbon transformation and commercialization). Oil pipelines undergo internal localized/uniform corrosion and stress corrosion cracking (SCC) due to the high currents of flow line contents. Corrosion adversely affects the microstructures of materials and this leads to fractures especially in sections with high temperature and turbulence. H_2S in oil and gas fields has been linked with surface pitting, hydrogen embrittlement and SCC [3–7]. Ren et al. [8] have reported that sweet uniform corrosion increases the severity of pitting corrosion at higher partial pressures of H_2S, pH and temperature. Apart from uniform corrosion in pipelines, galvanic corrosion problems associated with metals of dissimilar elemental makeup have gained more attention in material design for corrosion resistance [1]; galvanic corrosion is common in wellheads with tubing string (made of corrosion-resistant alloy) and steel casing [9].

Corrosion does not only remain a huge economic problem for most industrial countries of the world in areas of processing and production, it has also taken a toll on the transportation of industrial and commercial products as well as man. In US alone, $276 billion representing 3.1% GDP was the annual cost of corrosion in 2002 (See FHWA report in collaboration with NACE) [10,11]. Approximately half of this amount ($121 billion) was expended on mitigation techniques and procedures against corrosion in every sector of the economy, including transportation. MICC has also impacted negatively on sewer systems in most urban areas in the US. Brongers et al. [12] have estimated valuable assets in the zone of about $1 trillion and $35 billion for the USA and Australia, respectively, will be lost to MIC. The annual cost expended in water and wastewater infrastructures alone is $36 billion; and $14 billion per year is expended on the maintenance and reconstruction of concrete structures for new sewers and other aging infrastructures [12,13]. Failed sewer structures have been attributed to corrosion episodes brought about by increasing levels of H_2S in stored sewage, relative humidity and increased temperature. Many control technologies have been designed to estimate the service life of most sewer for maintenance purposes, but recent process models in modern sewers are designed to study the level of H_2S production and wastewater characteristics in the whole sewer networks [14,15]. Jiang et al. [16] have designed an artificial neural network (ANN) model for predicting MIC as a means of monitoring the service life of sewers. This analytical model takes into account possible changes in corrosion rates in alloys deployed in the concrete structures in varying sewer conditions. Besides natural precipitation (e.g. rain, condensation, seawater etc.) and the above enlisted corrosion-inducing processes, materials can also corrode due to exposure to corrosive environments during industrial processing; typical example of such operations is the industrial cleaning of metals using acid solutions. Hydrochloric acid (HCl) is deployed as oxidizing mixtures during pickling operations for alloyed and non-alloyed metals, during oil well acidification and other petrochemical processes. Other pickling operations involve the removal of rusts, scales and carbonate deposits from oil wells using some mineral acids [17,18]. Due to the complex nature of metal degradation processes and since corrosion is continuous, it is difficult to predict a perfect corrosion inhibition system without considering a lot of solution and substrate-based factors. Modern researches worldwide are focused on designing technologies that adequately predict the rates of corrosion in media as well as the kinetics of the degradation process in real-time. In some oilfield systems, the use of zinc primers (sacrificial anodes) is popular; cathodic protection is also deployed especially when it involves the application of a current opposing to the corrosion on the metal system [19,20]. Another mitigation technique involves the designing of corrosion-resistant alloy by a careful choice of alloying elements during the metallurgical processing of the materials. Most corrosion inhibition strategies also involve the use of protective devices with their treatments approaches based on the mechanism of the corrosion process. Anodizing, chromating and the use of protective organic coatings and anticorrosive paint composites on metals surfaces have also proved to be effective corrosion control techniques but not without some demerits [19]. In recent times, the use of organic inhibitor compounds has proven to be the most practical and effectives methods for protecting metals against corrosion in most aggressive media [20]. These compounds are deployed as principal