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Synergistic effects and hydrogen bonded interaction of alkyl benzimadazoles and thiourea pair on mild steel in hydrochloric acid

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ABSTRACT

Synergistic hydrogen bonded interaction and corrosion protection properties of alkyl benzimidazoles and thiourea pair on mild steel in hydrochloric acid at different temperatures have been studied by polarization, electrochemical impedance spectroscopic studies (EIS), adsorption, surface studies and computational methods. The extent of synergistic interaction increases with temperature. Quantum chemical approach was used to calculate some electronic properties of the molecules. The inhibition efficiencies and the global chemical reactivity relate to total energy, E_{HOMO}, E_{LUMO} and gap energy (ΔE). Thiourea interacts with benzimidazoles up to a bond length of approximately 2.20 Å. This interaction may be due to the development of a hydrogen bond between thiourea and benzimidazoles. This synergistic interaction offer extended inhibition efficiency toward mild steel in hydrochloric acid. The corrosion inhibition efficiencies and the global chemical reactivity relate to total energy, E_{HOMO}, E_{LUMO} and gap energy (ΔE).

1. Introduction

Mild steel and its alloys are widely used in oil and gas industries among others [1,2]. The stimulation process in petroleum industry involves different aspects, including the acidizing portion utilized to stimulate the carbonate reservoir or for dissolving fines. Concentrated acids of 5–28 wt%, usually used in refineries make the environment corrosive to steel and alloys. Hydrochloric acid, hydrofluoric acid, acetic acid or formic acids are injected into the well during the acidizing stimulation process which causes serious corrosion issues. In the absence of corrosion inhibitors, the general corrosion rate is extremely high which increases exponentially with increasing temperature and acid concentrations [3]. It has to be pointed out that the petroleum industry is the largest consumers of corrosion inhibitors [4,5]. Most of well-known acid inhibitors are organic compounds containing N, O, P and S in their structures [6–8]. The inhibiting action of organic compounds is usually attributed to their interactions with the metal surface through adsorption. The adsorption of organic molecules on metal surface or solution interface may take place through

(a) Electrostatic attraction between the charged molecules and the charged metal.
(b) Interaction of unshared electron pairs in the molecule with the metal.
(c) Interaction of Π (pi) electrons with the metal.
(d) Combination of (a) and (b) [9].

The adsorption ability of inhibitors onto metal surface depends on the nature and surface charge of metal, the chemical composition of electrolytes, the molecular structure and electronic characteristic of inhibitors molecules. Organic compounds containing functional electronegative groups and the Π (pi) electrons in triple or conjugated double bonds are usually good inhibitors [10–12].

Generally studies on corrosion inhibitors mainly focus on three domains:

(1) To find the appropriate inhibitors among the known compounds,
(2) To synthesize new compounds under the direction of theoretical calculation,
(3) To identify synergistic actions among various compounds to expand the range of inhibitor application.

Synergistic effect describes an increase in the effectiveness of corrosion inhibitors in the presence of another substance in the corrosive medium. Synergism is an effective method to improve the inhibitive performance, to decrease the amount of the usage of inhibitors and to diversify the application of inhibitors in acidic media [13]. Some authors reported the synergistic inhibition effects between different organic inhibitors and halide ions [14–18], organic inhibitors/metallic ion mixture [19–23], organic inhibitor/organic inhibitor mixture [24–28] on steel corrosion in acidic solutions.

The aim of the present investigation is to study the synergistic influence of mixture of thiourea (TU) and three different alkyl

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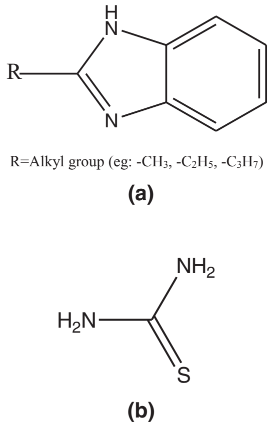

Fig. 1. Structure of inhibitors: (a) alkyl benzimidazole, (b) thiourea.

benzimidazoles [2-methyl benzimidazole (MBI), 2-ethyl benzimidazole (EBI), and 2-propyl benzimidazole (PBI)] on corrosion inhibition of mild steel in 1 M HCl. This work is a continuation of the study on the synergistic influence of ETU and benzimidazole derivatives on corrosion of mild steel in 1 M HCl [29].

2. Experimental

2.1. Inhibitor synthesis

Alkyl benzimidazoles were (Fig. 1a) synthesized from a mixture of *o*-phenylenediamine (10 g, 0.092 mol) and aliphatic acid (0.11 mol) in the presence of 4 M HCl (10 ml) and were refluxed at 373 K for 12 h. Completion of the reaction was monitored by thin layer chromatography (TLC). The contents were cooled to room temperature and neutralized with saturated solution of $NaHCO_3$. The solid separated was filtered and dried. Water soluble compounds were recrystallized and used. Commercially available thiourea (Fig. 1b) after re-crystallization was used for synergistic studies.

2.2. Medium

The medium for the study was prepared from reagent grade HCl (E. Merck) and doubly distilled water. All tests were performed in an aerated medium at different temperatures (303 K, 308 K, 313 K and 318 K).

2.3. Materials

The steel sample had the following composition (atom%): C (0.2%), Mn (1%),P (0.03%), S (0.02%) and Fe (98.75%). The mild steel specimens used in weight loss measurements were cut in 2.8 cm^2 × 1.9 cm^2 coupons. For electrochemical studies same type of coupons were used but only 1 cm^2 area was exposed in each test. Before measurements the samples were polished using different grade of emery papers and then subjected to the action of a buffing machine attached with a cotton wheel and a fiber wheel having buffing soap to ensure mirror bright finish, degreased by washing with ethanol, acetone and finally washed with distilled water.

2.4. Electrochemical measurements

Electrochemical studies were carried out at the open circuit potential (E_{ocp}), using a Gill AC computer controlled electrochemical work station (ACM, U.K. model no.: 1475). In the conventional three electrode assembly, a Pt foil auxiliary electrode and a saturated calomel reference electrode (SCE) were used. After immersion of the specimen, prior to the impedance measurement a stabilization period of 1 h was observed, which proved sufficient for E_{ocp} to attain a stable value. The AC frequency range extended from 10 kHz to 0.1 Hz, a 10 mV peak to peak sine wave being the excitation signal. Data processing was based on a non-linear least square fitting procedure as described elsewhere [30,31]. The same equipment as for the impedance measurements was used for polarization measurements. The polarization curves were obtained in the potential range from −250 mV to +250 mV with respect to SCE with a sweep rate of 60 mV/min.

2.5. Quantum chemical measurements

The correlation between theoretically calculated properties and experimentally determined inhibition efficiencies has been studied successfully for uniform corrosion [32–39]. Several theoretical parameters such as electronic properties of inhibitors, effect of the frontier molecular orbital energies, the difference between lowest unoccupied molecular orbital (LUMO) and highest occupied molecular orbital (HOMO) energies ($E_L - E_H$), electronic charges on reactive centers, dipole moments and confirmation of molecules were obtained using DFT methods. Density functional theory is used with beck's three parameter exchange functional along with Lee–Yang–Parr non-local correlation functional (B3LYP) with 6-31G* basis set implemented in Guassian03 program package. According to DFT – Koopman's theorem [40–42], the ionization potential (I) is approximated as the negative of the highest occupied molecular orbital energy (E_{HOMO}) and the negative of the lowest unoccupied molecular orbital energy (E_{LUMO}) is related to the electron affinity (A).

$$I = -E_{HOMO} \tag{1}$$

$$A = -E_{LUMO} \tag{2}$$

Natural bond orbital (NBO) analysis [43] was performed to evaluate the electron density distributions. The electron density plays an important role in calculating the chemical reactivity parameters. The global reactivities include electro negativity (χ), chemical potential (μ), global hardness (η) and the global softness (σ). They can be calculated from the following equations:

$$\chi = -\mu = \frac{I + A}{2} \tag{3}$$

$$\eta = \frac{I - A}{2} \tag{4}$$

$$\sigma = \frac{1}{\eta} \tag{5}$$

The fraction of electrons transferred from the inhibitor molecules to the metal surface was estimated as

$$\Delta N = \frac{\chi_m - \chi_{inh}}{2(\eta_m + \eta_{inh})} \tag{6}$$

where χ_{Fe} and χ_{inh} denote the absolute electro negativity of metal and inhibitor molecules respectively, η_{Fe} and η_{inh} denote the absolute hardness of metal and the inhibitor molecule respectively. In this study, we use the theoretical value of $\chi_{Fe} = 7.0$ eV and $\eta_{Fe} = 0$ for the computation of fraction electrons transferred from ligands to metal [44].

The local reactivity of the inhibitor molecules was analyzed through an evaluation of the Fukui indices. Fukui indices provide information about the local reactivity, as well as the nucleophilic and electrophilic behaviors of the molecule. Regions of molecules having large Fukui functions are chemically softer than the regions with smaller Fukui functions, and by invoking HSAB principle in a local sense; one can establish the behavior of different sites with respect to hard or soft reagents.

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