



Molecular dynamic and quantum chemical calculations for phthalazine derivatives as corrosion inhibitors of mild steel in 1 M HCl

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ABSTRACT

The abilities of phthalazine derivatives, including phthalazine (PT), phthalazone (PTO) and phthalhydrazide (PTD), to inhibit the corrosion of mild steel in 1 M HCl at 30 °C were studied using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Theoretical calculations were performed to investigate the electronic structures of the PT derivatives. Our results showed that the inhibition efficiencies of these derivatives improved with increases in concentration. The data also showed that $PTD < PT < PTO$ in terms of the inhibiting efficiency. Theoretical calculations also revealed that PTO is expected to be the best inhibitor among the studied phthalazine derivatives.

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1. Introduction

The corrosion of metals, including mild steel, is a serious problem in many industries, especially during processes such as the pickling of steel, acid washing and etching [1,2]. Corrosion inhibitors are chemical compounds that in small quantities can retard the degradation of metals in hostile environments. Because these inhibitors represent an economic and effective technique to prevent metal and alloys from being corrupted, inhibitors are widely used in chemical cleaning solutions, industrial water and petrochemical engineering production processes, applied to the atmosphere and environment and are becoming an indispensable protection measure during industrial production [3]. These inhibitors are believed to work by influencing the kinetics of the electrochemical reactions that constitute the corrosion process, thereby modifying the metal dissolution in acids. The existing data show that most organic inhibitors act by adsorption onto the metal surface [4]. Generally, organic inhibitor molecules might physically or chemically adsorb onto a corroding metal.

Theoretical chemistry, including quantum chemical calculations, has proved to be a very powerful tool for studying the mechanism of corrosion inhibition [5]. Because strong correlations have been found between the corrosion inhibition efficiencies of most compounds with several semi-empirical parameters, the quantum chemical principle is a useful tool to predict the inhibition potentials of structurally related organic compounds [6–10]. A better

understanding of how inhibitor molecules behave on a metal surface could greatly enhance our ability to control the essential interfacial properties of these systems in a wide variety of corrosion problems. As such, the adsorption of inhibitor molecules on surfaces has recently become the subject of intensive investigation in the field of corrosion research [11–22].

The objectives of this work were to study the inhibition performance of phthalazine derivatives, namely phthalazine (PT), phthalazone (PTO) and phthalhydrazide (PTD) (Fig. 1), using electrochemical impedance spectroscopy (EIS) and potentiodynamic polarization measurements. Properties of the molecular structure of these phthalazine derivatives were calculated using AM1, PM3 and MNDO semi-empirical equations implemented with Restricted Hartree–Fock (RHF). Monte Carlo molecular simulations were performed using an adsorption locator module to obtain adsorption energies of the phthalazine derivatives on the Fe_2O_3 surface.

2. Materials and methods

Mild steel specimens with an exposed area of 4.5 cm² were obtained from the Metal Samples Company (PA, USA) and were used as the working electrodes throughout this study. The compositions (wt.%) of mild steel in the electrodes are listed in Table 1. The studied inhibitors, PT, PTO and PTD, were supplied by Sigma–Aldrich Co. and were used without any further purification. The inhibitor concentrations ranged from 0.25 to 2 mM. The 1 M HCl solution was prepared by dilution of analytical grade 37% HCl with distilled water. Measurements were performed in a non-aerated and unstirred 1 M HCl acid solution at 30 °C (± 1 °C). The temperature

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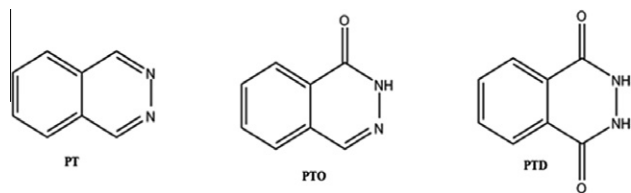


Fig. 1. Chemical structure of the investigated Phthalazine derivatives inhibitor.

was controlled using a thermostat [23]. The specimens were cleaned according to ASTM standard procedure G1-03 [24].

A 200 mL, Gamry water-jacketed glass cell was used in these experiments. The cell contained the three classic electrodes, namely the working, counter and reference electrodes, which were comprised of mild steel, a graphite bar and a saturated calomel electrode (SCE), respectively [25,26]. Measurements were performed using a Ref 600 model Gamry Instrument Potentiostat/Galvanostat/ZRA. The DC105 and EIS300 software by Gamry were used for electrochemical impedance spectroscopy (EIS) and potentiodynamic scans, respectively. The potentiodynamic current-potential curves were taken from -0.2 to $+0.2$ V_{SCE} at a scan rate of 0.5 $mV s^{-1}$. Impedance measurements were performed using AC signals with a 10 mV peak-to-peak amplitude at the open circuit potential in the frequency range of 10 kHz – 0.1 Hz . All impedance data were fitted to appropriate equivalent circuits (ECs) using Gamry Echem. Analyst software. Electrochemical measurements were initiated approximately 30 min after the working electrode was immersed in solution to stabilize the steady-state potential [25,27].

3. Theoretical calculations

Theoretical studies were performed to examine the electrostatic structures of the PT derivatives in order to compare the theoretical and experimental results. Our goal was to investigate the relationships between the PT derivatives' inhibition abilities and their quantum chemical parameters. Molecular simulation studies were performed using the Materials Studio software (Version 5.5) from Accelrys Inc. This software is a high-quality quantum mechanics computer program that is available from Accelrys (San Diego, CA) [28]. Our study employed three modules. As described on the Accelrys website, the VAMP module "is a semi-empirical molecular orbital package for molecular organic and inorganic systems." The Forcite module "is an advanced classical molecular mechanics tool that allows fast energy calculations and reliable geometry optimization of molecules and periodic systems." Finally, the Adsorption locator module "identifies possible adsorption configurations by carrying out Monte Carlo searches of the configurational space of the metal-adsorbate system as the temperature is slowly decreased (simulated annealing)." In this study, the molecules were sketched, the hydrogens were adjusted and the molecules were cleaned using sketch tools available in the Materials Visualizer.

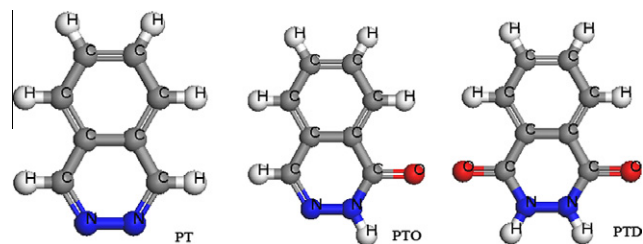


Fig. 2. Sketches of molecules of the PT derivatives.

The sketched molecules are shown in Fig. 2. All quantum calculations were performed with complete geometry optimization using the VAMP module and performed at the restricted Hartree–Fock (RHF) level using AM1, PM3 and MNDO semi-empirical methods in the Materials Studio software [29,30]. The molecules that are shown in Fig. 2 were optimized (i.e., energy minimizing) in the Monte Carlo simulations using the Forcite module and the Condensed-Phase Optimized Molecular Potentials for Atomistic Simulation Studies (COMPASS) force field, as shown in Fig 3. COMPASS is the first *ab initio* force field that has been parameterized and validated using condensed-phase properties in addition to various *ab initio* and empirical data for molecules in isolation. Consequently, this force field enables accurate and simultaneous prediction of structural, conformational, vibrational and thermophysical properties for a broad range of molecules in isolation and in condensed phases and under a wide range of temperatures and pressures. The unit cell structures of metal oxides with the associated experimental lattice parameters were available from Materials Studio. Using the surface builder module of Materials Studio, metal oxide surfaces were prepared by employing the desired cleavage planes hkl (1 1 0). This provided the fractional depth of the surface, which should be larger than the non-bonded cut-off distance of 9.5 Å [31].

The choice of cut-off is always a trade-off between the accuracy of the results and the time required for the calculation. Using a thickness of 4.3 Å, which produces a depth of approximately 10.83 Å for a Fe_2O_3 surface, a depth is obtained which is sufficient for the inhibitor molecules to only be involved in non-bonded interactions with the Fe_2O_3 atoms on the surface, and this calculation can be completed in a reasonable time. The surface must be large enough to accommodate the inhibitor molecules; therefore, a distance monitor was used to calculate the length of the optimized molecules, yielding 6.065 , 7.033 and 7.066 Å for PT, PTO and PTD, respectively, as shown in Fig. 3. We used super cell package to triple $U \times V$ (3×3) in order to expose a more realistic surface area for docking the inhibitor molecules. This step produced a surface with parameters of 16.25 and 18.5 Å, which is enough to accommodate the inhibitor molecules. It is important that the size of the vacuum is great enough such that the non-bonded calculation for the adsorbate does not interact with the periodic image of the bottom layer of atoms in the surface; thus, a vacuum slab with thickness 40 Å was built using Crystal Builder.

Table 1
Composition of the mild steel electrode.

Element	Content (wt.%)
Fe	99.21
C	0.21
Si	0.38
P	0.09
S	0.05
Mn	0.05
Al	0.01

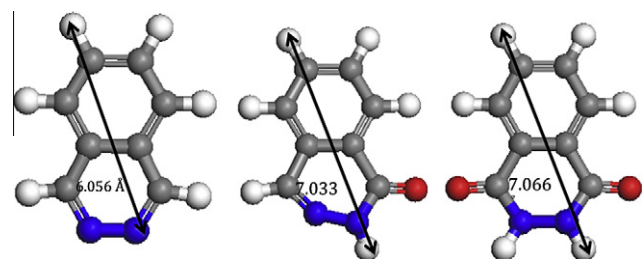


Fig. 3. Optimized structures of the PT derivatives using Forcite.

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