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Quantitative structure–activity relationship model for amino acids as corrosion inhibitors based on the support vector machine and molecular design

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ABSTRACT

The inhibition performance of nineteen amino acids was studied by theoretical methods. The affection of acidic solution and protonation of inhibitor were considered in molecular dynamics simulation and the results indicated that the protonated amino-group was not adsorbed on Fe (1 1 0) surface. Additionally, a nonlinear quantitative structure–activity relationship (QSAR) model was built by the support vector machine. The correlation coefficient was 0.97 and the root mean square error, the differences between predicted and experimental inhibition efficiencies (%), was 1.48. Furthermore, five new amino acids were theoretically designed and their inhibition efficiencies were predicted by the built QSAR model.

1. Introduction

The corrosion of metals and alloys usually results in huge financial losses and many potential safety issues, and anti-corrosion technology has aroused the great interests of the researchers. One of the most convenient and economic methods was the use of inhibitors, which can slow down corrosion rate or protect metal from corrupting, though used in a very small amount [1–3]. Most of the efficient corrosion inhibitors were compounds containing heteroatoms with lone pair of electrons (e.g., N, O, S and P), or π-systems, or conjugated bonds, or aromatic systems [4]. There were so many different kinds of organic corrosion inhibitors, such as imidazoline, amino acids, pyridine, alkynol, amides and thiourea [5–11]. Although many heterocyclic compounds have been successfully used as corrosion inhibitors in several metallic systems, most of them were toxicity and non-biodegradable [12]. With the trends of environmental protection, researches were focused on the environmentally friendly corrosion inhibitors. Amino acids, which were non-toxic, relatively cheap, easily available and completely soluble in aqueous media, were considered to be the most promising green inhibitors [13].

Many methods, including experimental and theoretical approaches, were usually employed to study the performance of amino acids as corrosion inhibitors. Though experimental measures, such as weight-loss method, potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) [14–17], are the most traditional means to test the inhibition performance, these researches were often high-cost, time-consuming, since large scale trial experiments were carried out [18,19]. Theoretical techniques, which can overcome these shortages, have attracted researchers' great attention in recent years. To investigate the inhibition performance of amino acids, quantum chemical calculations have been employed to obtain the structural properties, which were related to the corrosion inhibition efficiency [20–25]. In addition, to study the adsorption behavior of amino acids on metal surface, molecular dynamics simulation was used to research the adsorption configuration and adsorption strength of amino acids on metal surface [22–27]. For example, Hu [26] investigated the adsorption behavior of glutamic acid and aspartic acids on Cu (0 0 1) surface in vacuum and found that both of the two inhibitors could be adsorbed on the Cu surface firmly due to the interaction between polar groups and copper surface. Fu [23] researched the inhibition behavior of four amino acids compounds on Fe (1 1 0) surface in

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aqueous and found that these four amino acids compounds can be absorbed on the iron surface through the heteroatoms and heterocyclic ring. Though some useful information has been obtained from these studies, there still exists some disparity between the theoretical adsorption model and realistic inhibition systems. Various factors, such as the adsorption of the solvent molecules, the protonation of the inhibitor molecules, and the affection of the acidic solution, which would influence the adsorption behaviors of the amino acid compounds greatly, should also be considered in the molecular dynamics simulation.

Recently, quantitative structure–activity relationship (QSAR) has aroused many researchers' interest in the studies of corrosion inhibitors. The advantage of this approach lies in the fact that it requires only the knowledge of the chemical structure and is not dependent on any experimental properties. Additionally, it has been proved to be very helpful for predicting the inhibition efficiencies of novel corrosion inhibitors [28,29]. Some QSAR studies on amino acids have been carried out. Using three [30] or four [31] amino acids as samples, Eddy built nonlinear QASR models to correlate the inhibition efficiencies of theses amino acids with some chemical parameters (energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), energy gap (ΔE), the dipole moment (μ) etc.) by the statistical product and service solutions (SPSS) program. It was concluded that QSAR can adequately be used to model the inhibitive behavior of these amino acid. Using linear regression analysis, Gece [20] proposed equations to determine the relationship between the inhibition efficiencies of twelve amino acids and three quantum chemical descriptors (E_{HOMO}, E_{LUMO}, ΔE). In addition, the linear correlation [32] between the inhibition efficiencies of fifteen amino acids and ΔE was also found by the same research group. In order to build a reliable QSAR model, some influencing factors, such as sufficient number of samples, adequate descriptors which can provide enough useful imformation on the characteristics of the inhibition performance, suitable statistical method, should be considered. Though some useful models or equations have been got from these studies, these factors were not considered fully in the QSAR studies of amino acids. For the samples, the number of the studied samples, even less than five, was not enough to build an accurate QASR model. While for the descriptors, though some descriptors based on the structural properties of the samples, such as E_{HOMO} and E_{LUMO}, have been considered, some descriptors about the interaction between the amino acids and metal surface should not be neglected. Therefore, binding energy indicating the interaction strength between amino acids and metal surface should be taken as one of the descriptors to build QSAR model [33]. In addition, for the statistical method, due to the complexity of the corrosion protection, the performance of amino acids was affected by many factors and it was difficult to be explained clearly by linear or simple nonlinear QSAR model [34,35]. Thus, those factors mentioned above should be considered comprehensively to build a more accurate and reliable QSAR model.

In the present paper, nineteen amino acids were studied by quantum chemical calculation, molecular dynamics simulation and QSAR analysis. The affection of the acidic solution and protonation of the inhibitor molecules were taken into consideration in the molecular dynamics simulation of amino acids adsorbed on iron surface. In addition, the calculated binding energy was taken as one of the descriptors to build QSAR. As for the method of building QSAR model, the support vector machine (SVM) was used. SVM was a relatively novel machine learning technique based on a statistical learning theory (SLT) principle [36]. It has been used to solve regression problems in many fields, such as drug design [37], bioscience [38] and medicine [39], and also suitable for the QSAR studies of corrosion inhibitors. Furthermore, five new amino acids were theoretically designed and their inhibition efficiencies were predicted by the built QSAR model.

2. Experimental

2.1. Materials

Nineteen amino acids molecules were studied in present study and their molecular structures, the sequencing of non-hydrogen atoms and inhibition efficiencies were shown in Table 1. All these amino acids molecules were the alpha amino acids, which contain carboxyl and amino functionalities bonded to the same carbon atom. The inhibition efficiencies of all these molecules were obtained by potentiodynamic polarization curves in 1 mol/L hydrochloric acid with 0.01 mol/L concentration of the amino acids against iron corrosion [40]. As shown in Table 1, the inhibition efficiencies of all the nineteen amino acids molecules were from 16% to 87%. Among them, number 10 molecule, diiodotyrosine, to which benzyl and halogen were introduced, has the highest inhibition efficiency (87%) in this study.

2.2. Quantum chemical calculation

Quantum chemical calculations in gas and aqueous phases were performed with Gaussian 09 program [41]. Density Functional Theory (DFT) method, B3LYP combined with 6-311+G (d,p) basis set were used in this study. The B3LYP [42,43] was an appropriate calculation method to estimate the structural characteristics of organic corrosion inhibitors [44]. As for the description of aqueous environment, the self-consistent reaction field theory based on Tomasi's polarized continuum model (PCM) was utilized [45].

The global reactivity of the molecules was analyzed by the following quantum chemical parameters: energy of the highest occupied molecular orbital (E_{HOMO}), energy of the lowest unoccupied molecular orbital (E_{LUMO}), dipole moment (μ), the change in the number of electrons transferred (ΔN), the adiabatic ionization potential (I), the adiabatic electron affinity (A), and so on. The adiabatic ionization potential (I) [46] were estimated by the following manner:

$$I = E_{(\text{optimized cation})} - E_{(\text{optimized neutral})} \tag{1}$$

The adiabatic electron affinity (A) [46] was estimated by the following manner:

$$A = E_{(\text{optimized neutral})} - E_{(\text{optimized anion})} \tag{2}$$

The values of adiabatic electronegativity and adiabatic global hardness, χ and η, were calculated from Eqs. (3) and (4), respectively.

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

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

The change in the number of electrons transferred [47] ΔN was estimated through the following equation:

$$\Delta N = \frac{\chi_{Fe} - \chi}{2(\eta_{Fe} - \eta)} \tag{5}$$

The values of χ_{Fe} and η_{Fe} were taken as 7 eV and 0 eV, respectively [48]. The electrophilicity index ω was estimated through the following equations:

$$\omega = \frac{\chi^2}{2\eta} \tag{6}$$