VIETNAM NATIONAL UNIVERSITY – HCMC **SOCIALIST REPUBLIC OF VIETNAM**
UNIVERSITY OF TECHNOLOGY   **Independence – Liberty – Happiness**

DISSERTATION INFORMATION

Title: Influences of molecular structure on copper corrosion inhibition by organic compounds

Major: Kỹ thuật hóa học   **Major code:** 9520301

PhD candidate: Pham Thanh Hai

Advisors: Assoc. Prof. Do Ngoc Son, Assoc. Prof. Tran Tan Viet

University: Ho Chi Minh City University of Technology, VNU – HCMC

Major contributions of this dissertation:
Understanding the relationship between molecular structure and the corrosion inhibition efficiency of organic compounds is a fundamental issue in developing new-generation inhibitors. These inhibitors need to be more effective, less toxic, and environmentally friendly to meet the demands of environmental protection and sustainable development. Despite extensive research, a clear and consistent correlation between the structure of organic compounds and their corrosion inhibition efficiencies is still lacking. This thesis integrates experimental data analysis, including both published studies and new experiments, with advanced methodologies such as machine learning, density functional theory (DFT) calculations, and reaction kinetic simulations. The aim is to model how molecular structure influences corrosion inhibition efficiency and identify key structural features that determine the effectiveness of organic compounds as corrosion inhibitors for copper in acidic solutions.

1) Based on available experimental data, a machine learning approach has been employed to develop a quantitative structure-property relationship (QSPR) model that relates the organic compound molecular structure to their corrosion inhibition efficiency for copper. A novel machine learning workflow, combining the gradient-boosted decision trees (GB) algorithm with the permutation feature importance (PFI) feature selection technique, was proposed. The results showed that the QSPR model for carbon steel developed using the proposed machine learning workflow achieved high accuracy, with a mean absolute error (MAE) of 4.80%, a root mean square error (RMSE) of 6.42%, and a coefficient of determination (R^2) of 0.72. These metrics demonstrate superior performance compared to previously published models. At the same time, the constructed model is applied to predict the corrosion inhibition efficiency of the drug compound. The results showed that the model's predictions have high accuracy compared with published and self-performed experimental results. Based on these results for carbon steel, the proposed machine learning workflow was further applied to construct and analyze the correlation between the structure of organic compounds and their corrosion inhibition efficiency for copper in a 0.5 M H_2SO_4 solution. The limitation of the data set and the difference in inhibition mechanism compared to carbon steel resulted in the QSPR model on

copper still not being highly accurate, with MAE of 5.79%, RMSE of 8.22%, and R^2 of 0.44, suggesting that the relationship between structure and copper corrosion inhibition efficiency of organic compounds needs to be further clarified.

2) Combining DFT calculations and microkinetic simulations, a novel model was developed to simulate the potentiodynamic polarization curve of copper in an acidic solution in the presence of a corrosion inhibitor. This model accounts for the influence of inhibitors on the kinetics of the cathodic and anodic corrosion reactions on the copper surface, providing a quantitative relationship between the adsorption free energy of inhibitors on the copper surface and the concentration of the inhibitor in the solution with corrosion rate and corrosion inhibition efficiency. The results showed that the simulated polarization curve of copper in acid solution aligns with the published experimental data, with the simulated corrosion potential and current density values of -74 mV and 26.02 µA/cm², respectively, falling within the experimental value range. The effects of adsorption free energy and inhibitor concentration on corrosion inhibition efficiency are also consistent with the trends obtained in published experiments. Based on the simulation results of some published experimental data, the relationship between adsorption free energy and corrosion inhibition efficiency has been analyzed and clarified. Additionally, the model's limitations have been examined to evaluate its potential for predicting the copper corrosion inhibition efficiency of organic compounds.

3) Combining experiments and DFT calculations, the influence of some functional groups on the corrosion inhibition efficiency of benzotriazole (BTAH) and 2-mercaptobenzothiazole (MBTH) for copper in a 0.5 M H_2SO_4 solution was investigated.

i) Results of the mass loss test, potential polarization curves, and surface morphology (SEM, AFM, ATR-FTIR, and contact angle) revealed a clear difference between the corrosion inhibition efficiencies of BTAH and two derivatives containing $-NH_2$ and -Cl at the C5 position for copper in a 0.5 M H_2SO_4 solution. The derivative containing $-NH_2$ has a significantly poorer inhibition efficiency, while the derivative containing -Cl shows a better efficiency than BTAH. Specifically, the corrosion inhibition efficiency determined by the weight loss method for BTAH-5-NH_2, BTAH, and BTAH-5-Cl at a concentration of 5×10^{-4} M was 61.0%, 76.6%, and 86.6%, respectively. DFT calculation results showed that the electronic properties of the inhibitor molecule and the interaction energy of the inhibitor on the copper surface cannot explain the observed differences. The influence of the inhibitor layer adsorbed on the copper surface on the oxygen reduction reaction, especially the mass transfer steps such as O_2 adsorption, H_2O adsorption, diffusion, and desorption, are the decisive factors for the difference between derivatives. The derivative containing $-NH_2$ interacts very strongly with O_2 and H_2O due to the formation of hydrogen bonds, thereby limiting its ability to inhibit the oxygen reduction reaction at the cathode, while BTAH and the derivative containing -Cl interact weakly with O_2 and H_2O, especially the -Cl derivative tending to repel O_2, resulting in higher inhibition abilities.

2

ii) The experimental and DFT calculation results show similar trends for MBTH and two derivatives containing -NH$_2$ and -Cl at the C6 position. However, the corrosion inhibition efficiency of the MBTH group was better than that of the BTAH group; specifically, the corrosion inhibition efficiency determined by the weight loss method for MBTH-6-NH$_2$, MBTH, and MBTH-6-Cl at a concentration of 5×10^{-4} M was 64.4%, 92.3%, and 95.7%, respectively. The difference between these two groups of compounds indicated that both the structural part interacting with the environment and the structural part interacting with the copper surface simultaneously influence the inhibition efficiency. These influences were evaluated in detail through a comparative analysis of experimental and DFT calculation results for both groups, BTAH and MBTH. The obtained findings elucidate the copper corrosion inhibition mechanism of organic compounds and provide an important direction for designing new, effective copper corrosion inhibitors.

Scientific supervisors   **PhD. candidate**

Assoc. Prof. Do Ngoc Son   **Assoc. Prof. Tran Tan Viet**   **Pham Thanh Hai**