The electronic Supporting Information

Corrosion Inhibition Ability of L-tryptophan and 5-hydroxy-L-tryptophan for Mild Steel: A Combination of Experimental and Theoretical Methods

Dinh Quy Huong[1*], Nguyen Le My Linh[1], Le Quoc Thang[1], Duong Tuan Quang[1]

[1]Department of Chemistry, University of Education, Hue University, Hue, Vietnam

*Corresponding: dqhuong@hueuni.edu.vn

List of supporting information

Table S1.

Inhibitors	Concentration (M)	Temperatures			
		293 K	303 K	313 K	323 K
TP	10^{-4}	81.08 (0.95)	77.26 (1.12)	74.56 (0.93)	70.65 (1.13)
	5×10^{-4}	85.81 (1.02)	80.37 (1.01)	76.60 (1.14)	74.64 (0.95)
	10^{-3}	87.16 (0.98)	84.11 (0.86)	81.30 (1.04)	77.72 (0.89)
	5×10^{-3}	89.19 (0.79)	87.54 (0.95)	83.04 (0.76)	80.98 (0.92)
	10^{-2}	91.22 (0.85)	89.56 (0.72)	87.03 (0.85)	84.96 (1.16)
5-OH-TP	10^{-4}	85.81 (0.69)	81.62 (1.06)	75.31 (0.91)	73.55 (0.77)
	5×10^{-4}	87.84 (0.74)	84.74 (0.78)	79.56 (1.02)	77.36 (0.84)
	10^{-3}	89.86 (0.75)	86.60 (0.82)	82.29 (1.08)	80.07 (0.97)
	5×10^{-3}	92.57 (0.82)	88.47 (0.75)	85.79 (1.13)	83.88 (1.18)
	10^{-2}	94.05 (1.13)	91.28 (0.94)	89.03 (1.17)	87.50 (1.21)

Values in parenthesis are the mean absolute deviation of corrosion inhibition efficiencies.

Table S2. Details of Temkin and Langmuir adsorption isotherm models

Adsorption isotherm models play a crucial role in understanding the interaction between the mild steel surface and the solution, particularly in characterizing the adsorption behavior of inhibitors on the metal surface. Various adsorption isotherms, such as Temkin, Frumkin, Freundlich, Langmuir, and Flory-Huggins, have been widely employed. Among them, two adsorption isotherm models, namely Temkin and Langmuir, were investigated in this study to examine the adsorption of TP and 5-OH-TP on mild steel surfaces.

In the Temkin model, the adsorbed inhibitor molecules do not interact with each other and the free energy of their position on the surface depends on the surface coverage (θ). θ is determined using Equation (1'):

$$\theta = \frac{\%IE_{PP}}{100} \tag{1'}$$

In which $\%IE_{PP}$ is the corrosion inhibition efficiency obtained from the PP method.

The Temkin adsorption isotherm is described by Equation (2'), where a represents the adsorbate interaction parameter:

$$\ln K \times C = a \times \theta \tag{2'}$$

The study also explores the Langmuir adsorption isotherm, which assumes that each adsorbate occupies only one position on the mild steel surface and the surface free energy remains constant at all substrate positions. The Langmuir adsorption isotherm model is mathematically represented by Equation (3'):

$$\frac{C}{\theta} = \frac{1}{K} + C \tag{3'}$$

In which, K is adsorption constant, C is inhibitor concentration.

Table S3 Detailed calculations of thermodynamic quantities

The relationship between adsorption constant (K) and adsorption-free energy (ΔG^o) can be expressed using Equation (4'), where 55.5 represents the molar concentration of water in the solution (M), and T denotes the temperature under investigation (K).

$$\Delta G^o = -R \times T \times \ln(55.5 \times K) \quad (4')$$

From the equation indicating the relationship between lnK and 1/T, adsorption enthalpy values (ΔH^o) are determined. Additionally, the adsorption entropy (ΔS^o) values are calculated from the obtained ΔH^o and corresponding ΔG^o using Equation (5'):

$$\Delta G^o = \Delta H^o - T \times \Delta S^o \quad (5')$$

In equation (5'), R denotes the gas constant with a value of 8.314 $J.mol^{-1}K^{-1}$.

Table S4 Optimized structure of TP and 5-OH-TP in gas phase using B3LYP/6-311++G(d,p).

Stable Neutral form (TP)			**$C_{11}H_{12}N_2O_2$**
0 1			
O	1.64498300	-0.86499500	1.83848700
O	2.26799000	-1.91976700	-0.04587800
N	-1.81526900	2.03261400	0.49388200
N	3.80004500	0.51909200	-0.59691400
C	0.02448200	1.11745100	-0.44044200
C	1.41935900	0.96482000	-0.97488200
C	-1.02151100	0.12230500	-0.39944700
C	2.48697500	0.49362800	0.04652600
C	-2.16030900	0.73197700	0.19223000
C	-0.50766200	2.25690300	0.10684300
C	-1.11274200	-1.21735100	-0.81561600
C	-3.36412200	0.04768100	0.37752500
C	-2.30709400	-1.89929500	-0.63466700
C	-3.42191600	-1.27386800	-0.04257500
C	2.13053700	-0.89457200	0.57827600
H	1.78393500	1.91912800	-1.36265300
H	1.42454800	0.26280200	-1.81579400
H	2.49860500	1.18991200	0.88715000
H	-0.05444300	3.22670100	0.24698700
H	-2.42350900	2.71831900	0.90807000

H	-0.26109300	-1.71609700	-1.26400800
H	-4.22395700	0.52923300	0.83061400
H	-4.34135400	-1.83375200	0.08552300
H	3.85581400	-0.21463100	-1.29842000
H	4.53803700	0.34126400	0.07717100
H	1.39746300	-1.77241600	2.07644600
H	-2.38724600	-2.93238000	-0.95336400

Stable Neutral form (5-OH-TP)	**$C_{11}H_{12}N_2O_3$**

0 1			
O	-2.69562600	-2.64427100	-0.59036200
O	1.71735400	-0.76838800	1.90662800
O	2.16737500	-2.09183400	0.14654700
N	-1.21651200	2.56830500	0.34537800
N	4.01827200	0.01498900	-0.67466900
C	0.39901000	1.24408800	-0.51255000
C	1.72609700	0.79666000	-1.05342100
C	-0.79889500	0.45789500	-0.33941300
C	2.73934500	0.25882300	-0.00876600
C	-1.79140900	1.31945200	0.19911100
C	0.09098700	2.51357800	-0.08930900
C	-1.12214900	-0.88397000	-0.60079300
C	-3.08165600	0.87303800	0.47819900
C	-2.40717800	-1.32408900	-0.32369500

C	-3.38019800	-0.45698200	0.21241300
C	2.18668100	-0.99920900	0.66074800
H	2.23172300	1.62831100	-1.55022100
H	1.58069400	0.02070600	-1.81299800
H	2.88668800	1.02035500	0.75943000
H	0.71147200	3.39699300	-0.07086600
H	-1.68208700	3.39259400	0.68432500
H	-0.39816000	-1.58129700	-1.00436900
H	-3.83668400	1.53457300	0.88819800
H	-4.37712300	-0.83464800	0.41910600
H	3.93420300	-0.78112000	-1.30147600
H	4.73950600	-0.21722400	0.00110700
H	1.33736800	-1.59980100	2.23176200
H	-3.61655600	-2.82225900	-0.37660500

Table S5. Optimized structures of protonated TP and 5-OH-TP in gas phase using B3LYP/6-311G(d,p)

pTP-N3			**$[C_{11}H_{13}N_2O_2]^+$**
1 1			
O	1.74131500	-0.41159400	1.96955600
O	2.33620500	-1.91262100	0.40716500
N	-1.68179500	2.04747300	0.54533500
N	3.80516200	0.29044700	-0.83957700

C	0.04695200	0.94057800	-0.59283600
C	1.39697900	0.65292900	-1.17286400
C	-1.03274000	0.03262300	-0.46788600
C	2.53395400	0.44411400	-0.13569700
C	-2.13306300	0.68664700	0.14793600
C	-0.35690800	2.22154400	-0.15752400
C	-1.24568600	-1.31985400	-0.84356300
C	-3.35144600	0.11162000	0.41982300
C	-2.47344700	-1.91195600	-0.59537800
C	-3.53474200	-1.22334200	0.02983500
C	2.20238300	-0.76115500	0.74413400
H	1.72554900	1.47831100	-1.81231800
H	1.35397900	-0.23979200	-1.80567800
H	2.59592000	1.32775400	0.50251700
H	0.26473800	3.00753300	0.24831700
H	-2.35058400	2.76405400	0.26730000
H	-0.45199400	-1.89048100	-1.31127300
H	-4.14761200	0.66027200	0.91404500
H	-4.48216200	-1.71597000	0.20537100
H	3.81200800	-0.58671900	-1.35329700
H	4.58188400	0.25693400	-0.18671900
H	1.51910100	-1.23389000	2.43412600
H	-2.62425500	-2.94538200	-0.88945700

H	-1.59370800	2.10318000	1.57711300

p5-OH-TP-N4			**$[C_{11}H_{12}N_2O_3]^+$**
1 1			
O	-2.96960100	-2.60662300	-0.49636700
O	1.92350000	-0.24223000	1.98644700
O	2.30719400	-2.02945300	0.68007100
N	-1.05372800	2.55090300	0.35331200
N	3.98247700	-0.27921500	-0.93521900
C	0.39783500	1.01858100	-0.67177000
C	1.64709100	0.42194100	-1.24091400
C	-0.81783000	0.34271500	-0.40859400
C	2.79179100	0.17145700	-0.21947400
C	-1.75219200	1.25529300	0.14964900
C	0.25255000	2.39711800	-0.39393600
C	-1.27329100	-0.98345800	-0.61578200
C	-3.03822400	0.94179000	0.50620700
C	-2.57653200	-1.31044000	-0.27124500
C	-3.47467100	-0.37454700	0.28686800
C	2.32423500	-0.83259500	0.83368600
H	2.07358000	1.07875400	-2.00571400
H	1.42180000	-0.53050800	-1.73196900
H	3.02472400	1.11198700	0.28402100
H	1.02462900	3.08689400	-0.08012200

H	-1.59623000	3.33513300	-0.00579900
H	-0.63144600	-1.75033600	-1.03025700
H	-3.70965400	1.67287100	0.94558600
H	-4.48727200	-0.66627600	0.54033800
H	3.82330400	-1.20683000	-1.31952700
H	4.77719600	-0.35389300	-0.30787600
H	1.60120300	-0.94865700	2.56816400
H	-3.88969800	-2.71179800	-0.23514700
H	-0.90670400	2.72016300	1.36226800

pTP-N4	**$[C_{11}H_{13}N_2O_2]^+$**

1 1			
O	3.43018100	-1.14940600	0.63747800
O	2.07364400	-2.15422800	-0.86399200
N	-2.10011300	2.07707000	-0.16174500
N	3.97931700	1.87616200	1.69110200
C	-0.39149200	0.84671900	-0.96536700
C	0.91031500	0.45483100	-1.62601000
C	-1.32690200	-0.03558500	-0.30915500
C	1.97480200	0.20581300	-0.60893100
C	-2.38993400	0.77043800	0.17691400
C	-0.90114600	2.11417300	-0.84818200
C	-1.37493100	-1.42441600	-0.10160700
C	-3.48507800	0.23074100	0.85574900

C	-2.46132100	-1.96244000	0.57291700
C	-3.50531300	-1.14407900	1.04699000
C	2.45410400	-1.12447200	-0.33044200
H	1.22972700	1.26877800	-2.28736400
H	0.76980600	-0.43720300	-2.24091800
H	2.37463500	1.02912000	-0.02522200
H	-0.50131500	3.05100400	-1.20530700
H	-2.68430100	2.87374900	0.02763300
H	-0.57471000	-2.06205200	-0.46012100
H	-4.29124400	0.85875600	1.21928600
H	-4.34061100	-1.59598500	1.56987300
H	4.10538000	0.86804100	1.65213000
H	3.65488300	2.11313300	2.62325000
H	3.67689800	-2.07858400	0.75081500
H	-2.51112600	-3.03245400	0.73976900
H	4.88833300	2.30981800	1.56553500

p5-OH-TP-N5	**$[C_{11}H_{12}N_2O_3]^+$**

1 1			
O	-2.68663000	-2.79841500	0.41293800
O	3.43375600	-1.45714500	0.53504800
O	2.04975000	-2.10855400	-1.12780200
N	-1.60410800	2.57302400	-0.05987300
N	4.29284500	1.32406100	1.96748800

C	-0.04756700	1.19103600	-0.92628100
C	1.21201900	0.68606800	-1.59040000
C	-1.10715700	0.39031100	-0.36225500
C	2.19627200	0.19761900	-0.57944300
C	-2.06994900	1.28969500	0.16648100
C	-0.39357600	2.50263800	-0.71713800
C	-1.32791700	-0.99317500	-0.27330200
C	-3.23870100	0.83845700	0.77648600
C	-2.49188900	-1.43756400	0.33531000
C	-3.43942400	-0.53359900	0.85628900
C	2.51401100	-1.20268100	-0.45507800
H	1.66223200	1.50681900	-2.16179800
H	0.97670700	-0.11627600	-2.29374100
H	2.66012500	0.89481500	0.11123200
H	0.13634100	3.40231400	-0.99105600
H	-2.08692100	3.42263600	0.17738900
H	-0.61693800	-1.71173300	-0.66331900
H	-3.97455800	1.52626100	1.17798100
H	-4.34027100	-0.91653100	1.32658000
H	5.25437100	1.64560500	1.92072300
H	4.28947100	0.32154000	1.79787800
H	3.56878400	-2.41574200	0.53999300
H	-3.52738600	-2.97952300	0.84396200

H	3.96514000	1.48029200	2.91538000

p5-OH-TP-O1			**$[C_{11}H_{12}N_2O_3]^+$**
1 1			
O	-2.74194700	-2.51944300	-0.67479000
O	1.70976000	-0.82172100	1.88367000
O	2.12679000	-2.10696000	0.08749600
N	-1.13749300	2.62945400	0.39707000
N	4.03641100	-0.02709700	-0.66909000
C	0.44827500	1.28740500	-0.48826400
C	1.76601700	0.82095200	-1.03594100
C	-0.76953400	0.52728800	-0.33938200
C	2.76090600	0.23110600	-0.00194500
C	-1.74262600	1.39950200	0.21718900
C	0.17014900	2.55304900	-0.03394200
C	-1.12514300	-0.79894400	-0.63627800
C	-3.04483600	0.97869700	0.48016200
C	-2.42177800	-1.21338200	-0.37461300
C	-3.37516500	-0.33641800	0.18018700
C	2.17426600	-1.02999400	0.63203100
H	2.29425500	1.65222600	-1.50928300
H	1.60439200	0.06869700	-1.81579700
H	2.92371600	0.96830800	0.78657800
H	0.81236100	3.41991200	0.00928100

H	-1.58357200	3.45602800	0.75610100
H	-0.41713500	-1.50350700	-1.05533600
H	-3.78480300	1.64833600	0.90419900
H	-4.38171100	-0.69451500	0.37462100
H	3.93547900	-0.80417500	-1.31693800
H	4.74870000	-0.29461200	0.00311000
H	1.30818800	-1.65173700	2.18563200
H	-3.67176400	-2.67547900	-0.48307400
H	-1.88055300	-4.73654800	1.09880900