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'Pungent' Copper Surface Resists Acid Corrosion in Strong HCl Solutions

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S Supporting Information

ABSTRACT: Extensive efforts have been devoted to the qualification of plant extracts as green corrosion inhibitors for industrial metals, but studies that demonstrate the active component(s) of these extracts remain scarce. We report here that piperine, the major pungent component of peppers, has the best corrosion inhibitive efficiency for copper in HCl among four analogous amide alkaloids isolated from a traditional Chinese medicine. This compound inhibited HCl corrosion more efficiently than cysteine, and did not exhibit markedly decreased efficiency under several harsh experimental conditions. Electrochemical and microscopic analyses suggested that piperine could form a protective layer on the metal surface via both physisorption and chemisorption, reducing the corrosion rate. The adsorption energies of all the test compounds were calculated using a hybrid density functional theory.

INTRODUCTION

Copper, due to its good thermal and electrical properties, constitutes a multitude of metallic materials and equipments in industry. Despite its low corrosion rate in clean air and aqueous media, copper can be susceptible to acid corrosion during common industrial processes such as acid descaling, cleaning, and pickling. As a result, addition of corrosion inhibitors during these processes is necessary for mitigating the release of copper species deleterious to nature and for reducing overuse of acids. However, most of the commercial inorganic and organic inhibitors are toxic, raising a series of additional environmental issues.

Recently, much attention of both the academic and industrial communities has been paid to the qualification of the low-toxic natural products as green corrosion inhibitors.^{1,2} A number of natural primary (such as amino acids and sugars)^{3–6} and secondary metabolites (such as plant extracts)^{7–18} have been identified as corrosion inhibitors for various metals. Regarding the latter, however, mixtures consisting of structurally different compounds were directly employed for corrosion inhibition, which may cause ambiguity in elucidating the corrosion mechanism. As a consequence, determination of the active component that inhibits metal corrosion has become intriguing as the inhibitive mechanism could be better defined and the consumption of the inhibitor more accurately quantified.

With a continuing interest in the identification of green corrosion inhibitors,^{19–23} we reveal here that piperine (the pungent component of peppers) has the best inhibitive efficiency for copper corrosion in HCl among several analogous amide alkaloids isolated from *Piper longum* L., a traditional Chinese medicine. This compound also inhibited the corrosion more effectively than cysteine (a well-studied green corrosion inhibitor) at a low concentration and exhibited insignificant

decrease in efficiency under several harsh experimental conditions. Electrochemical and microscopic analyses suggested that piperine could form a protective layer on the metal surface via both physisorption and chemisorption to reduce the corrosion rate. The adsorption energies of all the test compounds were calculated using a hybrid density functional theory.

RESULTS AND DISCUSSION

Amide alkaloids (i.e. piperine (CL1), piperanine (CL2), pipernonatin (CL3), and (2E,4E,10E)-N-11-(3,4-methylenedioxypheylmdecatrienoyl)-piperidine (CL4)) used (Figure 1) for corrosion tests were isolated from a traditional Chinese medicine, *Piper longum* L. (Anguo, Hebei), according to our previously described method.²⁴

The protective efficiency of these natural products for copper against HCl corrosion was first assessed by scanning electron microscope (SEM). After immersion in 1 M HCl for 3 h, the surface of copper was severely corroded in the absence of an inhibitor (Figure 2b vs Figure 2a). In the presence of the compounds, however, the corrosion was tangibly inhibited due to formation of molecular coatings on the metal surface (Figure 2c–f). Notably, we observed that, among the four analogs, CL1 seems to have the best inhibitive efficiency as the CL1-protected copper surface (Figure 2c) exhibited unappreciable corrosion trace as compared to other counterparts (Figure 2d–f).

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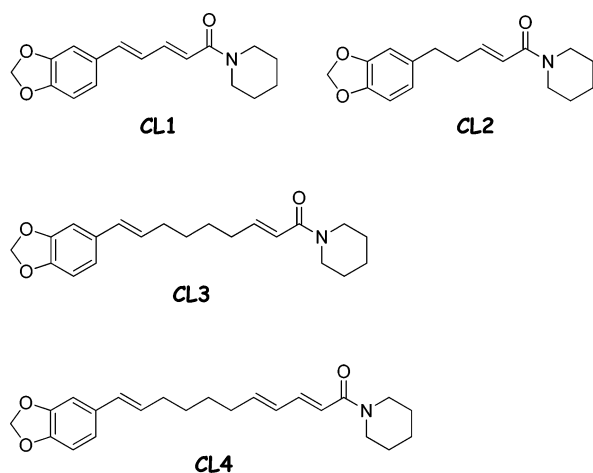


Figure 1. Structure of amide alkaloids CL1–CL4.

Next, electrochemical impedance spectroscopy (EIS) was used for quantification of the corrosion inhibitive efficiencies of the CL compounds (10^{-3} M each) for copper in 1 M HCl. The Nyquist and Bode plots shown in Figure 3 were recorded at the open-circuit potential. The capacitive loop of all the Nyquist plots in the absence (blank) and presence of an inhibitor exhibited as a depressed semicircle tailed with a straight line (the Warburg impedance) (Figure 3a). The depressed circle

might be caused by the inhomogeneity of the surface-adsorbed substance and the tailed line is indicative of copper dissolution controlled by diffusion and oxygen reduction at the electrode.^{20–22}

We observed that, in the presence of the alkaloids, the capacitive loops increased compared to that without an inhibitor, suggesting the formation of protective molecular films on the copper surface. This is in accordance with the SEM analysis. Circuit models with one (Figure 3b, upper, without inhibitor) or two time constants (Figure 3b, lower, with inhibitor) were used to fit the Nyquist plots.²⁵ The fitted data (line) are in good agreement with the experimental (dots), and the corresponding EIS parameters fitted by the circuits are shown in Table 1.

CL3 ($\eta = 44\%$) and CL4 ($\eta = 19\%$) with long carbon chains connecting the piperidine and methylenedioxybenzene moieties showed much lower inhibitive efficiencies for copper in HCl than did CL1 ($\eta = 78\%$) and CL2 ($\eta = 67\%$) with relatively shorter carbon chains. Moreover, despite the same chain length, CL1 with an additional double bond exhibited better protective effect for copper than CL2. These data imply that both chain length and structural rigidity may impact the copper-surface adsorptive ability of this series of compounds.

The Bode plots were then analyzed to further evaluate the corrosion inhibitive efficiency of the compounds. As shown in Figure 3c, the impedance modulus values ($|Z|$) for all compounds almost equaled to zero at the high frequency

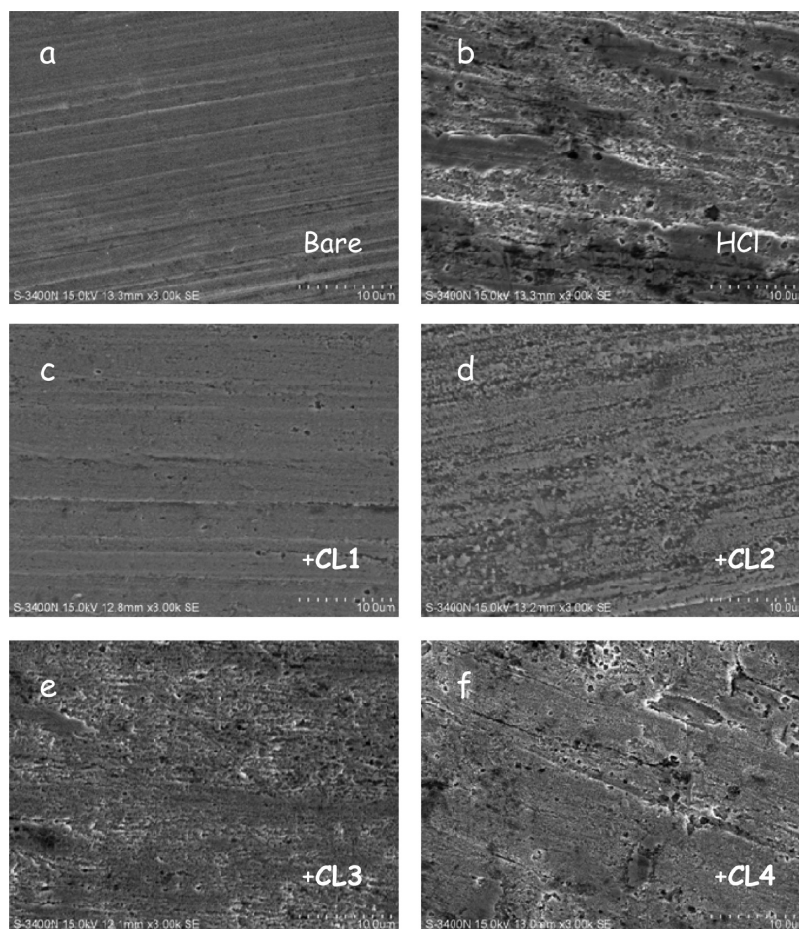


Figure 2. SEM images of abraded copper surface (a) and corroded copper surface after 3 h of immersion in 1 M HCl (b) and of copper surfaces after 3 h of immersion in 1 M HCl in the presence of 3.2×10^{-3} M of (c) CL1, (d) CL2, (e) CL3, and (f) CL4.

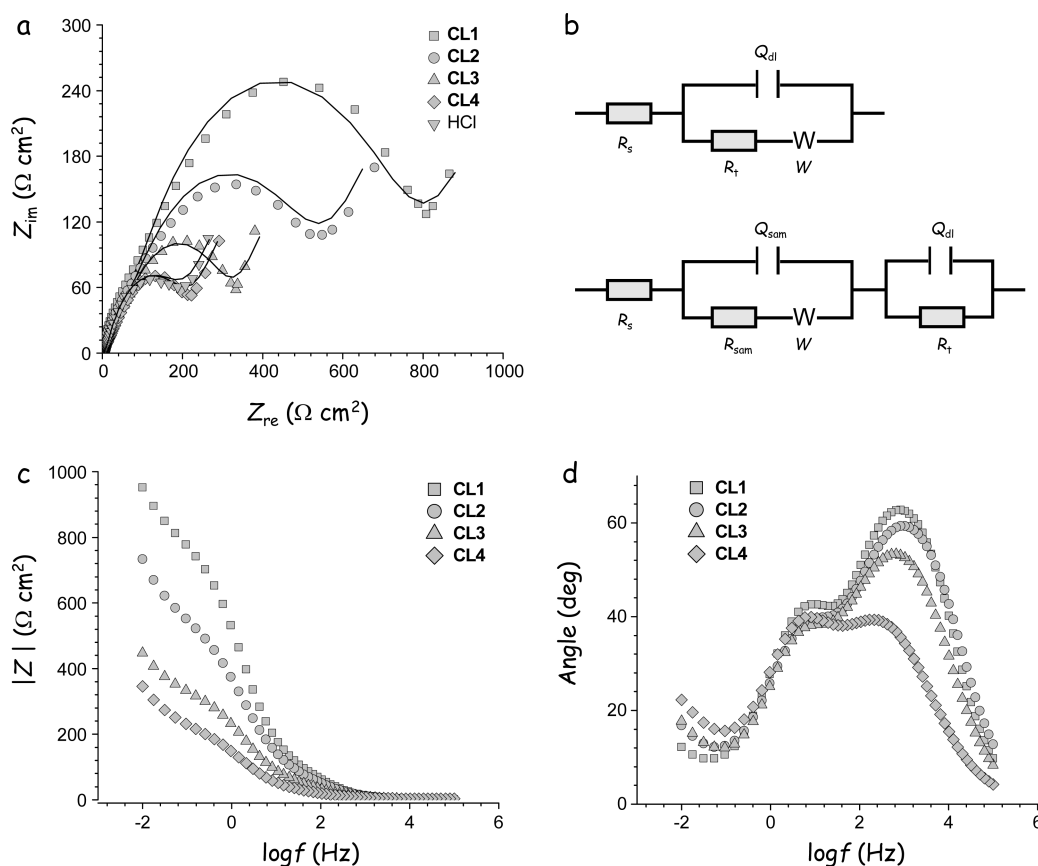


Figure 3. Experimental (dots) and fitted (line) Nyquist (a) and Bode (c and d) plots for copper in 1 M HCl in the absence or presence of the inhibitors (10^{-3} M). (b) Equivalent circuit models used to fit the obtained EIS data in the absence (upper) and presence (lower) of inhibitors, where R_s is the solution resistance, R_t the charge transfer resistance corresponding to the corrosion reaction at the copper/solution interface, R_{sam} the polarization resistance of transfer resistance of electrons through the layer, W the Warburg impedance, Q_{dl} the constant phase elements as a surrogate for the double-layer capacitance, and Q_{sam} the capacitance of the molecular film formed on copper.

Table 1. EIS Parameters Fitted for Copper Electrodes in 1 M HCl in the Absence (blank) and Presence of CLs (10^{-3} M) at 25 °C

compd.	R_s ($\Omega \text{ cm}^{-2}$)	Q_{sam} ($\mu\text{F cm}^{-2}$)	n_1	R_{sam} ($\Omega \text{ cm}^{-2}$)	W ($\text{m}\Omega^{-1} \text{ cm}^{-2} \text{ s}^{1/2}$)	Q_{dl} ($\mu\text{F cm}^{-2}$)	n_2	R_t ($\Omega \text{ cm}^{-2}$)	η (%)
blank	1.70	2522	0.72	n.a. ^a	52.7	n.a.	n.a.	165.5	n.a.
CL1	1.56	290.1	0.76	67.0	15.5	375.8	0.85	700.5	78.4
CL2	1.25	109.8	0.81	52.5	14.1	474.6	0.72	455.0	67.4
CL3	1.50	249.0	0.74	46.9	21.5	743.5	0.77	250.7	44.4
CL4	2.90	106.3	0.79	27.2	22.4	862.1	0.64	175.8	18.5

^an.a. means not available.

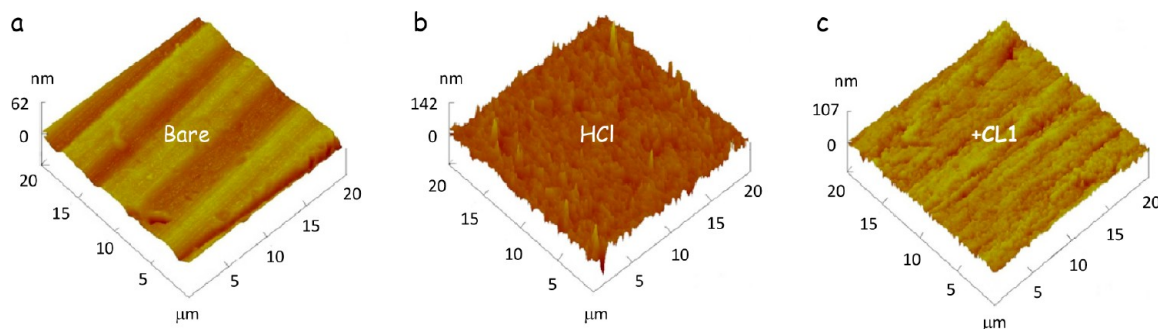


Figure 4. AFM images of bare (a) and HCl-corroded copper surface (b), and of copper surface protected by CL1 (3.2×10^{-3} M) in 1 M HCl.

range (>1 kHz), which indicates insignificant solution resistance. At the low frequency range (<1 Hz), all the $|Z|$ values increased tangibly, which are in an order of **CL1** $>$ **CL2**

$>$ **CL3** $>$ **CL4**. Figure 3d showed two time constants corresponding to the two circuits in series in the circuit model (Figure 3b, lower) used for copper in HCl in the

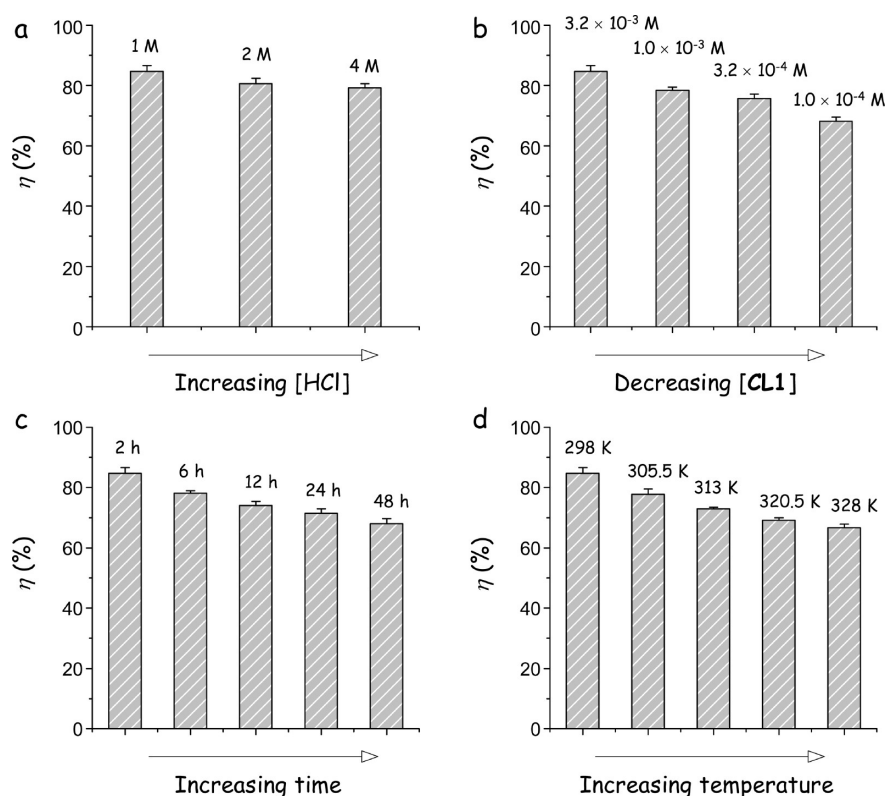


Figure 5. Inhibitive efficiency (η) of CL1 under different conditions: (a) with increasing HCl concentration; (b) in 1 M HCl with decreasing compound concentration; (c) in 1 M HCl with increasing immersion time; (d) in 1 M HCl with increasing temperature.

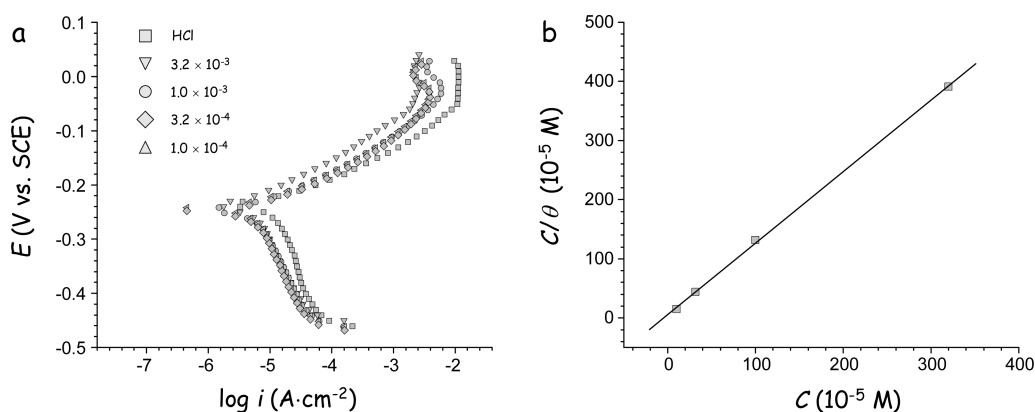


Figure 6. (a) Polarization curves in the absence or presence of CL1 of different concentrations, and (b) the Langmuir isotherm of CL1 with different concentrations at 25 °C for copper electrodes in 1 M HCl.

presence of inhibitors. The increased phase angles in the presence of the inhibitors probably indicate the formation of a molecular film on copper surface to block the corrodible areas.

CL1 with the best inhibitive efficiency was selected for detailed analyses. Atom force microscope (AFM) was primarily used to scrutinize the coating of the compound (3.2×10^{-3} M) on copper surface (Figure 4). While the surface morphology of copper corroded by HCl (likely by pitting, Figure 4b) is substantially different from that of bare (uncorroded) copper (Figure 4a), a thickened coating formed by CL1 could be observed for the protected copper surface (Figure 4c). This again manifests that the corrosion inhibition is due to formation of molecular layers on the metal surface. Additionally, an X-ray diffraction (XRD) analysis proved that generation of copper chloride due to exposure of the copper specimen to HCl could

be significantly suppressed by addition of CL1 (Supporting Information Figure S1).

The inhibitive performance of CL1 for copper was also interrogated under a variety of harsher experimental conditions (Figure 5 and Supporting Information Table S1). Increasing the concentration of CL1 (from 10^{-4} M to 3.2×10^{-3} M) in 1 M HCl led to gradually improved η (Figure 5b and Supporting Information Figure S2a), which means that the corrosion inhibition is concentration dependent. In stronger HCl solutions (2 and 4 M), CL1 displayed almost unaffected η (Figure 5a and Supporting Information Figure S2b), while by increasing the immersion time (Figure 5c and Supporting Information Figure S3) or by increasing the immersion temperature (Figure 5d and Supporting Information Figure S4), the inhibitor exhibited only slightly decreased efficiency.

Furthermore, under the same experimental condition, **CL1** displayed much better η than cysteine (a well-studied green corrosion inhibitor, Supporting Information Table S1). These data imply that piperine has the potential to become a promising green corrosion inhibitor for industrial applications.

To elaborate the inhibitive mechanism against corrosion, potentiodynamic polarization was performed. The polarization curves recorded for copper in 1 M with or without **CL1** are shown in Figure 6a. The calculated η values shown in Table 2

Table 2. Parameters Obtained from Polarization and Isotherm Analyses for Copper in 1 M HCl in the Absence (blank) or Presence of CL1 with Different Concentrations at 25 °C

CL1 (M)	E_{corr} (mV vs SCE)	$-\beta_c$ (mV dec $^{-1}$)	β_a (mV dec $^{-1}$)	i_{corr} ($\mu\text{A cm}^{-2}$)	η (%)
blank	−236.7	278.3	60.3	15.9	n.a. ^a
1.0×10^{-4}	−243.6	211.5	50.0	5.0	68.3
3.2×10^{-4}	−247.2	205.8	54.6	4.3	73.2
1.0×10^{-3}	−242.5	193.3	48.8	3.8	76.0
3.2×10^{-3}	−232.1	197.6	49.7	2.9	81.8
compd.	slope	R^2	K_{ads} (M $^{-1}$)	ΔG_{ads}^0 (kJ mol $^{-1}$)	
CL1	1.21	0.9998	1.8×10^4	−34.2	

^an.a. means not available.

are in good agreement with those obtained from EIS (Table 2). It was observed that both the anodic and cathodic curves shifted toward a lower corrosion current density (i_{corr}) with inappreciably changed potentials. This suggests that **CL1** is a mixed-type corrosion inhibitor for copper that suppresses both the anodic and cathodic reactions.²⁸

The adsorption behavior of **CL1** for copper in 1 M HCl was also elaborated by an isothermal analysis. The surface coverage degree (θ)^{26,27} of **CL1** with varying concentrations was first determined by the following equation:

$$\theta = (i_{\text{corr}(0)} - i_{\text{corr}}) / i_{\text{corr}} \quad (1)$$

where $i_{\text{corr}(0)}$ and i_{corr} are the corrosion current densities in the absence and presence of the inhibitor, respectively.

These values were then fitted to various isotherm models, and the best correlation between the experimental and fitted data was obtained using the Langmuir isotherm described by the following equation:

$$\frac{C}{\theta} = \frac{1}{K_{\text{ads}}} + C \quad (2)$$

where C is the inhibitor concentration in the electrolyte and K_{ads} is the equilibrium constant of the adsorption process. Plotting of C vs C/θ resulted in a linear correlation (Figure 6b), and the standard free energy of adsorption (ΔG_{ads}^0) was estimated by the following equation:

$$K_{\text{ads}} = \frac{1}{55.5} \exp \frac{-\Delta G_{\text{ads}}^0}{RT} \quad (3)$$

where 55.5 is the molar concentration of water in the solution expressed in molar unit (M).

It is known that while the absolute values of ΔG_{ads}^0 range from 20 to 40 kJ mol $^{-1}$, probably both physisorption and chemisorption are adopted by the inhibitor (while the value is greater than or equal to 40 kJ mol $^{-1}$, chemisorption is favored; while the value is less than or equal to 20 kJ mol $^{-1}$,

physisorption is favored).²⁹ As a result, the ΔG_{ads}^0 value (−34.2 kJ mol $^{-1}$, Table 2) determined for **CL1** suggests that this compound probably adopts both physi- and chemisorptions on copper surface.

Therefore, coating of the alkaloid compounds on copper might be attributed to the replacement of water molecules and/or other species originally absorbed on the metal surface by the inhibitor molecules, and/or to occupation of the d -orbital of copper by the O - or N -heteroatoms of the inhibitors. Additionally, the protonated form of the compounds might exert electrostatic interactions with the $[\text{CuCl}]$ species generated by HCl corrosion. After coating, the corrodible areas could be protected, reducing the corrosion rate.

A modeling study was eventually performed to simulate the adsorptive ability of the amide alkaloids for copper.³⁰ The adsorption energy (E_{ad}) of the nitrogen atom of piperidine was determined to be lower than that of the oxygen atoms of methylenedioxybenzene, suggesting that the piperidine fragment might contribute predominantly to the protective film formation over the copper surface. The proposed complexation modes of the **CL** compounds with a copper cluster are shown in Figure 7, and the E_{ad} value of **CL1** was calculated to be the

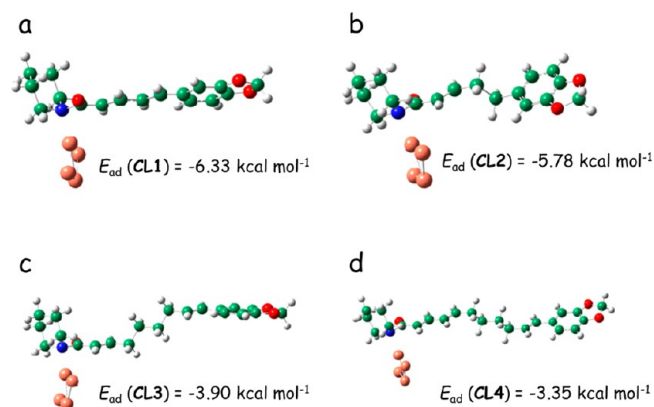


Figure 7. Calculated complexation mode and adsorption energy (E_{ad}) of **CL1**–**CL4** for copper, where the dark green balls stand for carbon, gray for hydrogen, red for oxygen, blue for nitrogen, and orange for copper.

lowest among the alkaloid compounds. This indicates that **CL1** has the strongest adsorption capacity toward copper among the four analogs, which accords with the experimental results.

CONCLUSION

In summary, we have reported the identification of piperidine (**CL1**), an amide alkaloid isolated from a traditional Chinese medicine, as a new green corrosion inhibitor for copper in HCl. It was determined that among four analogous amide alkaloids, **CL1** has the best corrosion inhibitive efficiency as delineated by various microscopic and electrochemical techniques. Notably, this compound has a much better inhibitive efficiency than cysteine (a well-studied green corrosion inhibitor for copper), and the efficiency does not lower notably under several harsh experimental conditions. Therefore, piperine that can be abundantly purified from the rich pepper plants might have the potential to serve as a promising green copper corrosion inhibitor for use in industry. Identification of active components for corrosion inhibition from other plant extracts is currently underway in our laboratories.

■ ASSOCIATED CONTENT

■ Supporting Information

Experimental section, Figures S1–S4 and Table S1. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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