Comparative study of the copper inhibition of two [H₄L]calixarenic molecules in sulfuric acid medium

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Abstract

This is a comparative study of the inhibition and adsorption properties of two Calixarenic organic molecules of the type H₄L named Calix1 and Calix2 as good corrosion inhibitors in 0.5 M sulfuric acid by electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The experimental data showed that Calix1 and Calix2 are effective against copper corrosion in 0.5 M H₂SO₄ and the inhibitory efficiency which has been reached at an optimum value is 96.8% for Calix2. The results of EIS measurements have shown that the copper dissolution process occurs under diffusion control. The copper corrosion rates and additive inhibition efficiency were calculated. The results obtained showed that the combination could serve as effective inhibitors of copper corrosion in the sulfuric acid medium. The inhibition mechanisms are estimated from the inhibition efficiency as a function of concentration and immersion time. It is suggested that the molecular and the protonated organic species of both Calix contributed to the observed inhibitory action. In addition, the scanning electron microscope analysis confirmed the inhibitory effect of these two compounds. Furthermore, the SEM images showed that both compounds are adsorbed on the copper surface. Moreover, the increase in immersion time does not significantly affect the inhibitory efficiency values, which confirms the high resistance of the composite.

Keywords: Electrochemical impedance spectroscopy, calixarene, corrosion of copper, potentiodynamic polarization, H₂SO₄.

Received: February 6, 2020. Published: August 28, 2020

doi: [10.17675/2305-6894-2020-9-3-16](https://doi.org/10.17675/2305-6894-2020-9-3-16)

1. Introduction

Copper is widely used in many applications in the electronics and communications industries as a conductor in power lines, pipelines for domestic and industrial water utilities, including seawater, heat conductors, heat exchangers, *etc.* It has been one of the most important metals in the industry due to its high electrical and thermal conductivities, mechanical workability and relatively noble properties.

This material is more used in heating and cooling systems. Decreasing the heating efficiency of the equipment is caused by scaling and corrosion products that have a negative effect on heat transfer. This is why periodic cleaning with acidic solutions as sulfuric acid is necessary. The corrosion inhibitors eliminate effectively the undesirable destructive effect and prevent the metal dissolution. Most commercially available stripping inhibitors are toxic compounds that should be replaced by new, environmentally friendly inhibitors [1].

The use of copper corrosion inhibitors in such conditions is necessary since no protective passive layer can be expected. The possibility of preventing copper corrosion in different aqueous solutions has attracted many researchers so far, many inhibitors have been studied. These studies are indicated that there are many organic and inorganic compounds that can protect copper from corrosion [2–6]. The presence of hetero-atoms such as nitrogen, sulfur, phosphorous in the organic compound molecule improved its action as copper corrosion inhibitor. But, among these organic compounds and their derivatives such as azoles [7, 8], amino acids [9] and many others are very toxic compounds.

In general, the nature and surface charge of the metal, the adsorption mode, the chemical structure and the electrolyte solution type depend on the inhibitor adsorption on a metal surface [10]. However, the use of inorganic or organic compounds and their derivatives provide an effective protection to copper and its alloys in aggressive medium [11, 12]. This protection is ascribed to the chelate formation with the metal ion, leading to the formation of a barrier layer between the inhibitor and the metal surface preventing the reaction and dissolution of the metal. The barrier layer is attributed either to the presence of vacant d-orbitals in copper atom that form coordinative bonds with atoms which donate electron such as nitrogen, sulfur, phosphorous, or to strong π -interaction between the aromatic rings through the nitrogen-containing heterocyclic part of the inhibitor [13].

Organic compounds are commonly used to protect metal against corrosion as inhibitors in acidic media [14–32]. These inhibition efficiencies of organic compounds have been shown to depend on [33, 34]: (I) the chemical structure of the compound, (II) the metal surface charge and (III) the type of interactions between the organic molecules and the metal surface.

In this work, we investigated the ability of two calixarenic molecules to inhibit copper corrosion in a 0.5 M sulfuric acid solution. This study was also conducted using electrochemical impedance spectroscopy diagrams and a scanning electron microscopy (SEM) technique to examine changes in corroded copper surfaces in the test solution with and without inhibitor.

2. Experimental work

A conventional three-electrode cell was utilized with a large area Pt counter and Ag/AgCl reference electrodes. The chemical composition of copper, which is used such as working electrode, is shown below. The rod was mounted into glass tube of appropriate internal diameter by epoxy resin leaving a front surface area of 1 cm² to contact the test solution. Before each experiment, the surface electrode was abraded using emery paper in different grades (from 100 to 1200), cleaned with acetone, washed with distilled water, and dried in hot air. All potentials were measured and referred to the Ag/AgCl reference electrode.

In this study, the commercial copper used had the following chemical composition (by weight %): 0.019 P, <0.001 Fe, <0.001 As, <0.001 Mn, <0.002 Sb, <0.001 Al, 0.009 Sn, 0.003 Ni, 0.015 Pb, <0.005 Ag, <0.001 Bi, <0.001 S, <0.005 C, the balance being Cu. The corrosive medium is a sulfuric acid solution H₂SO₄ with a concentration of 2.0 M, obtained by diluting 98% concentrated commercial acid with distilled water.

The calix[4]arene molecules have been synthesized in Laboratory of the Molecular Engineering in Applied Analysis at the University of Strasbourg, France, following the literature [35]. Its molecular structure was presented in Table 1. Therefore, each additive was dissolved in dichloromethane and added, at different concentration in the range 10⁻³ M to 10⁻⁶ M. Furthermore, the electrochemical impedance spectroscopy measurements were carried out using a transfer function analyzer, over the frequency range from 100 kHz to 10 mHz with 10 points per decade. All experiments were performed at the open circuit potential and the applied amplitude of AC signal was 10 mV_{rms}. These measurements were made using Potentiostat/Galvanostat/Volta Lab PGZ 100 monitored by a personal computer and Voltalab 4.0 software. The obtained impedance data were analyzed in terms of equivalent electrical circuit using Z-view program. The molecular formulas of the inhibitors examined are presented in Table 1.

Table 1. Names, chemical structures and abbreviations of the studied calixarenic compounds.

Name of the additive	Tetrametylester-P- tertbutylcalix[4]arene	Tetraacid-P-tert- butylcalix[4]arene
Formula of the additive
Abbreviation used	Calix1	Calix2
Molar Mass (g/mol)	937.18	881.07

3. Results and Discussion

3.1. Electrochemical impedance spectroscopy

The effects of varying the concentrations of two inhibitors on the impedance behavior of copper in 0.5 M H_2SO_4 are presented in Figure 1. The curves show a similar type of Nyquist plot for copper in the presence of various concentrations of Calixarene (Calix1 and Calix2). The simple Randle equivalent circuit for the studies has been shown in Figure 2, where R_s represents the solution resistance of the corrosion product film, R_{ct} is the charge transfer resistance and Q_{ct} is the constant phase element of the double layer. The existence of a single semicircle has shown the unique charge transfer process during dissolution, which is affected by the presence of the inhibitory molecule. The diameter of the capacitive loop in 0.5 M of sulfuric acid increased with the additive concentration proposing that the formed inhibitive film was reinforced by the addition of Calix1 and Calix2 [36–41]. The frequency dispersion of the interfacial impedance resulting from roughness and non-homogeneous surface is often referred to as perfectly circular deviations [42, 43]. But in solution, the inhibitory efficiency of 0.5 M H_2SO_4 increased when the additive concentration decreased and reached a high efficiency of 94.7% for Calix1 and 96.8% for Calix2 at 10^{-5} M concentration of additives. On the other hand, the decrease in C_{dl} values with increasing inhibitor concentration is probably due to the diminution of the local dielectric constant and/or the increase in the thickness of the electric double layer. This suggests that the Calixarenes act by adsorption on the metal/solution interface [44, 45].

Figure 1. Nyquist plots of copper in 0.5 M H_2SO_4 with different concentrations of Calix1.

Figure 2. Nyquist plots of copper in 0.5 M H₂SO₄ with different concentrations of Calix2.

Table 2. Electrochemical parameters and corresponding inhibition efficiency for corrosion of copper in 0.5 M H₂SO₄ in the absence and the presence of different concentrations of Calix1 and Calix2 at 298 K.

	Conc. M	R_s $\Omega \cdot \text{cm}^2$	Q_f $\mu\text{F} \cdot \text{cm}^2$	n_f	R_f $\Omega \cdot \text{cm}^2$	Q_{ct} $\mu\text{F} \cdot \text{cm}^2$	n_{ct}	R_{ct} $\Omega \cdot \text{cm}^2$	R_p $\Omega \cdot \text{cm}^2$	$E\%$
Blank	—	0.7	—	—	—	475	0.720	350	349	—
Calix1	10^{-3}	1.6	151	0.775	464	212	0.640	2514	2978	88.2
	10^{-4}	3.6	77	0.688	1612	280	0.767	1390	3002	88.3
	10^{-5}	1.0	52	0.837	3562	169	0.850	3078	6640	94.7
	10^{-6}	2.1	127	0.984	538	211	0.661	2659	3197	89.1
Blank	—	0.7	—	—	—	475	0.720	350	349	—
Calix2	10^{-3}	1.6	38.2	0.857	5302	155	0.723	1980	7282	95.2
	10^{-4}	1.2	36.3	0.727	7786	309	0.984	742	8528	95.9
	10^{-5}	1.4	52.5	0.788	3396	32	0.683	7577	10973	96.8
	10^{-6}	1.7	78.2	0.827	1398	131	0.668	2826	4224	91.7

The EIS data are analyzed by equivalent circuits models (Figure 3).

Figure 3. Equivalent circuit for the electrochemical impedance spectra.

As shown above, this is a two-time constant model due to the presence of both the passive and the corroding regions on these surfaces. The passive regions refer to the oxide layer on copper surface, while the corroding regions refer to the oxide layer breakdown. R_s stands for the solution resistance, R_f and R_{ct} are attributed to the surface film resistance, and the charge transfer resistance which is related to the corrosion process taking place on copper surface. Q_f and Q_{dl} are the constant phase elements, which represent the capacitance of the surface film and the double layer capacitance. The impedance spectrums were fitted and their parameters were calculated according to the chosen model and listed in Table 2. CPE was used as the substitute for capacitor to fit more accurately impedance. The impedance of the CPE is expressed as [46, 47].

$$Z_{GPE} = Y^{-1} (j\omega)^n$$

where Y is the magnitude of the CPE; ω the angular frequency; n is an empirical exponent which measures the deviation from the ideal capacitive behavior [48, 49]. Depending on the values of n , CPE can represent resistance ($n=0$), capacitance ($n=1$), inductance ($n=-1$) and Warburg impedance ($n=0.5$) [50–52].

3.2. Effect of immersion time

Figures 4 and 5 show the impedance spectra at different immersion times in 0.5 M H_2SO_4 containing 10^{-5} M Calix1 and Calix2.

Table 3 summarizes the evolution parameters as a function of time. The diameter of the capacitive loop decreased slightly depending on the immersion time. On the other hand, at 10^{-5} M of Calix1, the capacity of the film decreased with immersion time.

Figure 4. Electrochemical impedance spectra obtained after different immersion time in 0.5 M H_2SO_4 .

Figure 5. Electrochemical impedance spectra obtained after different immersion time in 0.5 M H_2SO_4 with 10^{-5} M of Calix1 and Calix2.

To continue the electrochemical study at different concentrations and to link the results obtained with the proven effectiveness, the corrosion inhibiting properties of Calix1 were studied with precision. However, it would be more important to evaluate the temporal behavior of the inhibitor through the kinetics associated with relatively long immersion times. Figures 4 and 5 show the impedance results with values for Calix1 reaching ($8146 \Omega \cdot \text{cm}^2$) after 16 h immersion. The impedance spectrum has described clearly two time constants, one linked to the substrate, and other to the charge transfer resistance of the organic molecules (Calix1). Table 3 shows the variation of the R_{ct} data obtained as a function of the immersion time. According to the results of Table 3, the inhibitory efficiency IE decreased with immersion time and reached 87% after 16 h.

The electrochemical parameters of Calix2 showed that the inhibitory efficiency decreased with immersion time and it had a value of 84% efficiency after 16 h.

Table 3. Electrochemical parameters and the corresponding inhibition efficiencies at various immersion time of copper in 0.5 M H_2SO_4 , in the absence and the presence of 10^{-5} M of Calix1 and Calix2 at 298 K.

	Time, h	R_s , $\Omega \cdot \text{cm}^2$	Q_t , $\mu\text{F} \cdot \text{cm}^2$	n_t	R_t , $\Omega \cdot \text{cm}^2$	Q_{ct} , $\mu\text{F} \cdot \text{cm}^2$	n_{ct}	R_{ct} , $\Omega \cdot \text{cm}^2$	R_p , $\Omega \cdot \text{cm}^2$	E%
Blank	0.5	0.7	—	—	—	475	0.720	350	349	—
	1	1.8	112.9	0.750	318	296	0.474	627	945	—
	2	1.4	20.32	0.946	359	155	0.559	799	1159	—
	4	1.8	24.88	0.893	825	346	0.514	871	1697	—
	6	2.7	22.9	0.905	691	246	0.499	1061	1753	—
	12	2.5	20.21	0.918	780	197	0.484	1220	2000	—
	16	1.4	32.89	0.819	1330	777	0.917	348	1678	—

	Time, h	R_s , $\Omega \cdot \text{cm}^2$	Q_t , $\mu\text{F} \cdot \text{cm}^2$	n_t	R_t , $\Omega \cdot \text{cm}^2$	Q_{ct} , $\mu\text{F} \cdot \text{cm}^2$	n_{ct}	R_{ct} , $\Omega \cdot \text{cm}^2$	R_p , $\Omega \cdot \text{cm}^2$	$E\%$
Calix1	0.5	1.0	52	0.837	3562	169	0.850	3078	6640	94.7
	1	1.7	17.6	0.908	2907	84	0.532	4838	7745	87.8
	2	1.5	15.9	0.916	4442	103	0.583	4875	9317	87.5
	4	0.7	15.2	0.919	4987	105	0.580	5444	10431	83.7
	6	0.8	15.4	0.912	5673	117	0.596	5516	11189	84.3
	12	0.7	14.9	0.918	5949	119	0.617	5777	11726	82.9
	16	1.8	12.4	0.954	4121	80	0.512	8146	12267	86.3
Calix2	0.5	1.4	52.5	0.788	3396	32	0.683	7577	10973	96.8
	1	2.3	18.8	0.915	4583	67	0.431	8590	13173	92.8
	2	3.7	16.5	0.936	4193	53	0.446	9701	13894	91.6
	4	1.5	18.9	0.892	8961	160	0.476	7229	16190	89.5
	6	1.3	18.5	0.893	9785	167	0.453	8393	18178	90.3
	12	1.8	16.8	0.912	9771	130	0.532	8053	17824	88.7
	16	2.1	22.5	0.905	6072	162	0.562	4411	10483	83.9

3.3. Scanning electron microscopy observations

Figure 6 (a, b and c) shows the scanning electron microscope (SEM) images of the copper surface exposed in the sulfuric acid solution (0.5 M) for 6 hours, in the absence and in the presence of the Calix1 and Calix2 organic molecules at 10^{-5} M concentration.

In the absence of inhibitors, the images of the copper surface have shown that copper substrates have been severely damaged in immersion tests because the corrosion products are multilayered.

The morphology of the outer layer of the corroded substrate appeared uneven and rough, which is adsorbed compactly to the inner layer. In addition, it should be noted that these images showed a heterogeneous layer of the scale product formation.

Furthermore, the SEM images of copper surface morphology in the presence of Calix1 and Calix2 (Figure 6 b and c) show a large surface without corrosion products (no pits or cracks except polishing lines) and the surface had become smooth. It is clear that the inhibitor molecules can be adsorbed on the copper surface and has protected it. These figures have confirmed the formation of a protective film by Calix on the copper surface in sulfuric acid solutions [53].

Figure 6. SEM microphotographs of copper in 0.5 M H₂SO₄ without (a) and with (b) Calix1 and (c) Calix2 after 6 h of immersion.

Conclusion

In summary, the spectroscopic and electrochemical results corresponding to the calixarene mechanisms (Calix1 and Calix2) as copper corrosion inhibitors in 0.5 M sulfuric medium are explained by the presence of oxygen functional group and other aromatic compounds in these inhibitors molecules. Calixarenic additives act on both cathodic and anodic domains. Moreover, the inhibitory efficiency have increased with concentration and reached a maximum efficiency at 10^{-5} M concentration in H₂SO₄ at 25°C. Inhibition mechanisms, estimated from the dependence as a function of immersion time shows that the additives functioned *via* a mixed inhibition mechanism. The effect of the immersion time in the medium shows that the inhibition of copper reaches a maximum at 12 hours.

Finally, the SEM images have confirmed all the previous results and showed that the copper corrosion in 0.5 M H₂SO₄ could be inhibited by the addition of Calix. The obtained results show that the additive could serve as a corrosion inhibitor for the protection of copper in other aggressive media.

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