Calixarene molecule as an effective inhibitor of copper corrosion in 2.0 M H_3PO_4 and 0.5 M H_2SO_4 solutions

N. M'Hanni,¹ M. Galai,¹ * M. Ouakki,² M. Ebn Touhami,¹ E.H. Rifi¹ and Z. Asfari³

¹Advanced Materials and Process Engineering, Faculty of Sciences, Ibn Tofail University, PO Box 133, 14000, Kenitra, Morocco

²Laboratory of Organic, Inorganic Chemistry, Electrochemistry and Environment, Faculty of Sciences, Ibn Tofail University, PO Box 133, 14000, Kenitra, Morocco

³Laboratory of Molecular Engineering Applied to the Analysis, IPHC, UMR 7178 CNRS, University of Strasbourg, ECPM, 25 street Becquerel, 67087 Strasbourg Cedex 2, France

*E-mail: galaimouhsine@gmail.com

Abstract

The comparative study of the inhibition and adsorption properties of organic molecule Calixarene (Calix) as a corrosion inhibitor in 2.0 M phosphoric acid and 0.5 M sulfuric acid solutions was done using several methods such as polarization curves, electrochemical impedance spectroscopy (EIS) and scanning electron microscopy (SEM). The results of EIS and polarization measurements showed that the dissolution process of copper occurs under diffusion control. Potentiodynamic polarization curves indicated that the Calixarene behaves as cathodic-type inhibitor. The corrosion rates of copper and the inhibition efficiencies of the additive were calculated. The results obtained show that the calix could serve as an effective copper corrosion inhibitor in both media. However, the sulfuric acid medium shows better results compared to phosphoric acid. The inhibition mechanisms, estimated from the temperature dependence of inhibition efficiency as well as from kinetic and activation parameters, show that the additive operates according to a mixed inhibition mechanism. It is suggested that molecular as well as protonated organic species in the Calix contribute to the observed inhibiting action.

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1. Introduction

Copper is widely used in many applications such as electronic and communication industries as a conductor in power lines, in 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.

Owing to its excellent thermal conductivity and good mechanical workability, copper 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 and cleaning solutions with sulfuric acid are necessary. Corrosion inhibitors effectively eliminate the undesirable destructive effect and prevent the dissolution of the metal. Most commercially available stripping inhibitors are toxic compounds that should be replaced by new, environment 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 the copper corrosion prevention in different aqueous solutions has attracted many researchers, and many inhibitors have been investigated. These studies reported that many organic and inorganic compounds can contribute in the improvement of copper corrosion [2–6]. The presence of hetero-atoms such as nitrogen, sulfur, phosphorous in the organic compound molecule improves its action as copper corrosion inhibitor. Amongst these organic compounds and their derivatives, we find azoles [7, 8], amino acids [9] and many others, but these compounds are highly toxic.

In general, nature and surface charge of the metal, the mode of adsorption, the chemical structure and the type of electrolyte solution depends on the adsorption of an inhibitor on a metal surface [10]. However, the use of inorganic or organic compounds and their derivatives provides an effective protection to copper and its alloys in an aggressive medium [11, 12]. This protection is ascribed to the chelating action of the heterocyclic part of the chemical compound and the formation of a barrier layer between the inhibitor and the metal surface, preventing metal reaction and dissolution. The barrier layer is attributed either to the presence of vacant d orbitals in the copper atom that form coordinative bonds with atoms donating electron such as nitrogen, sulfur, phosphorous, or very 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 acid mediums [14–32]. These inhibition abilities of organic compounds have been shown to depend on [33, 34]: (i) the chemical structure of the compound, (ii) the surface charge of the metal, and (iii) the type of interactions between the organic molecules and the metal surface.

In this work, we investigated the ability of the calixarene molecule to inhibit copper corrosion in two different acid solutions (0.5 M sulfuric acid and 2.0 M phosphoric acid).

This study was also conducted by using potentiodynamic polarization curves, electrochemical impedance spectroscopy diagrams and scanning electron microscopy (SEM) technique to examine the changes of the corroded copper surfaces in test solutions without and in the presence of the 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, as a working electrode, is showed below. The rod was mounted into a 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 at 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.

The commercial copper used in this study 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 test solutions were prepared from analytical grade reagent and distilled water: 98% H₂SO₄. The aggressive solution of 2.0 M H₃PO₄ was prepared by dilution of analytical grade 85% H₃PO₄ ($d = 1.71$ and $PM = 98$) with distilled water.

The calix[4]arene molecule was synthesized in the laboratory of the Molecular Engineering in Applied Analysis at the University of Strasbourg, France, according to the literature [35]. Its molecular structure was presented in Table 1. The additive was dissolved in dichloromethane and added at different concentration in the range 10^{-3} M to 10^{-6} M. In addition, 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/VoltaLab PGZ 100 monitored by a personal computer and Volta lab 4.0 software. The obtained impedance data were analyzed in terms of equivalent electrical circuit using Z-view program.

The molecular formula of the examined inhibitor is shown in Table 1.

Table 1. Name, chemical structure and abbreviation of the studied calixarenic compound.

Abbreviation	Chemical structure	Molar Mass (g/mol)
Calix		964

3. Results and Discussion

3.1 Effect of Calixarene molecule concentration in 2.0 M H₃PO₄ and 0.5 M H₂SO₄

Tafel polarization method was used to evaluate the corrosion rate of the copper sample in the presence and absence of Calixarene. Tafel polarization curves of the copper in 2.0 M H₃PO₄ solution with and without the addition of various concentrations of Calix are shown in Figure 1. The different parameters are calculated from the graphs and are reported in Table 2.

This decrease is more marked when the concentration of the compound added to the H_3PO_4 solution is high. The cathodic curves show a wide range of linearity, indicating that the Tafel law is well verified in the cathode zone. Generally, an inhibitor can be classified as a cathodic or anodic type if the offset of potential for corrosion in the presence of the inhibitor is greater than 85 mV compared to that in the absence of inhibitor [36, 37]. In the presence of Calix, E_{corr} goes to minus negative, and the offset is small (from -120 to -71 mV), which indicates that this additive can be arranged as a cathodic type inhibitor with a predominant cathodic efficiency. The cathodic polarization curves give rise to parallel Tafel lines, which indicate that hydrogen evolution reaction is activation controlled.

The copper inhibition study in the absence and presence of Calixarene at different concentrations in 0.5 M sulfuric acid medium, given in Figure 2, showed that the polarization curves are shifted in the cathodic versus white domain with a wide range of $[-0.7, -0.3 \text{ V}]$ which is due to oxygen diffusion. The results obtained from table 2 in the solution of 2 M H_3PO_4 containing 10^{-3} M Calix at 25°C indicate the decrease in copper corrosion current density from $16.4 \mu\text{A}/\text{cm}^2$ to $2.85 \mu\text{A}/\text{cm}^2$ and the addition of this organic compound causes a displacement of the corrosion potential to more cathodic values. This displacement is accompanied by a net decrease in the cathodic current density and the increase in corrosion inhibition efficiency to 83%. Similar results were obtained in 0.5 M H_2SO_4 medium; we notice that copper corrosion current density decreases from $29 \mu\text{A}/\text{cm}^2$ to $1.7 \mu\text{A}/\text{cm}^2$ with a corrosion inhibition efficiency of 94% at an inhibitor concentration of 10^{-5} M. This behavior can be explained by the good coverage of the metal surface by the Calix molecule which blocks the active sites on the metallic surface [38–40]. It can be concluded that the 2 M phosphoric medium is more aggressive than the 0.5 M sulfuric medium.

Figure 1. Typical polarization curves for copper in 2.0 M H_3PO_4 for various concentrations of Calixarene at 298 K.

Figure 2. Typical polarization curves for copper in 0.5 M H₂SO₄ for various concentrations of Calixarene at 298 K.

Table 2. Electrochemical parameters and corresponding inhibition efficiency for corrosion of the copper in 2.0 M H₃PO₄ and 0.5 M H₂SO₄ in the absence and the presence of different concentrations of Calixarene at 298 K.

Inhibitor Calix	Concentration M	E_{corr} , mV vs. Ag/AgCl	i_{corr} , ($\mu\text{F}/\text{cm}^2$)	$-\beta_c$, mV	β_a , mV	EI%
2 M H ₃ PO ₄	0	-50.7	16.4	146	107	—
	10^{-3}	-120	2.85	131	80	82.6
	10^{-4}	-119	3.1	148	84	81.1
	10^{-5}	-70	5.7	151	86	65.2
	10^{-6}	-71	7.5	156	81	54.3
0.5 M H ₂ SO ₄	0	-79	29.0	204	59.0	—
	10^{-3}	-156	2.3	195	56.0	92.0
	10^{-4}	-172	1.9	209	54.4	93.4
	10^{-5}	-187	1.7	205	53.0	94.1
	10^{-6}	-164	2.4	200	55.0	91.7

3.2 Electrochemical impedance spectroscopy

The effect of inhibitor concentration on the impedance behavior of copper in 2.0 M H₃PO₄ solution at 298 K is presented in Figure 3, and 0.5 M H₂SO₄ are shown in Figure 4. The curves show a similar type of Nyquist plot for copper in the presence of various concentrations of Calixarene. The simple Randle equivalent circuit for the studies has been shown in Figure 5, where $R(\Omega)$ represents the solution resistance, R_{ct} , is the resistance of the corrosion product film and the capacitor C_{dl} represents the corrosion interface. The existence

of a single semicircle shows that the unique charge transfer process during dissolution is unaffected by the presence of the inhibitory molecule. The diameter of the capacitive loop in the solution 2 M H_3PO_4 increases with the increase of additive concentration proposing that the formed inhibitive film was strengthened by the addition of Calix [41]. Perfectly circular deviations are often referred to as the frequency dispersion of the interfacial impedance resulting from roughness and inhomogeneity of the surface [42, 43]. But in solution 0.5 M, H_2SO_4 inhibitory efficacy increases when the concentration of additive decreases. On the other hand, C_{dl} values are decreased with increasing inhibitor concentration which is probably due to the decrease of the local dielectric constant and/or the increase in the thickness of the electric double layer, suggesting that Calixarene acts by adsorption on metal/solution interface [44, 45].

Figure 3. Nyquist plots of copper in 2.0 M H_3PO_4 with different concentrations of Calixarene.

Figure 4. Nyquist plots of copper in 0.5 M H_2SO_4 with different concentrations of Calixarene.

Table 3. Electrochemical impedance parameters and inhibition efficiency for copper in 2.0 M H₃PO₄ and 0.5 M H₂SO₄ solution with Calix at 298K.

Medium	Conc. of inh. 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 $\Omega \cdot \text{cm}^2$	$E\%$
2 M H ₃ PO ₄	0	7.67	88.49	0.823	1575	932	0.617	1402	2969.33	–
	10 ⁻³	5.51	40.53	0.887	10178	139.9	0.813	6360	16532.49	82.0
	10 ⁻⁴	6.68	44.01	0.847	3005	92.07	0.609	12650	15648.32	81.0
	10 ⁻⁵	6.06	63.58	0.814	2800	90.5	0.391	5489	8282.94	64.1
	10 ⁻⁶	5.72	52.86	0.833	3113	243.6	0.770	3319	6426.28	53.8
0.5 M H ₂ SO ₄	0	0.7	–	–	–	475	0.720	350	349	–
	10 ⁻³	3.04	41.64	0.868	2842	416	0.730	1421	4259.96	91.8
	10 ⁻⁴	2.66	28.00	0.880	3248	217	0.715	1962	5207.34	93.3
	10 ⁻⁵	3.03	29.72	0.902	4010	371	0.829	1765	5771.97	93.9
	10 ⁻⁶	3.08	34.67	0.873	2703	291	0.814	1385	4084.92	91.4

The values of charge-transfer resistance (R_{ct}) and double-layer capacitance (C_{dl}) obtained from the Nyquist plots, and the calculated inhibition efficiency values ($E\%$) is reported in Table 3. The Nyquist diagrams have a similar shape with different concentration of the inhibitor molecule. The values of R_{ct} in 2.0 M H₃PO₄ solution increases with increasing inhibitor concentration which indicates that the adsorption of inhibitor molecules occurs on the metal surface. The data (Table 3) suggests that increasing charge transfer resistance is associated with a decrease in the double-layer capacitance and an increase in the percentage of the inhibition efficiency. The reduction in C_{dl} values could be attributed to the adsorption of the inhibitor molecules at the metal surface. It has been reported that the adsorption of organic inhibitor on the metal surface is characterized by a decrease in C_{dl} [46]. These results confirm that copper in the presence of Calix is a good inhibitor in 0.5 M sulfuric acid compared to 2.0 M phosphoric acid.

3.3 Effect of temperature

The adsorption phenomenon has been successfully explained on the basis of thermodynamic data. To elucidate the inhibition property of the molecule and its mechanism, the kinetic model is another useful tool. Because many changes can occur on the metal surface, for example, rapid etching and desorption of the inhibitor, the inhibitor itself may undergo decomposition, the effect of temperature on inhibition of the acid-metal reaction is very complicated [47]. For this purpose, Figure 5 represents the polarization curves of copper in the presence of Calixarene at different temperatures (298, 308, 318 and 328 K) in the acidic

medium 2.0 M H_3PO_4 and 0.5 M H_2SO_4 . The inhibition efficiency decreased with the increase of temperature from 82.6% to 75.2% in the 2.0 M phosphoric medium and from 94.1% to 87.7% for the 0.5 M sulfuric medium. Figure 5 shows that the increase in temperature has a significant effect on the corrosion potential because the E_{corr} values are more negative in the cathode range but leads to a high corrosion rate (I_{corr}). The values of the corrosion potential (E_{corr}), the corrosion current density (I_{corr}), the β_c and anodic β_a cathode slopes and the inhibition efficiency (η_{EIS}) are shown in Table 4.

Figure 5. Tafel polarization curves for copper in 2.0 M H_3PO_4 in the absence (a) and presence of 10^{-3} M of Calixarene (b) and 0.5 M H_2SO_4 in the absence (c) and presence of 10^{-5} M of Calixarene (d) with different temperatures.

Table 4. Electrochemical parameters for copper in 1.0 M H₃PO₄ and 0.5 M H₂SO₄ with different temperatures.

Compounds	Temp., K	$-E_{\text{corr}}$ mV, Ag/AgCl	i_{corr} $\mu\text{A cm}^{-2}$	$-\beta_{\text{c}}$ mV dec ⁻¹	β_{a} mV dec ⁻¹	η_{P} %
Blank H ₃ PO ₄ 2.0 M	298	50.7	16.4	146	107	–
	308	146	21.4	132	94	–
	318	155	28.9	136	98	–
	328	171	39.5	142	101	–
Calix 10 ⁻³ M	298	120	2.85	131	80	82.6
	308	102	4.2	165	87	80.3
	318	97	6.4	143	71	77.8
	328	95	9.8	133	85	75.2
Blank H ₂ SO ₄ 0.5 M	298	79	29.0	204	59	–
	308	105	35.0	178	64	–
	318	142	56.0	164	77	–
	328	166	77.0	182	52	–
Calix 10 ⁻⁵ M	298	187	1.7	205	53.0	94.1
	308	192	2.8	180	59	92.0
	318	185	5.7	187	67	89.8
	328	172	9.4	177	73	87.7

The activation parameters for the corrosion process were calculated from the Arrhenius-type plot according to the following equation:

$$i_{\text{corr}} = K \cdot \exp(-E_{\text{a}} / RT)$$

E_{a} is the apparent activation corrosion energy, R is the universal gas constant, and K is the Arrhenius pre-exponential constant. In the following, Arrhenius diagrams for copper corrosion density have been shown below, in the case of Calix for both acidic media and are given in Figure 6. Values of apparent activation energy of corrosion (E_{a}) in the absence and in the presence of Calix at the optimal concentration of 10⁻³ M and 10⁻⁵ M, respectively for copper in 2.0 M H₃PO₄ and 0.5 M H₂SO₄, were determined from the slope of $\ln(I_{\text{corr}})$ with respect to the 1000/ T plots and are shown in Table 6.

3.4 Thermodynamic study

The thermodynamic study makes it possible to quantify the inhibition efficiency against corrosion and facilitates the calculation of the thermodynamic parameters and the activation energy in order to determine and interpret the type of adsorption adopted by the inhibitor.

Figure 6. Arrhenius curves corresponding to the corrosion of copper in 2.0 M H_3PO_4 (a) and 0.5 M H_2SO_4 (b) in the absence and presence of Calixarene.

The Arrhenius curves are plotted by calculating the logarithm of the corrosion rates ($\ln I_{\text{corr}}$) with respect to the absolute temperature ($1000/T$) for the acidic medium 2.0 M H_3PO_4 and 0.5 M H_2SO_4 (Figure 6). The Arrhenius equation (*) is as follows [48]:

$$\ln I_{\text{corr}} = -E_a / RT + \ln A \quad (*)$$

Where A is the pre-exponential constant of Arrhenius, R is the universal gas constant, E_a is the apparent activation energy, and T is the absolute temperature.

From Table 5, E_a increases with the addition of Calix over the control solutions. The change in corrosion rate with temperature increase was studied in 2.0 M H_3PO_4 in the absence and presence of 10⁻³ M of Calix and in 0.5 M H_2SO_4 media in the absence and presence of 10⁻³ M of Calix inhibitor. Table 6 contains the different data obtained from the curves.

The increase in corrosion rate is more shown with the rise in both acid solutions in the absence of Calix. But with the addition of Calix, the corrosion rate decreases rapidly.

Table 5. Activation parameters for copper in H_3PO_4 2.0 M and H_2SO_4 0.5 M.

Medium	Concentration	E_a , kJ mol^{-1}
H_3PO_4 2.0 M	Blank	23.8
	10 ⁻³ M	33.5
H_2SO_4 0.5 M	Blank	27.5
	10 ⁻⁵ M	47.4

3.5 Scanning electron microscopy (SEM)

SEM microphotographs of the surface of the copper samples after immersion in 2.0 M H_3PO_4 solution and in 0.5 M H_2SO_4 in the absence and presence of Calix are revealed in Figures 6 and 7. The microphotographs of copper surface in the absence of inhibitor are given in Figure 6a and Figure 7a and represent the polished metal sample; the whole surface is plane. Figure 6b and Figure 7b represent the inhibited samples immersed for 12h. in 2.0 M H_3PO_4 and 0.5 M H_2SO_4 containing an optimum concentration of the inhibitor. The image of the surface exposed to the inhibitor-free aggressive solution (Figure 6a) shows the heterogeneous layer of corrosion products (dark appearance clusters, pits and cracks), but in (Figure 6b), the surface is cleaner and free of any pits compared to the one without inhibitor.

Moreover, the SEM image in the presence of 10^{-3} M of Calix (Figure 7b) shows a large area free of corrosion products (no pits or cracks except polishing lines), and the surface became smooth. It is clear that the inhibitor molecules can be adsorbed on the copper surface and protect it.

These figures confirm the formation of a protective film by Calix on the copper surface in both acid solutions [49].

Figure 6. SEM microphotographs of copper in 2.0 M H_3PO_4 without (a) and with (b) Calix after 12 h of immersion.

Figure 7. SEM microphotographs of copper in 2.0 M H_3PO_4 without (a) and with (b) Calix after 12 h of immersion.

3.6 Effect of immersion time

Figure 8 shows the obtained impedance spectra at different immersion time in 2.0 M H₃PO₄ and in 0.5 M H₂SO₄ containing 10⁻³ M and 10⁻⁵ M of Calix respectively. It is noted that the Nyquist plot of copper in the presence of inhibitor for one hour of immersion contains slightly depressed semi-circular shape, and only one-time constant appeared, indicating that a charge transfer process mainly controls the copper corrosion. The corresponding parameters are shown in Table 6. We can see that all the diagrams are composed of a capacitive loop. Indeed, we see that the values of the charge transfer resistance R_{ct} increase with immersion time up to 12 h. in both environments and then decrease slightly. The inhibitory efficiency of the two media, 2.0 M H₃PO₄ and 0.5 M H₂SO₄, respectively reaches 82% and 94% after half an hour and then decreases with time; it is important to note that the inhibitory efficiency remains of the order of 87% at 12 h. for H₂SO₄ medium. We can notice that the value of Q_{ct} decreases with the immersion time, indicating that more inhibitory molecules are adsorbed on the metal surface and provide better surface coverage and/or improved thickness of the protective layer metal/solution interface.

In addition, the change in Q_{ct} values may be caused by the progressive replacement of water molecules by the adsorption of the inhibitory molecules on the metal surface, decreasing the extent of the dissolution reaction. So, the whole active sites become saturated with inhibitor. Moreover, C_{ct} can be expressed as:

$$C_{ct} = \varepsilon \cdot \varepsilon_0 S/d$$

Where ε is the relative dielectric constant, ε_0 is the dielectric constant in the vacuum, S and d are the surface and the thickness of the film, respectively [50]. Thus, the decrease of the capacitance values of the film can be explained by the thickening of the film [51].

Conclusion

To conclude, the spectroscopic, electrochemical results corresponding to the mechanisms of Calixarene (Calix) as a corrosion inhibitor for copper in 2.0 M H₃PO₄ and 0.5 M H₂SO₄ acid are explained by the fact that the inhibitor contains the group functional oxygen-containing and other aromatic components, which explains the inhibitory effect of this molecule. The additive Calix acts on the cathodic domain. In addition, the inhibitory efficiency increases with increasing concentration with maximum efficiency at a concentration of 10⁻³ M for H₃PO₄ and 10⁻⁵ M for H₂SO₄ at 25 °C. The inhibition mechanisms, estimated from the temperature dependence of inhibition efficiency as well as from kinetic and activation parameters, show that the additive functioned *via* a mixed inhibition mechanism. The thermodynamic data calculated for Calix confirm the physical adsorption on the metal surface for the two acid media 2.0 M H₃PO₄ and 0.5 M H₂SO₄. The study of the effect of immersion time in both media showed that the inhibition of copper achieved the best efficiency for the first 12 h.

Finally, the SEM method confirmed all previous results and showed that copper corrosion in 2.0 M H_3PO_4 and 0.5 M H_2SO_4 could be inhibited by Calix. The results obtained showed that the additive could serve as an effective inhibitor for the corrosion of copper, especially in sulphuric acid media, since it displayed better results compared to phosphoric acid media.

Figure 8. Electrochemical impedance spectra obtained after different immersion time in corrosion of copper in 2.0 M H_3PO_4 (a, b) and 0.5 M H_2SO_4 (c, d) in the absence and presence of Calixarene.

Table 6. Electrochemical parameters and the corresponding inhibition efficiencies at various immersion time of copper in 1.0 M H₃PO₄ and 0.5 M H₂SO₄.

	Time, h	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 2.0 M H ₃ PO ₄	½	7.67	88.49	0.823	1575	932	0.617	1402	2969.33	–
	1	6.35	54.76	0.816	2340	300	0.510	4299	6632.65	–
	2	6.23	111.8	0.743	1453	164	0.575	5918	7364.77	–
	4	6.51	20.44	0.910	3992	199	0.554	3888	7873.49	–
	6	6.51	17.23	0.924	4029	135	0.488	5999	10021.49	–
	12	6.53	15.56	0.932	4588	108	0.520	7208	11789.47	–
	16	6.52	23.72	0.897	3696	268	0.617	2951	6640.48	–
Calix 10 ^{–3} M	½	5.51	40.53	0.887	10178	139.9	0.813	6360	16532.49	82.0
	1	6.33	23.8	0.790	18651	72.49	0.871	10818	29462.67	77.5
	2	6.26	22.22	0.796	17034	56.48	0.786	14895	31922.74	76.9
	4	6.13	22.65	0.800	9641	32.94	0.699	23386	33020.87	76.1
	6	6.18	22.22	0.798	13013	40.41	0.724	20099	33105.82	69.7
	12	6.15	22.4	0.807	8370	33.28	0.690	22661	31024.85	62.0
	16	6.27	21.11	0.838	5034	32.75	0.670	20010	25037.73	73.5
Blank 0.5 M H ₂ SO ₄	½	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	–
Calix 10 ^{–5} M	½	3.03	29.72	0.902	4010	371	0.829	1765	5772	93.9
	1	2.8	19.94	0.929	6856	63.98	0.780	6729	13585	93.0
	2	2.8	17.25	0.939	8125	57.21	0.807	8909	17034	93.2
	4	2.7	16.6	0.943	6816	55.53	0.760	10855	17671	90.4
	6	2.1	20.99	0.908	6700	63.29	0.541	14534	21234	91.7
	12	2.7	16.82	0.950	5410	48.22	0.689	9831	15241	86.8
	16	2.7	17.67	0.945	8175	104	0.837	4388	12563	86.6

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