ORIGINAL PAPER

Novel calixarene derivatives as inhibitors of mild C-38 steel corrosion in 1 M HCl

M. Kaddouri · N. Cheriaa · R. Souane · M. Bouklah · A. Aouniti · R. Abidi · B. Hammouti · J. Vicens

Abstract Calixarenes **CA1–CA4** containing one to four 4-imidazolylethylamidocarbonyl groups were synthesized and tested as inhibitors for the corrosion of mild steel in 1 M HCl at 308 K. The study was made using Tafel polarisation and weight-loss methods. In contrast to **CA1**, calixarenes **CA2–CA4** were good inhibitors, reaching inhibition efficiencies (E%) of 94 to 100% at 10^{-4} M. The values of the inhibition efficiency calculated by the two techniques were in acceptable agreement. E% increased with the number of 4-imidazolylethylamidocarbonyl groups attached to the calixarene. Polarisation curves showed that **CA2–CA4** act as mixed-type inhibitors. Their adsorption on the steel surface followed a Langmuir isotherm. Thermodynamic parameters of adsorption were also deduced.

Keywords Corrosion · Steel · Calixarene · Inhibition · Hydrochloric acid · Chemisorption

1 Introduction

Corrosion inhibitors are often added to secure metal dissolution in acid solutions used for removal of wastes and deposits. By inhibiting metal dissolution they of course also reduce acid consumption. Many aspects of the molecular structure of organic molecules used as corrosion inhibitors have been associated with their activity and, in particular, *N*-heterocyclic compounds offer good protection of steel and iron in acidic media [1–4]. It is commonly assumed that surface coordination occurs involving lone pairs on N and/or the π-electrons of the heterocycle. Of the azoles shown to give the most effective inhibition [5–9], imidazole and amide derivatives have the advantage of also being environmentally friendly [10–15].

Calixarenes are amphiphilic molecules and their interfacial activity has been widely studied. Their adsorption on surfaces has been shown to offer useful control of surface reactivity [16, 17] and in particular we have recently shown [18] that various derivatives of calix[6]-arene offer promise as corrosion inhibitors for mild steel. In extension of this work, we now describe the inhibitory activity of a series of calix[4]arene derivatives, **CA1–CA4**, in which a number of 4-imidazolylethylcarboxamide substituents, varying from one to four, have been introduced. These molecules combine the natural amphiphilicity of calixarenes with the particular properties of an imidazole unit. The study was carried out by the gravimetric method and the potentiodynamic polarisation technique.

2 Experimental

### 2.1 Synthesis of **CA1–CA4**

CA1–CA4 (see Fig. 1) are new compounds and were prepared according to the following procedures:

M. Kaddouri · R. Souane · M. Bouklah · A. Aouniti · B. Hammouti
Laboratoire de Chimie Appliquée et Environnement, Faculté des Sciences, Oujda, Morocco
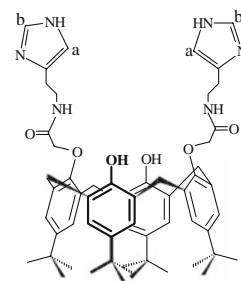
N. Cheriaa · R. Souane · J. Vicens (✉)
ECPM, IPCH, UMR 7178 du CNRS-ULP, 25 rue Becquerel, 67087 Strasbourg Cedex 2, France
e-mail: vicens@chimie.u-strasbg.fr

N. Cheriaa · R. Abidi
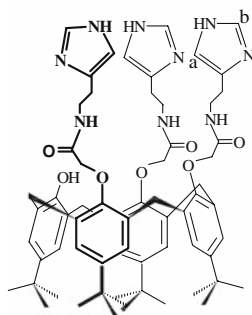Faculté des Sciences de Bizerte, 7021 Zarouna-Bizerte, Tunisie

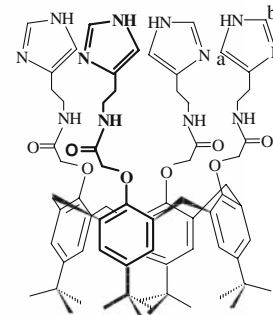**Fig. 1** Chemical formulae of calixarenes **CA1–CA4**
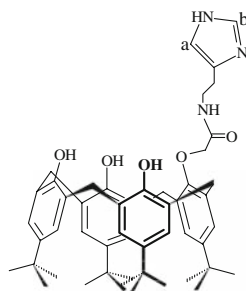
CA1 : C$_{51}$H$_{65}$O$_5$N$_3$ MM = 800,09 g mol^{-1}   **CA2 :C$_{58}$H$_{74}$O$_6$N$_6$ MM = 951,26 g mol^{-1}**

CA3 : C$_{65}$H$_{83}$O$_7$N$_9$ MM = 1102,43 g mol^{-1}   **CA4 : C$_{72}$H$_{92}$O$_8$N$_{12}$ MM = 1253,60 g mol^{-1}**

2.1.1 5,11,17,23-tetra(t-butyl)-25-(2-(4-imidazolyl) ethylamidocarbonylmethyl)calix[4]arene (*CA1*)

A mixture of the mono(methoxycarbonylmethyl) ether of t-butylcalix[4]arene (**1**) (1.441 g, 2.0 mmol) and histamine (0.277 g, 2.5 mmol) in 16 mL of a 1:1 mixture of methanol:toluene was refluxed for 6 days. The solvents were evaporated under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na$_2$SO$_4$. After filtration and evaporation, the resulting oil was purified by chromatography on a column (SiO$_2$: 9:1 CH$_2$Cl$_2$–MeOH) to yield **CA1** (1.053 g, 64%) as a white solid. Mp 148–149 °C. ^{1}H-NMR (CDCl$_3$):9.30 (t, 1H, $J = 2.5$ Hz, N*H* amide), 7.55 (s, 1H, C*H* imidazolyl-*Ha*), 7.09 (d, 2H, $J = 1.0$ Hz, Ar*H*), 7.07 (s, 2H, Ar*H*), 7.06 (s, 2H, Ar*H*), 7.02 (d, 2H, $J = 1.0$ Hz, Ar*H*), 6.93 (s, 1H, C*H* imidazolyl-*Hb*), 4.56 (s, 2H, ArOC*H$_2$*), 4.26 (d, 2H, $J = 10.1$ Hz, AB system, ArC*H$_2$*Ar), 4.18 (d, 2H, $J = 10.1$ Hz, A′B′ system, ArC*H$_2$*Ar), 3.50 (d, 2H, $J = 10.1$ Hz, AB system, ArC*H$_2$*Ar), 3.48 (d, 2H, $J = 10.1$ Hz, A′B′ system, ArC*H$_2$*Ar), 3.86 (q, 2H, $J = 5.2$ Hz, NHC*H$_2$*CH$_2$-imidazole), 3.10 (t, 2H, $J = 5.2$ Hz, C*H$_2$*-imidazole), 1.24 (s, 9H, *tert*-butyl), 1.23 (s, 18H, *tert*-butyl), 1.17 (s, 9H, *tert*-butyl). Anal.calcd. For C$_{51}$H$_{65}$O$_5$N$_3$ · 2 CH$_3$OH: C, 73.65; H, 8.52. Found: C, 73.48; H, 8.60.

2.1.2 5,11,17,23-tetra(tert-butyl)-25,27-di-2-(4-imidazolyl) ethylamidocarbonylmethyl)calix[4]arene (*CA2*)

Using the same procedure as for **CA1**: the 25,27-*bis*(methoxycarbonylmethyl) ether of t-butylcalix[4]arene

(**2**) (1.030 g, 1.3 mmol), histamine (0.288 g, 2.6 mmol) in 16 mL of a 1:1 mixture of methanol:toluene was refluxed for 4 days. The solvents were removed by evaporation under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na$_2$SO$_4$. The residue was precipitated with diethyl ether to give pure **CA2** (0.751 g, 68%) as a white solid. Mp 154–155 °C. ^{1}H-NMR (CDCl$_3$):9.11 (broad t, 2H, N*H* amide), 7.84 (s, 2H, OH), 7.46 (s, 2H, C*H* imidazolyl-*Ha*), 7.08 (s, 4H, Ar*H*), 6.95 (s, 4H, Ar*H*), 6.77 (s, 2H, C*H* imidazolyl-*Hb*), 4.58 (s, 4H, ArOC*H$_2$*), 4.13 (d, 4H, $J = 13.3$ Hz, AB system, ArC*H$_2$*Ar), 3.69 (q, 4H, $J = 7.7$ Hz, NHC*H$_2$*CH$_2$-imidazole), 3.45 (d, 4H, $J = 13.3$ Hz, AB system, ArC*H$_2$*Ar), 2.94 (t, 4H, $J = 7.7$ Hz, C*H$_2$*-imidazole), 1.28 (s, 18H, *tert*-butyl), 1.07 (s, 18H, *tert*-butyl). Anal.calcd. For C$_{58}$H$_{74}$O$_6$N$_6$ · CH$_3$OH: C, 72.05; H, 8.00; N, 8.55. Found: C, 72.43; H, 7.74; N, 8.75.

2.1.3 5,11,17,23-tetra(t-butyl)-25,26,27-tris(2-(4-imidazolyl)ethylamidocarbonylmethyl)calix[4]arene (*CA3*)

Using the same procedure as for **CA1**: the 25,26,27-*tris*(methoxycarbonylmethyl) ether of t-butylcalix[4]arene (**3**) (0.995 g, 1.15 mmol), histamine (0.771 g, 6.94 mmol) in 16 mL of a 1:1 mixture of methanol:toluene was refluxed for 5 days. The solvents were removed under reduced pressure. The residue was dissolved in dichloromethane and washed with was added. The organic layer

was dried over Na_2SO_4. The residue was precipitated with hexane-diethyl ether to give pure **CA3** (0.702 g, 68%) as a white solid. Mp 203–204 °C. ^{1}H-NMR (CDCl$_3$):8.31(broad s, 1H, N*H* amide), 7.93 (broad s, 2H, N*H* amide), 7.45 (broad s, 1H, C*H* imidazolyl-*Ha*), 7.40 (broad s, 2H, C*H* imidazolyl-*Ha*), 7.16 (s, 2H, Ar*H*), 7.07 (s, 2H, Ar*H*), 6.70 (broad s, 1H, C*H* imidazolyl-*Hb*), 6.66 (broad s, 2H, C*H* imidazolyl-*Hb*), 6.59 (s, 2H, Ar*H*), 6.53 (s, 2H, Ar*H*), 6.03 (s, 1H, O*H*), 4.41–4.35 (m, 6H, ArOC*H*$_2$), 4.27 (d, 4H, $J = 10.9$ Hz, AB system, ArC*H*$_2$Ar), 3.70–3.44 (m, 6H, NHC*H*$_2$C*H*$_2$-imidazole), 3.24 (d, 4H, $J = 10.9$ Hz, AB system, ArC*H*$_2$Ar), 2.89–2.72 (m, 6H, C*H*$_2$-imidazole), 1.32 (s, 18H, *tert*-butyl), 0.83 (s, 18H, *tert*-butyl). Anal.calcd. For $C_{65}H_{83}O_7N_9 \cdot 4\ CH_3OH$: C, 66.86; H, 7.55; N, 11.65. Found: C, 66.86; H, 7.48; N, 10.17.

2.1.4 5,11,17,23-tetra(t-butyl)-25,26,27,28-tetrakis-2-(4-imidazolyl)ethylamidocarbonylmethyl)-calix[4]arene (CA4)

Using the same procedure as for **CA1**: the 25,26,27,28-*tetrakis*(methoxycarbonylmethyl) ether of t-butylcalix[4]arene (**4**) (0.937 g, 1.0 mmol), histamine (0.889 g, 8.0 mmol) in 16 mL of a 1:1 mixture of methanol : toluene was refluxed for 6 days. The solvents were removed under reduced pressure. The residue was dissolved in dichloromethane and washed with water. The organic layer was dried over Na_2SO_4. The residue was precipitated with hexane to give pure **CA4** (0.752 g, 56%) as a white solid. Mp ≥ 300 °C. ^{1}H-NMR (insoluble in chloroform, CD$_3$OD): 7.56 (s, 4H, C*H* imidazolyl-*Ha*), 6.85 (s, 8H, Ar*H*), 6.77 (s, 4H, C*H* imidazolyl-*Hb*), 4.53 (d, 4H, $J = 13.3$ Hz, AB system, ArC*H*$_2$Ar), 4.48 (s, 8H, ArOC*H*$_2$), 3.53 (t, 8H, $J = 7.3$ Hz, NHC*H*$_2$C*H*$_2$-imidazole), 3.23 (d, 4H, $J = 13.3$ Hz, AB system, ArC*H*$_2$Ar), 2.82 (t, 8H, $J = 7.3$ Hz, C*H*$_2$-imidazole), 1.09 (s, 36H *tert*-butyl). Anal.calcd. For $C_{72}H_{92}O_8N_{12} \cdot 2\ CH_3OH$: C, 67.44; H, 7.65; N, 12.76, Found C, 67.98; H, 7.25; N, 12.34.

2.2 Gravimetric and polarisation measurements

The mild C38-steel used had the following chemical composition (wt%): 0.09 P; 0.38 Si; 0.01 Al; 0.05 Mn; 0.21 C; 0.05 S and Fe to balance. Prior to all measurements, samples were polished with different emery papers up to 1200 grade, washed thoroughly with bi-distilled water, degreased with AR grade ethanol and acetone, and then dried at room temperature. The corrosion medium (1 M HCl) was prepared by dilution of Analytical Grade 37% HCl with bi-distilled water.

Gravimetric measurements were carried out in a double-walled glass cell equipped with a thermostat-cooling condenser. The solution volume was 100 mL. The steel

specimens had a rectangular form (2 cm × 2 cm × 0.05 cm). The immersion time for the loss of weight was 6 h at 308 K. After the corrosion test, the specimens were carefully washed in bi-distilled water, dried and weighed. The rinse removed loose segments of any corrosion films. Duplicate experiments were performed in each case and the mean value of the weight loss is reported. The different weight losses were used to calculate a mean rate value expressed in mg cm^{-2} h^{-1}.

Electrochemical measurements were carried out in a conventional cylindrical, three-electrode Pyrex-glass cell. The steel working electrode (WE) was cut circular with a geometrical area of 1 cm^2 and was embedded in PTFE (polytetrafluoroethylene). A saturated calomel electrode (SCE) and a platinum disc electrode were used as reference and auxiliary electrodes, respectively. The temperature was controlled at 308 ± 1 K. The WE was abraded with silicon carbide paper (grade 1200), degreased with ethanol and acetone, and rinsed with bi-distilled water before use.

3 Results and discussion

3.1 Weight-loss tests

Although the neutral calix[4]arenes **CA1–CA4** are of very low solubility in water, their solubility is enhanced by protonation of the imidazole units, so that concentrations in the range 10^{-4}–10^{-6} M used in the corrosion tests were readily obtained. The weight-loss results for steel in 1 M HCl at different calixarene concentrations after 6 h immersion at 308 K are given in Table 1. The inhibition efficiency (E$_w$%) values were calculated from the equation:

$$E_w\% = \frac{W_{corr} - W_{corr(inh)}}{W_{corr}} \times 100 \qquad (1)$$

where $W_{corr(inh)}$ and W_{corr} are the corrosion rates of steel in the presence and absence, respectively, of the inhibitor.
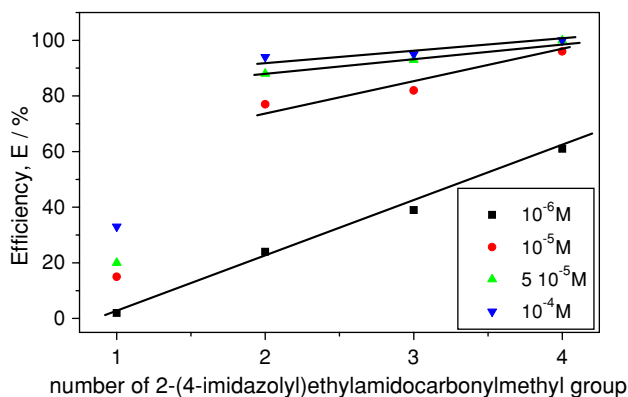
Clearly, all the calixarenes produce some degree of corrosion inhibition, though this depends upon the concentration and the number of substituents, so that E$_w$% increases with increasing inhibitor concentration to reach 33, 94, 95 and 100% at 10^{-4} M of **CA1–CA4**, respectively. The most effective corrosion protection agent is **CA4**, which provides complete protection (over 6 h) at a concentration as low as $\sim 5 \times 10^{-5}$ M. The inhibition efficiency indeed appears to be a linear function of the number of imidazole-containing substituents (Fig. 2).

3.2 Polarisation measurements

Figure 3 depicts the polarisation curves of mild steel in 1 M HCl as a function of the concentration of **CA4**. The values of

Table 1 Weight-loss measurements for mild steel after 6 h immersion in 1 M HCl at 308 K in the presence of various concentrations of calix[4]arene derivatives
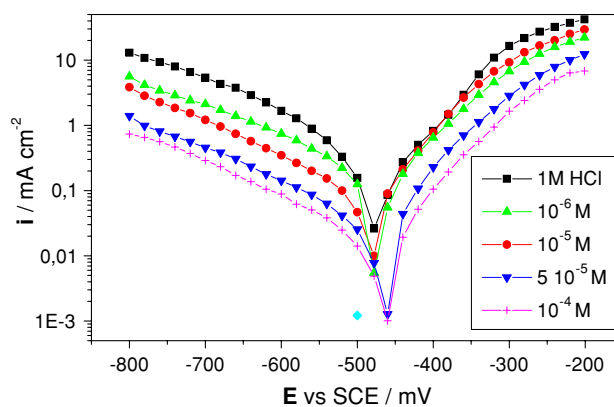
Inhibitor	Concentration (M)	W (mg cm^{-2} h^{-1})	E$_w$ (%)	θ
HCl	1	4.406	–	–
CA1	10^{-6}	4.338	1.5	0.02
	10^{-5}	3.787	14.0	0.14
	5×10^{-5}	3.509	20.3	0.20
	10^{-4}	2.938	33.3	0.33
CA2	10^{-6}	3.354	23.8	0.24
	10^{-5}	1.011	77.1	0.77
	5×10^{-5}	0.563	87.2	0.87
	10^{-4}	0.274	93.7	0.94
CA3	10^{-6}	2.699	38.7	0.39
	10^{-5}	0.803	81.7	0.82
	5×10^{-5}	0.303	93.1	0.93
	10^{-4}	0.286	93.5	0.94
CA4	10^{-6}	1.751	60.2	0.60
	10^{-5}	0.156	96.4	0.96
	5×10^{-5}	0.0023	99.9	1.00
	10^{-4}	0.000	100	1.00

Fig. 3 Polarisation plots of steel in 1 M HCl at various concentrations of **CA4**

Fig. 2 Variation of E$_w$% with the number of 2-(4-imidazolyl)ethylamidocarbonylmethyl groups

Table 2 Electrochemical parameters and deduced corrosion inhibition efficiencies of steel under various concentrations of **CA1–CA4** in 1 M HCl at 308 K

Inhibitors	Conc (M)	E$_{corr}$ versus SCE (mV)	b$_c$ (mVdec^{-1})	I$_{corr}$ (µA cm^{-2})	E (%)
HCl	1	485	176	495	–
CA1	10^{-4}	470	255	255	48
CA2	10^{-6}	475	226	210	57
	10^{-5}	478	189	76	85
	5×10^{-5}	455	190	65	87
	10^{-4}	465	185	50	90
CA3	10^{-6}	480	226	349	30
	10^{-5}	495	190	80	83
	5×10^{-5}	480	191	60	87
	10^{-4}	470	203	47	90
CA4	10^{-6}	480	218	280	43
	10^{-5}	475	203	200	60
	5×10^{-5}	470	246	90	81
	10^{-4}	468	182	18	96

the corrosion parameters E$_{corr}$, I$_{corr}$ and β_c obtained from potentiodynamic polarization curves for the steel in 1 M HCl containing different concentrations of **CA1–CA4** are summarised in Table 2. From these measurements, the inhibition efficiencies (E$_I$%) were estimated from the expression:

$$EI\% = \frac{I_{corr} - I_{corr(inh)}}{I_{corr}} \times 100 \qquad (2)$$

where I$_{corr}$ and I$_{corr (inh)}$ are the corrosion current density values with and without the inhibitor, respectively, determined by extrapolation of cathodic Tafel lines to the corrosion potential.

The corrosion current density (i$_{corr}$) of the steel electrode under these conditions was 495 µA cm^{-1}. It is clear that i$_{corr}$ decreased with increasing calixarene concentration. Addition of calixarene compounds to the acid solution affected both the cathodic and anodic parts of the curves. However, the corrosion potentials of specimens in acid containing the inhibitors were almost constant and not shifted in anodic or cathodic directions. The cathodic Tafel plots indicated that hydrogen evolution was activation-controlled and the change of β_c towards higher values indicated that the reduction mechanism was affected by the presence of inhibitors. Thus, both hydrogen evolution and
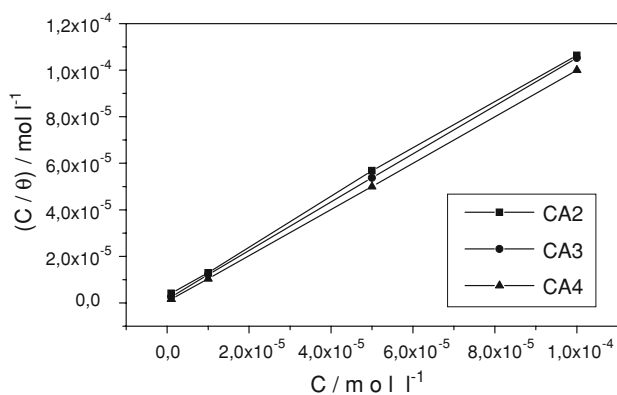
Fig. 4 Langmuir isotherm adsorption model of **CA2**–**CA4** on the surface of steel in 1 M HCl

steel dissolution were inhibited, so that **CA1**–**CA4** can be described as mixed-type inhibitors.

3.3 Adsorption isotherms

A Langmuir adsorption isotherm [19] was found to provide the best description of the adsorption behaviour

$$\frac{C_{inh}}{\theta} = \frac{1}{k} + C_{inh} \tag{3}$$

$$k = \frac{1}{55.5} \cdot \exp\left(-\frac{\Delta G_{ads}^{\circ}}{R \cdot T}\right) \tag{4}$$

where C_{inh} is the inhibitor concentration; θ is the fraction of the surface covered, k is the adsorption equilibrium and ΔG_{ads}° is standard free energy of adsorption. This equation applies in principle only to smooth surfaces where the adsorbing particles do not interact [20].

Figure 4 shows the dependence of the ratio C/θ of the covered surface as function of the concentration (C) of **CA2**–**CA4**. The degree of surface coverage θ for different concentrations of the inhibitors in acidic media was evaluated from the weight loss measurements using the equation [21]:

$$\theta = \frac{W_{(\theta=0)} - W_{\theta}}{W_{(\theta=0)} - W_{(\theta=1)}} \tag{5}$$

While various mechanisms for the adsorption of nitrogen-containing molecules on metal surfaces have been proposed [22–24], protonation of the imidazole units under the acidic conditions used presently would appear to exclude the involvement of N lone pairs of **C1**–**C4** in coordination to Fe. (See ahead for further discussion of this issue.)

The plots in Fig. 4 are linear with slopes to close to unity and regression coefficients R > 0.999. Thus, it would appear that the inhibitor molecules do not interact on the steel surface. The intercept allows the calculation of the equilibrium constant K and so of ΔG_{ads}° (Table 3).

Table 3 Adsorption parameters for **CA2**–**CA4** in HCl solution

	Linear regression coefficient (r)	Slope	K	$\Delta G_{ads}^{\circ}/kJ\ mol^{-1}$
CA2	0.9997	1.038	302571.9	−42.63
CA3	0.99999	1.036	578837.7	−44.29
CA4	0.99999	0.994	1953239.4	−47.41

Stronger adsorption (more negative ΔG_{ads}°) can be associated with higher inhibition efficiency [25, 26]. Values of ΔG_{ads}° of less than–40 kJ mol^{-1} are usually taken as indicative of chemisorption, i.e., the formation of a bond between the inhibitor and the surface [27]. The ΔG_{ads}° values presently obtained are therefore taken as indicative of this situation and indeed we observed the formation of an adherent yellow film on the surface of the steel immediately following its immersion in inhibitor-containing solutions. Although interaction via coordination of imidazole-N to iron is possible [28], the fact that the imidazole units of **C1**–**C4** would be protonated in 1 M HCl probably excludes such coordination and thus it may be that the surface binding involves π-coordination of the calixarene to Fe [29]. Given that Cl$^-$ is well known to catalyse electron transfer reactions involved in the corrosion of iron, it is possible that not only do the calixarenes block the surface by their adsorption but that they prevent close approach of Cl$^-$ to the surface by forming inclusion complexes involving H-bonding of the anion to the protonated imidazole units [30].

4 Conclusion

The principal conclusions are drawn from the present study are:

- **CA1**–**CA4** act as mixed-type inhibitors and their inhibition efficiencies increase with increasing inhibitor concentration.
- The protection ability of these inhibitors decreases in the order of **CA4** > **CA3** > **CA2** > **CA1**, with **CA4** providing essentially complete protection over extended periods at concentrations below 10^{-4} M.
- The inhibition order **CA4** > **CA3** > **CA2** > **CA1** reflects the strength of their adsorption on the mild steel surface. The adsorption fits the Langmuir isotherm model.

The actual mechanism of corrosion inhibition by calixarenes remains a subject for further investigation but it is possible that it involves both blockage of the surface by film formation and inhibition of electron transfer by the binding of catalytically active anions.

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