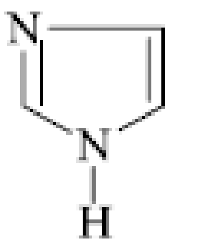
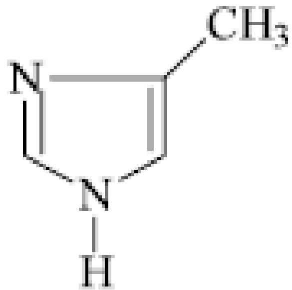
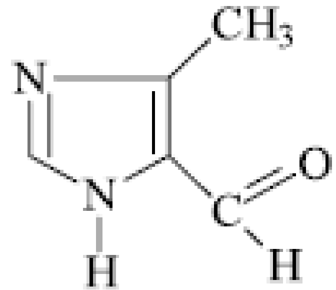
CORROSION INHIBITORS



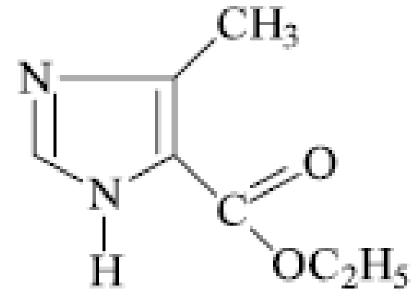
Imidazole
Inh1



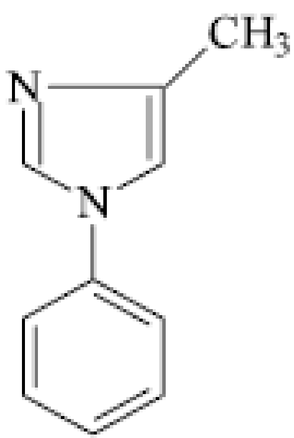
4-methylimidazole
Inh2



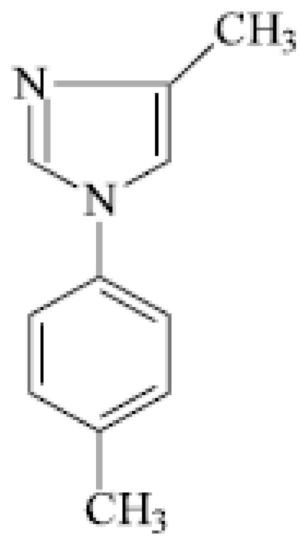
4-methyl-5-imidazole
carbaldehyd



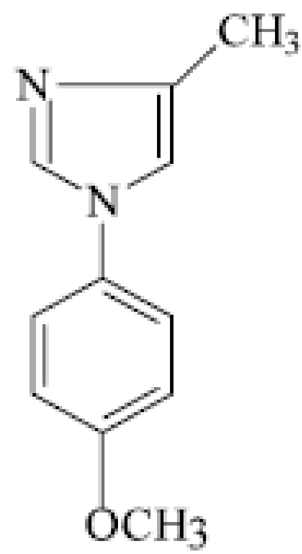
ethyl-4-methyl-5-
imidazole carboxylate
Inh4



1-phenyl-4-methyl
imidazole
Inh5

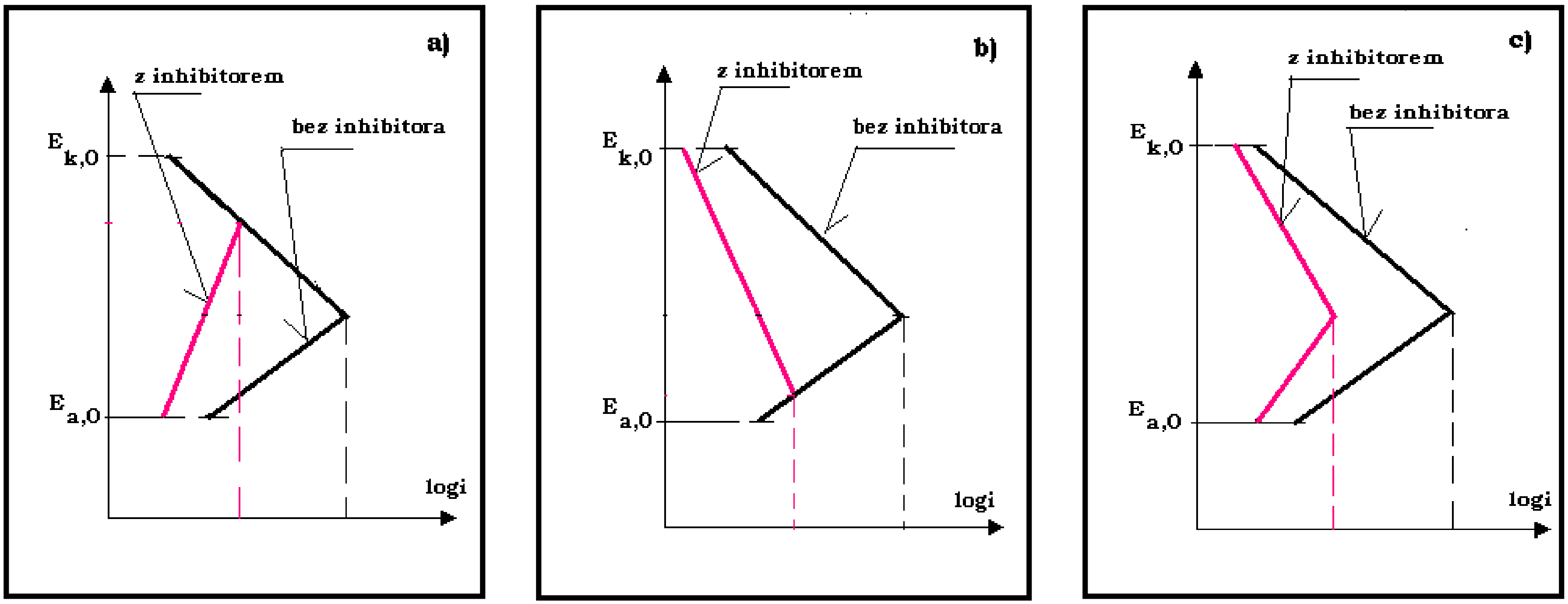


1-(p-tolyl)-4-methyl
imidazole
Inh6



4-methyl-1(4-methoxyphenyl)
imidazole
Inh7

Inhibitors



(a) **anodic inhibitors**:
phosphates
silicate compounds

(b) **Cathodic inhibitors**
poly-phosphates
Ca(HCO3)2
methylamino-phosphate

(c) **mixed anodic and cathodic inhibitors**
amines
selenides

Inhibitors

Types of Corrosion Inhibitors

Organic

These materials are characterized by high molecular weight structures, incorporating nitrogen or phosphorous groups. They are usually highly polar molecules.

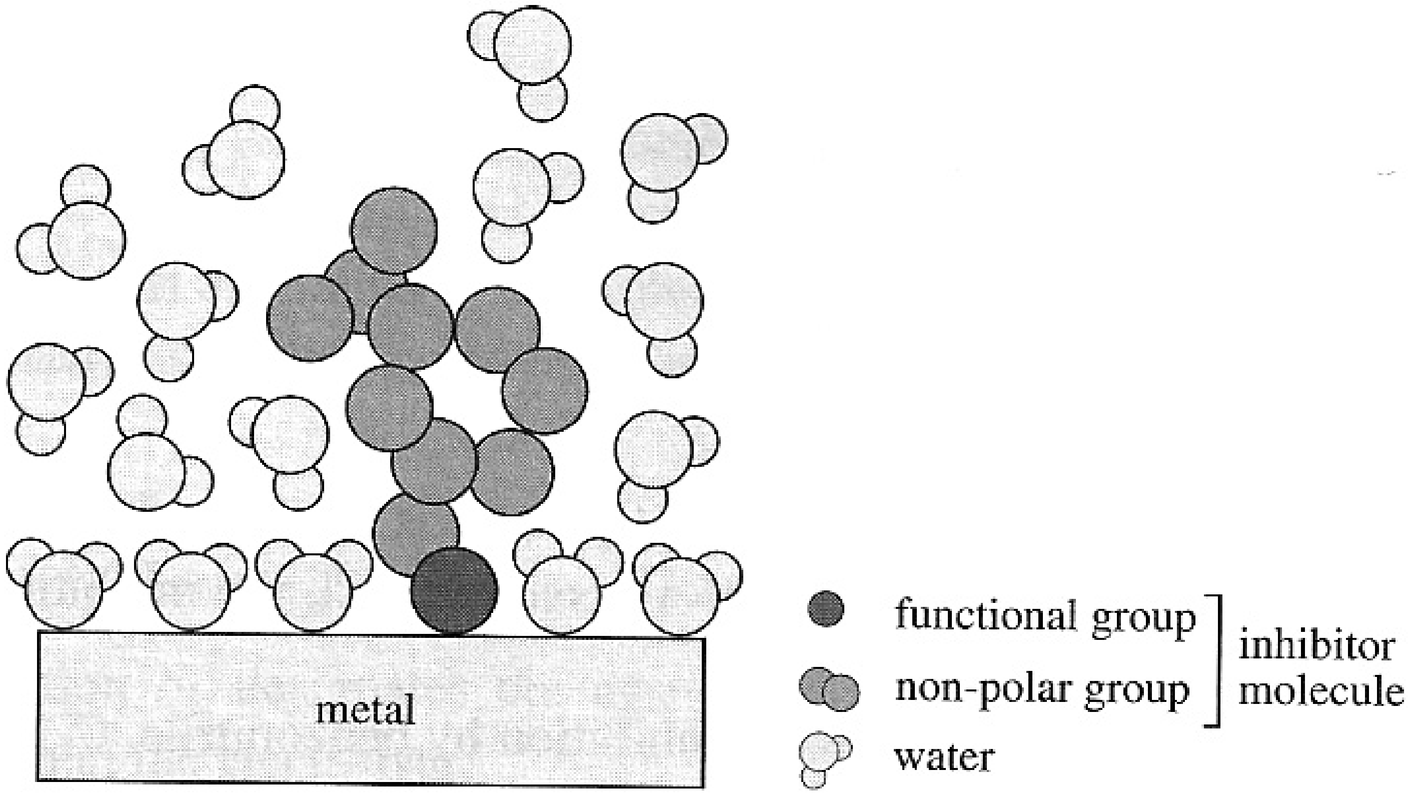
Phosphate Esters
Phosphonates

Inorganic

Salts of some metals and amphoteric elements act as corrosion inhibitors. Quite often these materials have tenacious filmforming or passivation effects. In some instances, they react with the metal surface.

Chromate Salts
Zinc Salts
Molybdate Compounds
Phosphates
Nitrite Salts
Silicate Compounds

Inhibitors



Adsorption of organic inhibitor onto a metal surface in aqueous environment

Inhibitor efficiency

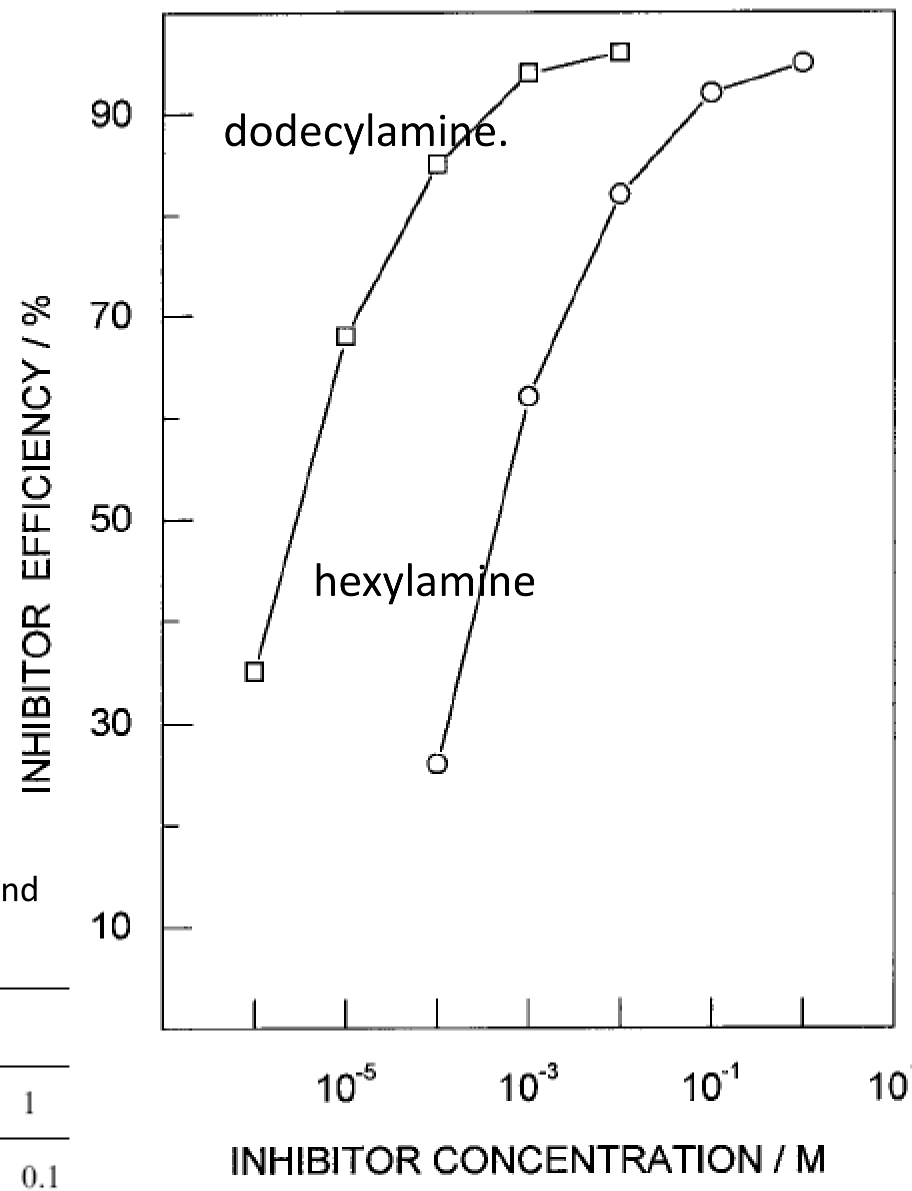
The percentage inhibitor efficiency is given by:

$$\frac{W_o - W_i}{W_o} \times 100$$

where Wo and Wi represent weight loss in the absence and presence of inhibitor, respectively.

Mild steel corrosion rate in 2.0 M HCl in the presence and absence of inhibitor

Inhibitor concentration/M	Corrosion rate × 10^6/kg m^{-2} s^{-1}							
	0	10^{-6}	10^{-5}	10^{-4}	10^{-3}	10^{-2}	10^{-1}	1
Hexylamine	2.8	–	–	2.1	1.1	0.5	0.2	0.1
Dodecylamine	2.8	1.8	0.9	0.4	0.2	0.1	–	–



Mechanism of inhibition

According to Bockris and Drazic, the inhibition mechanism can be explained by the Fe±(Inh)ads reaction intermediates

$$\mathrm{Fe} + \mathrm{Inh} \leftrightarrow \mathrm{Fe{-}(Inh)_{ads}} \leftrightarrow \mathrm{Fe}^{n+} + n\mathrm{e}^- + \mathrm{Inh}$$

This Fe-(Inh)ads intermediate forms an adsorption layer through the nitrogen atom of the inhibitor. The adsorption layer acts as a hindrance to the solution and enhances the protection of the metal surface.

The adsorption of an organic compound on the surface of a mild steel electrode is regarded as a substitutional adsorption process between the organic compound in the aqueous phase (Org_{ad}) and the water molecules adsorbed on the mild steel surface (H_2O_{ad})

$$\mathrm{Org_{aq}} + X\,\mathrm{H_2O_{ad}} \leftrightarrow \mathrm{Org_{ad}} + X\,\mathrm{H_2O_{aq}}$$

where X is the size ratio, that is, the number of water molecules replaced by one organic molecule.

The degree of surface coverage θ can be plotted as a function of the concentration of hexylamine or dodecylamine inhibitors in the hydrochloric acid solution. The value of θ was calculated from the inhibitor eciency relationship:

$$\theta = \frac{W_\mathrm{o} - W_\mathrm{i}}{W_\mathrm{o}}$$

Adsorption isotherm

Interaction between the organic compounds and metal surfaces

Temkin isotherm

$$\exp(f \cdot \theta) = k_{\text{ads}} \cdot C$$

Langmuir isotherm

$$\frac{\theta}{1-\theta} = k_{\text{ads}} \cdot C$$

Frumkin isotherm

$$\frac{\theta}{1-\theta} \cdot \exp(-2f \cdot \theta) = k_{\text{ads}} \cdot C$$

Freundluich isotherm

$$\theta = k_{\text{ads}} \cdot C$$

Adsorption isotherm plots

The most commonly used substitutional isotherms:

Flory-Huggins $$kc = \frac{\theta}{X(1-\theta)^X}$$ H.P. Dhar, B.E. Conway and K.M. Joshi, Electrochim. Acta 18 (1973) 789.

Dhar-Flory-Huggins $$kc = \frac{\theta}{e^{(X-1)}(1-\theta)^X}$$ H.P. Dhar, B.E. Conway and K.M. Joshi, Electrochim. Acta 18 (1973) 789.

Bockris-Swinkels $$kc = \frac{\theta}{(1-\theta)^X}\frac{[\theta + X(1-\theta)]^{(X-1)}}{X^X}$$ J. O'M. Bockris and D.A.J. Swinkels, J. Electrochem. Soc. 111 (1964) 736.

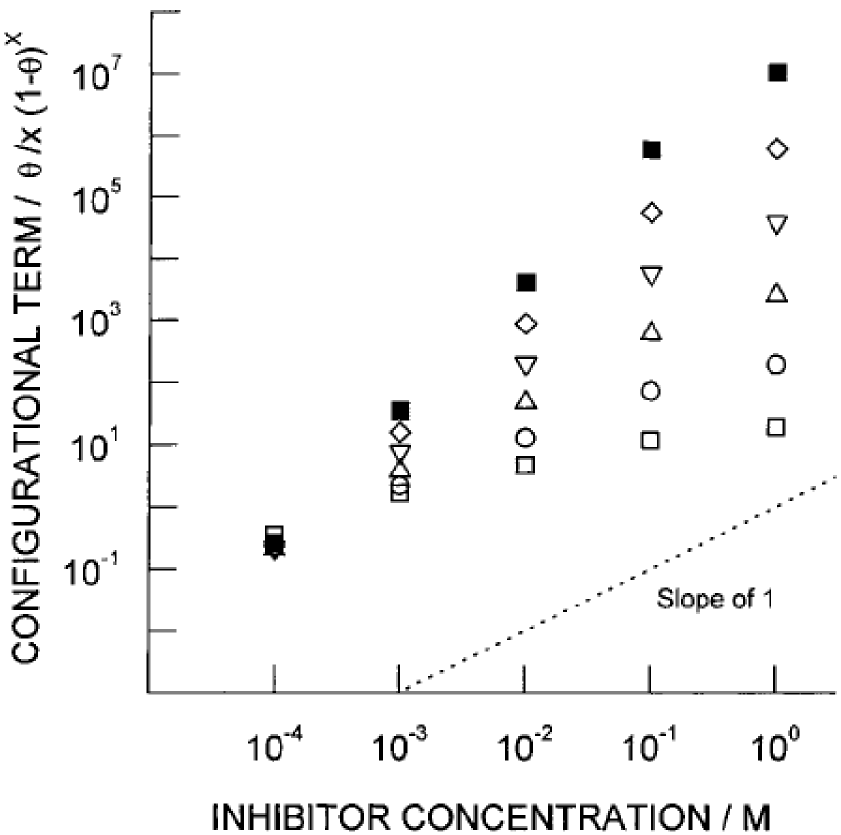
where *X* is the number of water molecules replaced by one molecule of organic compound, c is the inhibitor concentration and k is the equilibrium constant of the adsorption reaction given by: k_c = 1/55.5[exp($-\Delta G_{ads}^0$/RT)].

Equations at the top may be written as:

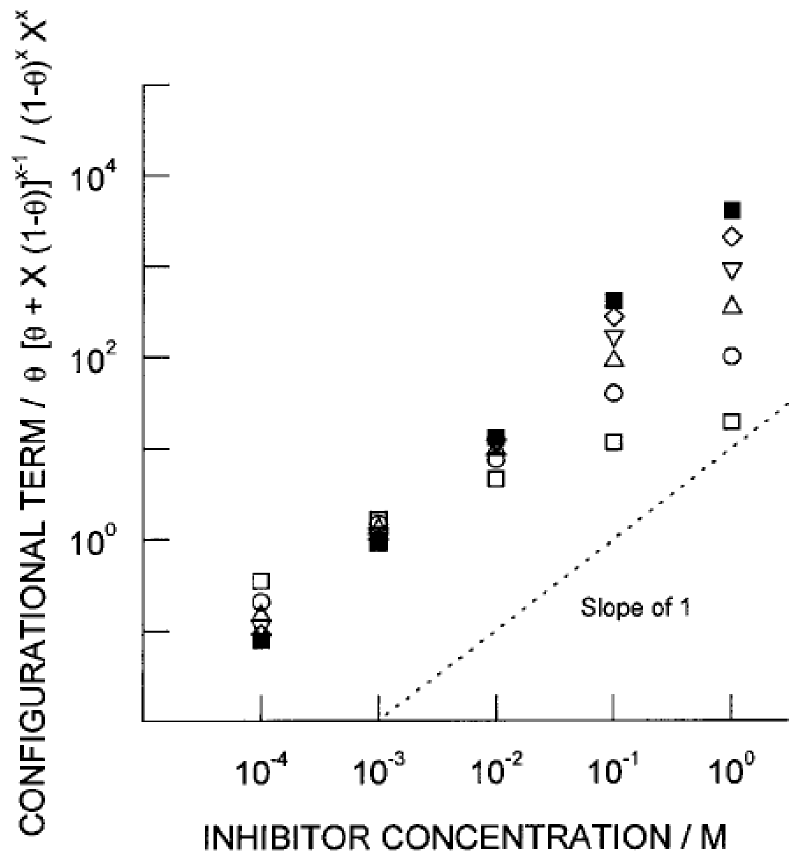
$$\log[f(\theta, X)] = \log\ c + \log\ k$$

where f (θ, X) is the configurational term, which depends essentially on the physical model and assumptions underlying the derivation of the isotherm .

A plot of log f (θ, X) against log c, for a specified value of X, is a straight line with a slope of unity, and the ordinate axis intercept gives the log k value.



Flory-Huggins isotherm plot



Bockris-Swinkels isotherm plot

for mild steel in 2.0 M HCl acid solution, at 298 K, for 24 h experimentation and for values of X up to 6. Key: (□) $X = 1$, (○) $X = 2$, (△) $X = 3$, (▽) $X = 4$, (◇) $X = 5$ and (■) $X = 6$.

J.M. BASTIDAS, J.L. POLO and E. CANO , Journal of Applied Electrochemistry 30: 1173±1177, 2000.

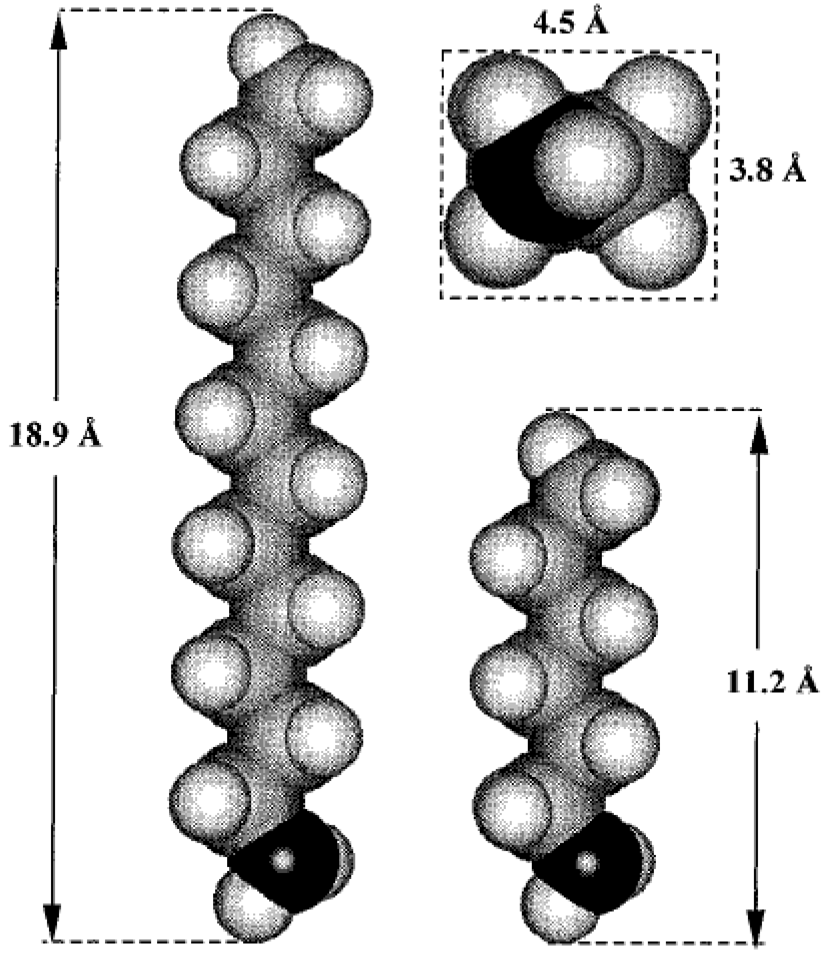
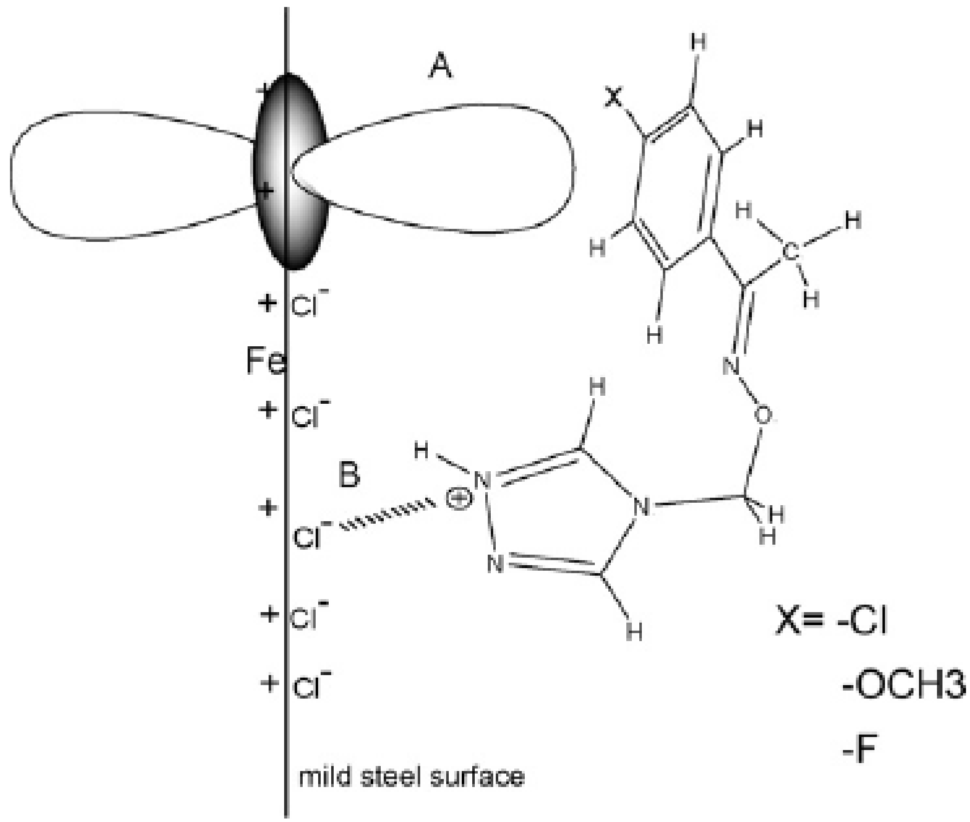


Fig. 5. Front view of hexylamine (bottom right) and dodecylamine (left) molecules adsorbed onto mild steel electrode. Top view (upper right corner).

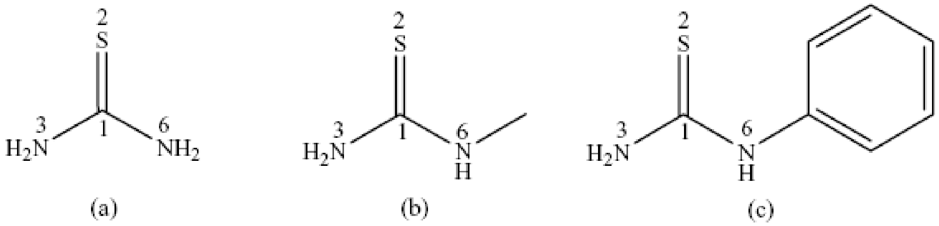
the area occupied by a vertically-oriented adsorbed hexylamine/dodecylamine molecule is about 17 $A^{o\,2}$ (the projected area of a rectangle surrounding a molecule), as compared with 50 $A^{o\,2}$ for hexylamine and 85 $A^{o\,2}$ for dodecylamine for the horizontal orientations

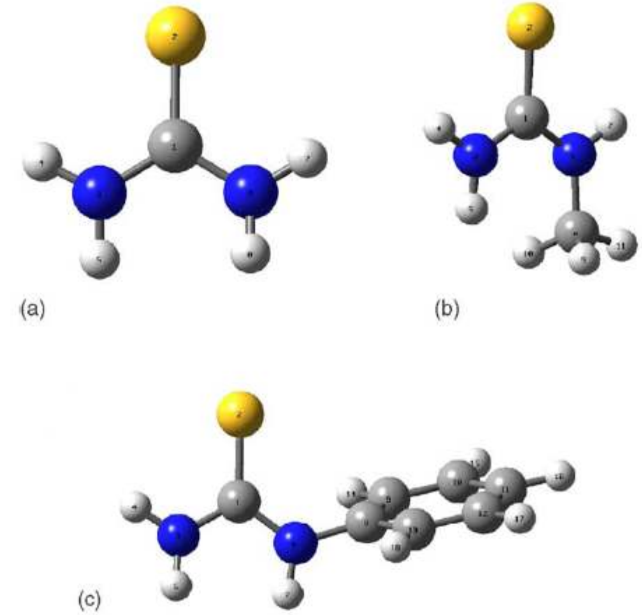


Two kinds of adsorption can be acting on steel surface:

Type A means the interaction between the benzene ring, C N and the vacant, low energy d-orbitals of Fe surface atoms, this process is called chemisorption. Type B shows the electrostatic interaction between the positively charged N atom and the negatively charged Cl− on mild steel surface, which is regard as physisorption.

Weihua Li a, *, *Qiao Heb, Changling Pei c, Baorong Houa,* Electrochimica Acta 52 (2007) 6386–6394





M. Özcan, I˙. Dehri, M. Erbil, Applied Surface Science 236 (2004) 155–164

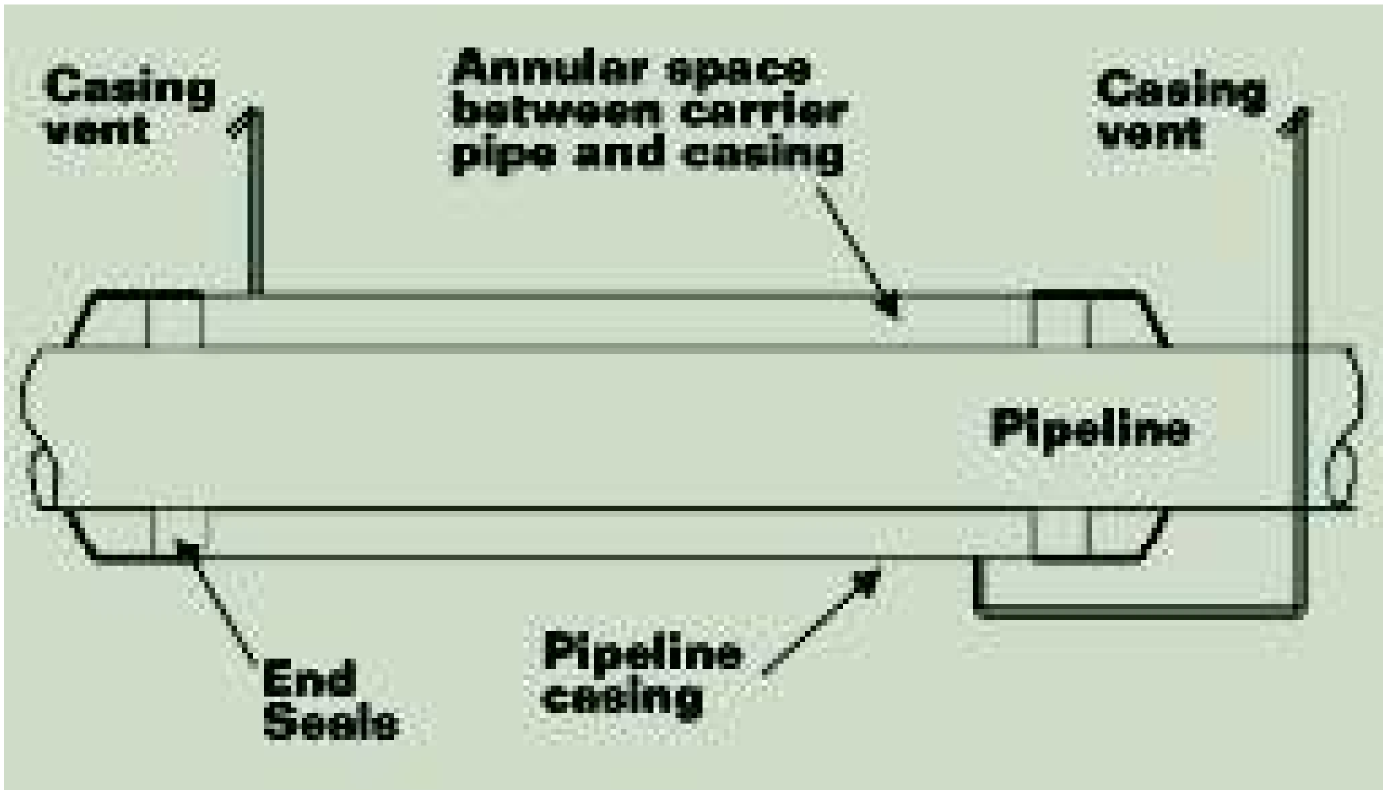
Impedance parameters and inhibition efficiency for the corrosion of mild steel in 0.1 M H_2SO_4 with and without addition of various concentrations of TU, MTU and PTU

Molecule	Inhibition concentration (M)	E_{corr} vs. Ag/AgCl (V)	R_p (Ω)[a]	R_p (Ω)[b]	C_{dl} (μF)	IE (%)
Blank	–	−0.526	36	25	137	–
TU	10^{-4}	−0.532	66	52	53.3	51.9
	10^{-3}	−0.521	224	192	39.0	87.0
	10^{-2}	−0.511	376	351	31.6	92.9
MTU	10^{-4}	−0.520	62	51	32.0	51.0
	10^{-3}	−0.505	293	330	18.8	92.4
	10^{-2}	−0.494	577	563	16.2	95.6
PTU	10^{-4}	−0.520	62	49	86.5	49.0
	10^{-3}	−0.497	820	788	7.86	96.8
	10^{-2}	−0.454	905	896	8.37	97.2

[a] R_p from polarisation resistance measurements.
[b] R_p from Nyquist diagrams.

Application of corrosion inhibitors

A vapor phase corrosion inhibitor is used to protect the annular space in road crossings.



Below ground road casing. Annular space between the casing and the carrier pipe can be protected with a VpCI or filled to mitigate corrosion in the annular space.

Application of corrosion inhibitors

Engine coolants	Sodium chromate	Fe, Pb, Cu, Zn	0.1-1%
..	Sodium nitrite	Fe	0.1-1%
..	Borax	..	1%
Glycol/water	Borax + MBT	All	1% + 0.1%
Oil field brines	Sodium silicate	Fe	0.01%
..	Quaternaries	..	10-25 ppm
..	Imidazoline	..	10-25ppm
Seawater	Sodium silicate	Zn	10 ppm
..	Sodium nitrite	Fe	0.5%
..	Calcium bicarbonate	All	pH dependent
..	Sodium phosphate monobasic + Sodium nitrite	Fe	10 ppm + 0.5%

System	Inhibitor	Metals	Concentration
Acids			
HCl	Ethylaniline	Fe	0.5%
..	Mercaptobenzotriazole	..	1%
..	Pyridine + phenylhydrazine	..	0.5% + 0.5%
..	Rosin amine + ethylene oxide	..	0.2%
Sulfuric	Phenylacridine	..	0.5%
Phosphoric	Sodium iodide	..	200 ppm
Others	Thiourea	..	1%
..	Sulfonated castor oil	..	0.5-1.0%
..	Arsenic Oxide	..	0.5%
..	Sodium arsenate	..	0.5%
Water			
Potable	Calcium bicarbonate	Steel, cast iron	10 ppm
..	Polyphosphate	Fe, Zn, Cu, Al	5-10 ppm
..	Calcium hydroxide	Fe, Zn, Cu	10 ppm
..	Sodium silicate	..	10-20 ppm
Cooling	Calcium bicarbonate	Steel, cast iron	10 ppm
..	Sodium chromate	Fe, Zn, Cu	0.1%
..	Sodium nitrite	Fe	0.05%
..	Sodium phosphate monobasic	..	1%
..	Morpholine	..	0.2%
Boilers	Sodium phosphate monobasic	Fe, Zn, Cu	10 ppm
..	Polyphosphate	..	10 ppm
..	Morpholine	Fe	variable
..	Hydrazine	..	O2 scavenger
..	Ammonia	..	neutralizer
..	Octadecylamine	..	variable