Some Aminoacids and Aminoesters as Non Toxic Inhibitors for the Corrosion of Iron in 0.5M H_2SO_4

D. Bouzidi[1], S. Kertit[2], H. Hammouti[1] and M. Brighli[1]

1. Laboratoire de Chimie Analytique appliqué, Faculte des Science d'Oujda, Morocco

2. Laboratoire de Physico-Chimie des materiaux, LAF 502, Ecole Normale Superieure de Takaddoum, B.P. 5118, Rabat, Morocco.

The study of the effect of some aminoacids and aminoesters as non toxic inhibitors on the corrosion behaviour of iron in 0.5M H_2SO_4 show that (i) inhibition efficiency increases with concentration and reaches a maximum value at 10^{-2}M (ii) these compounds are adsorbed on iron surface and obey Langmuir isotherm (iii) the order of inhibition efficiency is: $METOC_2H_5$ = $METOCH_3$ = METOH > LYS > HIS > THR > PHE > GLU > SER (iv) inhibition efficiency increases with substitution of one hydrogen in α position by a functional group containing sulphur atom. Polarisation measurements indicate the METOH, $METOCH_3$ and $METOC_2H_5$ as cathodic inhibitor and act by simple adsorption mode without changing the mechanism of the hydrogen evolution reaction.

The inhibition of corrosion of metals and alloys in acid solutions is of great economic and scientifc interest [1]. The inhibitor appears to act by the adsorption of molecules or ions at the iron / solution interface. However, detailed mechanism of inhibition is still not clear. The adsorption depends on (a) the chemical structure of inhibitors (b) the type of aggressive acid and (c) the nature and surface charge of the metal. The presence of electronegative functional groups as well as triple bond or aromatic ring in their structure increases the adsorption process [2-4].

Unfortunately, the use of organic inhibitor has recently been the subject of ecological concern due to their toxicity. Their toxic properties are caused by the aromatic and nitrogen containing heterocyclic compounds which find large application in pickling processes and in the oil industry [5,6]. The researches are reoriented to other type of non-toxic molecules. Some aminoacid type compounds have been used as good corrosion inhibitors [7,8].

In continuation of our study on the inhibitory action of some non toxic aminoacids and aminoesters [9,10], we are reporting in the present work, the application of some aminoacids and aminoesters as corrosion inhibitor for iron in 0.5M H_2SO_4 using electrochemical steady-state and gravimetric methods. The molecular structure of these compounds are given in Table 1.

EXPERIMENTAL

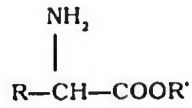
The iron specimens used were cut from a commerical iron "Ref. LS99376JV. Fe 000405 / 14" from Good Fellow, England. Some tests were carried out with Armco type iron for comparison. Prior to

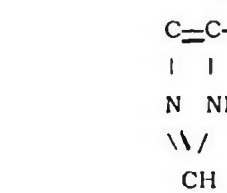
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Table 1

The Formulae of Aminoacids and Aminoesters studied

General formula



Compound	R	R'
D-serine (SER)	$HO-CH_2-$	H
L-glutamine (GLU)	$NH_2-(O)C-CH_2-CH_2-$	H
L-phenylalanine (PHE)	$Phenyl-CH_2-$	H
L-threonine (THR),	$CH_3-CH(OH)-$	H
L-histidine		H
L-lysine (LYS)	$NH_2-CH_2-CH_2-CH_2-CH_2-$	H
L-methionine (METOH)	$CH_3-S-CH_2-CH_2-$	H
L-methionine methylester ($METOCH_3$)	$CH_3-S-CH_2-CH_2-$	CH_3
L-methionine ethyl ester ($METOC_2H_5$)	$CH_3-S-CH_2-CH_2-$	C_2H_5

electrochemical and gravimetric measurements, the iron specimens were polished with different emery papers, washed thoroughly with doubly distilled water, rinsed with acetone and dried in air.

The aggressive solutions (0.5M H_2SO_4) were prepared by diluting analytical grade H_2SO_4 with doubly distilled water. All tests were made in magnetically stirred and deaerated solutions. The aminoacids and aminoesters are from the "Aldrich" commercial products.

Electrochemical measurements were carried out in a conventional cylindrical pyrex glass cell with three electrodes. A disc cut from iron (99.5%, d=0.05cm) sheet with a geometric area of 1.0 cm^2 was the working electrode. A saturated calomel electrode (SCE) and platinum electrode were the reference and auxiliary electrodes. The temperature was thermostatically controlled.

The polarization curves were recorded with an Amel potentiostat and an Amel linear sweep generator using a scan rate of 20 mV/min. Before recording the cathodic polarisation curves, the iron electrode was polarized at -800 mV *vs* SCE for 10 min. For anodic curves, the electrode was

maintained at its corrosion potential for 30 min and swept to more positive values.

The weight loss was measured with iron sheets of 2 cm^2 apparent surface area in 100 ml of acid. The corrosion rate was determined by the relation

$$W = \Delta m / St \qquad .....(1)$$

were Δm is the weightloss, S the surface area of specimen and t is the duration of experiment.

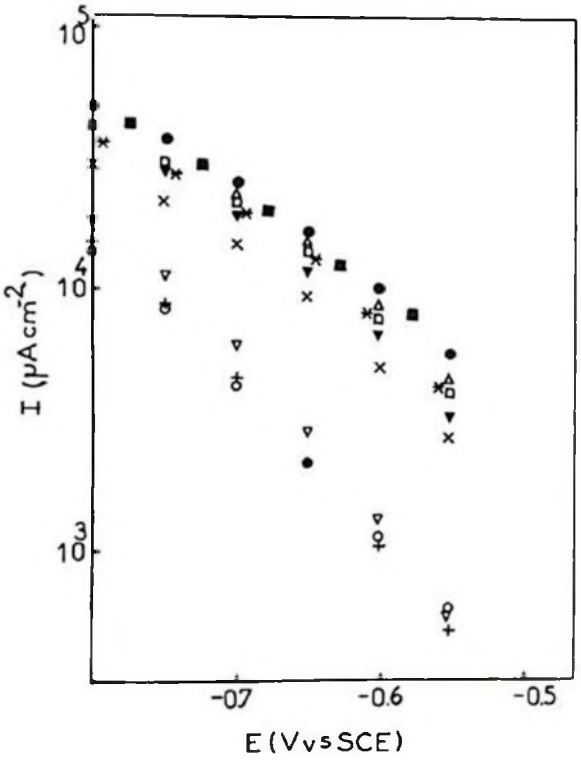


Fig.1. Cathodic potentiokinetic current-potential curves of iron in 0.5M H_2SO_4 without and with different aminoacid and aminoesters none (●), METOH (o), $METOCH_3$ (▽), $METOC_2H_5$ (+), GLU (Δ), PHE (□), THR (♥), HIS (✱), LYS (x) SER (□).

RESULTS

Electrochemical measurements

Comparative studies

The aminoacids and aminoesters tested are given in Table 1.

The cathodic polarisation data of iron in 0.5M H_2SO_4 in the absence and presence of 10^{-2} M of these compounds are presented in Fig.1. The inhibition efficiency is defined as:

$$E\% = [1 - (I'_{cor} / I_{cor})] \times 100 \qquad ... (2)$$

where I_{cor} and I'_{cor} are uninhibited and inhibited corrosion current densities, determined by extrapolation of cathodic Tafel lines to corrosion potential. The electrochemical parameters and corrosion inhibition efficiencies (%) are given in Table 2.

Table 2

Electrochemical Parameters and Corrosion Efficiency (ε%)

Medium 0.5M Sulphuric acid without & with 10^{-2} M inhibitor ; Specimen pure iron; (ε% determined by extrapolation of Tafel plots)

Inhibitor	E_{corr}	I_{corr}	b_c	ε %
Nil	-495	3800	240	-
SER	-501	3800	240	0.0
GLU	-492	3350	240	11.5
PHE	-500	3100	240	18.4
THR	-505	3000	240	21.0
HIS	-493	2990	240	23.7
LYS	-501	2200	230	42.1
METOH	-596	430	228	88.7
$METOCH_3$	-484	420	200	89.0
$METOC_2H_5$	-473	320	200	91.6

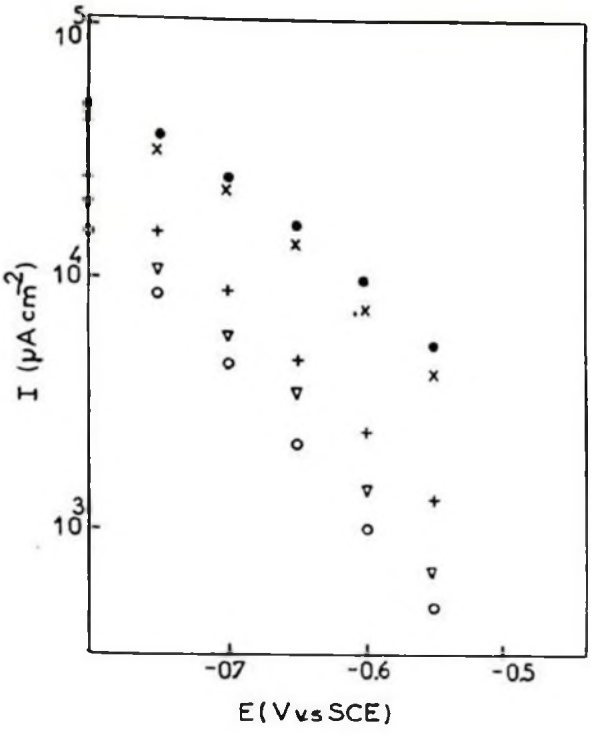


Fig.2. Cathodic potentiokinetic polarisation curves of iron in 0.5M H_2SO_4 in the presence of different concentrations of $METOC_2H_5$ inhibitor

(●) 0.0: (x) 10^{-4}: (+) 10^{-3}. (▽) 5.10^{-3} (o) 10^{-2}M.

As can be seen from Fig.1, current-potential curves gave rise to parallel Tafel lines indicating that the hydrogen evolution reaction is activation controlled and the addition of compounds tested does not change the mechanism of discharge of proton. The values of corrosion potential are not much changed in presence of aminoesters and aminoacids studied. But the cathodic current and corrosion current densities decrease - particularly with METOH, $METOCH_3$ and $METOC_2H_5$; in case of $METOC_2H_5$ solution, the inhibition efficiency was maximum (92%). The inhibition efficiency of compounds investigated decreases in the order:

$METOC_2H_5$ = $METOCH_3$ = METOH > LYS > HIS > THR > PHE > GLU > SER.

Influence of Concentration of Inhibitor

Cathodic curves of iron in 0.5M H_2SO_4 in the absence and presence of $METOC_2H_5$ at various concentrations (10^{-5} - 10^{-2} M) are shown in Fig.2. The electrochemical parameters and inhibition efficiencies of METOH, $METOCH_3$ and $METOC_2H_5$ are given in Table 3.

Table 3

Electrochemical Parameters and Corrosion Efficiency (ε%) with Three of the Inhibitors at Different Concentrations

Specimen pure iron: Medium 0.5M Sulphuric acid
Inhibitor Concentration varying
(ε% determined by extrapolation of Tafel plots)

Inhibitor conc. M	E_{corr} mV/SCE	I_{corr} μA.cm^{-2}	b_c mV/dec	ε%
nil	-495	3800	240	-
Inhibitor METOH				
10^{-5}	-506	3700	238	2.7
10^{-4}	-510	2800	232	26.3
10^{-3}	-506	1500	226	60.5
$5x10^{-3}$	-502	800	220	79.0
10^{-2}	-496	430	228	88.7
Inhibitor $METOCH_3$				
10^{-5}	-511	3700	247	2.7
10^{-4}	-509	2700	240	29.0
10^{-3}	-506	1900	235	50.0
$5x10^{-3}$	-496	1000	220	73.7
10^{-2}	-484	420	220	89.0
Inhibitor $METOC_2H_5$				
10^{-5}	-502	3700	245	2.7
10^{-4}	-511	3500	240	7.9
10^{-3}	-492	1220	240	67.9
$5x10^{-3}$	-498	500	220	86.8
10^{-2}	-495	320	220	91.6

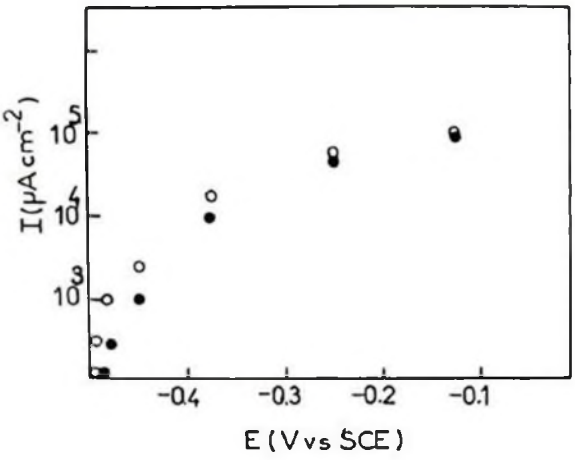


Fig.3. Anodic current -potential curves of the iron
0.5M H_2SO_4 (o) : 0.5M H_2SO_4+10^{-2}M of $METOC_2H_5$ (●)

These results demonstrate that the hydrogen evolution reaction is inhibited and the inhibition efficiency increases with the concentration. Corrosion current density decreases with increasing inhibitor concentraions and inhibition efficiency reaches a maximum value at 10^{-2} M.

In the anodic range the polarisation curves of iron in 1 M HCl without and with 10^{-2} M $METOC_2H_5$ show an increase of overvoltage at approximately corrosion potential. For the overvoltage higher than -250 mV/SCE. the preseene of $METOC_2H_5$ does not change the current-potential characteristics (Fig.3). The same result have been obtained with METOH and $METOCH_3$. This fact means that the inhibition mode of METOH, $METOCH_3$ and $METOC_2H_5$ depend on electrode potential and these compounds act primarily as cathodic inhibitor.

Gravimetric measurements

The electrochemical results have been confirmed by mass loss deteminations. The corrosion rate (W) in 0.5 M H_2SO_4 at various concentrations of each compound tested is determined after 2 hours of immersion. Typical values of W and inhibition efficiencies ($METOC_2H_5$) are given in Table 4. The inhibition efficiency is calculated, in this case, by the relation:

$$\varepsilon\% = [(1 - W') / W] \times 100 \quad \ldots (3)$$

where W and W' are the uninhibited and inhibited corrosion rate, respectively.

Table 4

Corrosion rate (W) & Inhibitor Efficiency (ε%) of Iron as a function of $METOC_2H_5$ Concentration (by Gravimetry)
Medium 0.5 M Sulphuric acid

$METOC_2H_5$ Concentration	W $mg.cm^{-2}.h^{-1}$	ε%
0 M	5.87	-
10^{-5} M	5.62	5
$5x\ 10^{-5}$ M	5.09	14
10^{-4} M	4.51	24
$5x\ 10^{-4}$ M	3.51	40
10^{-3} M	2.62	56
$5x\ 10^{-3}$ M	1.25	79
10^{-2} M	0.65	90

Table 3 shows that the corrosion rate decrease with $METOC_2H_5$ concentration. ε% attains 90% at 10^{-2}M of $METOC_2H_5$. The gravimetric measurements (Table 4) are in good agreement with electrochemical method.

Comparison between the behaviour of $METOC_2H_5$ at pure iron and Armco iron

To obtain information about the effect of composition of iron on the inhibitory action of $METOC_2H_5$, cathodic polarisation and gravimetric measurements were carried out. Results obtained are given in Table 5.

According to these tables, it is clear that, inhibition efficiency of $METOC_2H_5$ is higher with pure iron than that of Armco iron. $METOC_2H_5$ act without modifying the Tafel slope values in both the cases.

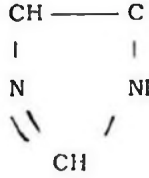
DISCUSSION

The inhibitors investigated are the α aminoacids or aminoesters with carboxyl / ester and amino functions bonded to the same carbon atom. The group "R" bonded to α carbon may contain aromatic ring, S atoms or other functional groups (Table 1).

Results (Table 2) indicate that only some aminoacids and aminoestrs are good cathodic inhibitors for the corrosion of iron in 0.5M H_2SO_4. Others show poor inhibition or even no inhibition.

The influence of the nature of substituents are in the following sequence:

$HO—CH_2—$(in SER 0%) <
$NH_2—(O)C—CH_2—CH_2—$(in GLU 11.5%) <
$Phenyl—CH_2—$(in PHE 18.4%) <
CH_3-CH(OH)—(in THR 21.1%) <



< $NH_2—(CH_2)_3—CH_2—$(in LYS 42.1%) <
$H—S—CH_2—CH_2—$(in METOH 88.7%)

Table 5

Electrochemical parameters & E% of Different samples of Iron

Medium 0.5 M Sulphuric acid; Inhibitor $METOC_2H_5$

Method	Polarisation				mass loss	
Inhibitor conc. M	E_{corr} mV/SCE	I_{corr} μA.cm^{-2}	b_c mV/dec	ε%	W mg/cm^2/h	ε%
Sample Pure Iron						
nil	-495	3800	240	-	5.87	-
10^{-2} M	-495	320	200	91.6	0.65	90
Sample Armco Iron						
nil	-516	1300	195	-	0.62	-
10^{-2}M	-500	400	192	69.3	0.22	65

METOH, $METOCH_3$ and $METOC_2H_5$ are more efficient corrosion inhibitors than other aminoacids tested here. This could be related to their sulphur atom. The presence of sulphur atom in the structure of aminoacids or aminoesters appears to be indispensable for good inhibiting effect. The sulphur atom and the large substituents facilitate adsorption and confer a good surface protection. The low inhibition efficiency of sulphur - free aminoacid confirm the role of sulphur atom. The presence of free electron pairs in sulphur has the major role in the adsorption.

Comparing inhibition efficiency of METOH, $METOCH_3$ and $METOC_2H_5$ makes it is clear that the methyl / ethyl substitution hardly affects the inhibition efficiency.

The efficiency of some inhibitors do depend on degree of purity of iron [11-14]. Epelboin [12] compared the inhibition of corrosion of high-purity iron and Armco-type iron by 2-butyne-1,4-diol in 0.5M H_2SO_4 and concluded that the inhibitory action is shown only in the armco iron case; 2-butyne-1,4-diol does not modify the corrosion behaviour of high-purity iron. A similar study in the present case shows that inhibition efficiency of $METOC_2H_5$ for pure iron is higher than that for Armco iron (Table 5). Thus the inhibitory action of $METOC_2H_5$ is shown to depend markedly on the purity of iron used.

As can be seen in Table 2, the inhibition efficiency of LYS at 10^{-2}M is 42.1%. This result indicates that LYS acts as weak inhibitor. However, Benkirane *et. al.* have shown that LYS acts as good anodic inhibitor for the corrosion of Armco type - iron in aerated 0.9% NaCl medium (ε% 90%). The inhibitory action of LYS has been interpreted as due to adsorption followed by reduction of LYS molecule at active sites of iron surface [15].

In the presence of METOH, $METOCH_3$, the cathodic Tafel slopes do not change with respect to blank. This result indicates that the addition of these molecules do not modify the hydrogen evolution reaction mechanism but act by the simple adsorption mode. This adsorption is favoured by the presence of electron donor groups such as nitrogen and sulphur in their structure.

The fraction (θ) of surface covered by adsorbed molecules of inhibitor is determined by the ratio ε% / 100. The relation log [θ/(1-θ)] *vs* log [inhibitor] is linear (Fig.4). The same result is obtained with METOH and $METOCH_3$. Thus the Langmuir isotherm

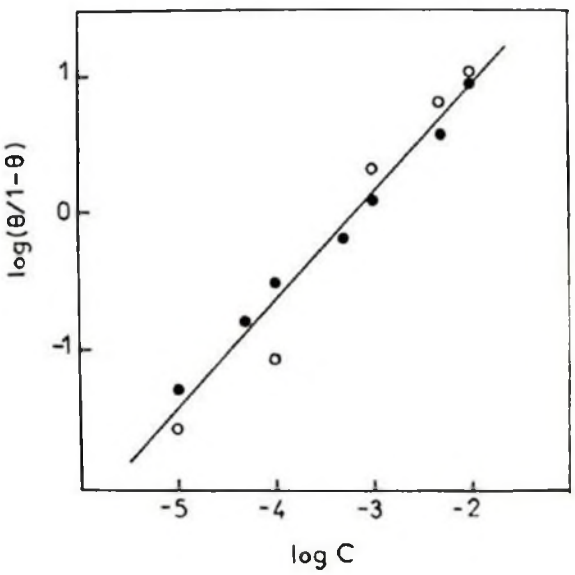


Fig.4. Lagmuir isotherm adsorption model of $METOC_2H_5$ on the surface of iron in 0.5M H_2SO_4.

(o) electrochemical results; (•) gravimetric results.

$[\theta/(1-\theta)] = kC$ .... (4)

is obeyed. It is interesting to note that in 1M HCl solution, $METOCH_3$ was adsorbed at iron surface according to Frumkin's model [10]. So it appears that the action of $METOCH_3$ depends on the type of aggressive solution used.

CONCLUSIONS

On the basis of results and discussions, the following conclusions can be drawn.

(i) Some aminoacids and aminoesters are good, non toxic, cathodic inhibitors for the corrosion of iron in 0.5M H_2SO_4. However, others show poor inhibition characteristic or even no inhibition.

(ii) Inhibition efficiency depends on molecular structure of compounds tested; it increases with substitution of one hydrogen in α position by a functional group containing sulphur atom.

(iii) Among the aminoacids / aminoesters studied, L-methionine (METOH), L-methionine methyl ester ($METOCH_3$) and L-methionine ethyl ester ($METOC_2H_5$) act as the best inhibitors and their inhibition efficiency attains a maximum value at 10^{-2}M. The adsorption of METOH, $METOCH_3$ and $METOC_2H_5$ on the iron surface obeys Langmuir's adsorption isotherm. The inhibitory effect is the result of the interaction between the molecule and the metallic surface thus decreasing the active surface.

(iv) The addition of these aminoacids and aminoesters do not change the hydrogen reduction mechanism.

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