

THE STABILITY OF THE LOW ALLOY STEELS IN ORGANIC SYSTEMS WITH SUCCINIC AND ADIPIC ACIDS

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The behaviour of three type of steel, with a variable carbon concentration (from 0.20 to 0.40 %) is studied in medium of methanol – 10 % ethylene glycol – 5 % succinic or adipic acids with water concentration varying between 1 % to 5 %. The weight losses are measured; also the polarisation curves are plotted and the corrosion parameters are established. SEM visualised the metallic surface. The corrosion compounds are analysed by IR spectroscopy, X-ray diffraction and chemical analysis.

Keywords: steel corrosion, organic acid medium

Introduction

In organic medium, in which water is present like impurity, the corrosion mechanisms of metals, in general, and iron, in particular, are different than those that occur in aqueous electrolyte solutions. In non-aqueous medium the formation of oxyhydroxylic layer does not use the HO⁻ groups derived from water as it happens in aqueous solutions [1-4]. This is possible only if the number of water moles is higher than the corrosive acid, meaning the ratio water/acid being higher than 4/1 [5-6]. It is known that the H⁺ ion co-ordinates 4 water molecules. Also, some other impurities contained in organic medium presented a much higher influence over the corrosion process than their presence in aqueous solutions. Their influence is shown in changes that appear in the conductivity values and also in the dissociation constant [7-8].

This paper continues the study about the influence of water concentration over steels with different carbon concentration. The steels have the composition situated at the limit between cementite and Fe-C solution. The corrosion reagents are organic acids and the medium in methanol with 10 % ethylene glycol [9-13]. In this paper, succinic and adipic acids are the corrosion reagents.

Experimental

The steels samples that are used for the corrosion, OL 37, OL 50 and OL 60 have the chemical composition

presented in *Table 1*. The steels samples of 5 cm² active metallic surface were cut up from a cylindrical bar. They were polished and dyeing protected the surface that should not be corroded. The corrosion system contained methanol, 10 % ethylene glycol, 5 % succinic or adipic acids, HOOC-(CH₂)_n-COOH, (n = 2 and 4) and the water concentration varied between 1 % and 5 %. Karl-Fisher method was used to determine the water content. We used Merck reagents and the water was bi-distilled, having electrical conductivity of 12 μS cm⁻¹. Also the pH-variation of the corrosion medium was measured with a HACH pH-meter.

Before introducing the samples in the corrosive system, they were submitted to a degreasing process in boiling benzene for 30 minutes and then degreased in a solution of hydrochloric acid 3 % for 3 minutes. The corrosive system was open, allowing the permanent access of oxygen from the atmosphere.

For every value of the water concentration, six metallic samples were used and were placed in the same time in the corrosive system, being subsequently taken off from 10 to 10 days, degreased with hydrochloric acid (3 %) for 15 seconds and then were weighed by an analytical balance. From the values of weight losses, the gravimetric figure K (g m⁻² h⁻¹) and the penetration figure P (mm year⁻¹) were calculated.

The metallic surfaces were visualised by electron microscopy on a TESLA B300 microscope.

For the value of 5 % of water concentration, the polarisation curves were plotted on a Digital Electrochemical Analyser DEA 332, made by RADIOMETER, Copenhagen, Denmark. From the

Table 1 The composition of the tested steels

Steel	% C	% Mn	% S	% Si	% P
OL 37	0.20	0.80	0.06	0.40	0.06
OL 50	0.30	0.80	0.05	0.40	0.05
OL 60	0.40	0.80	0.05	0.40	0.05

Table 2 The values of K and P figures in the system methanol- 10 % ethylene glycol- 5 % organic dicarboxylic acids

%	OL 37		OL 50		OL 60	
	K/P		K/P		K/P	
H ₂ O	Succinic acid	Adipic acid	Succinic acid	Adipic acid	Succinic acid	Adipic acid
1	0.296/ 0.27	0.093/ 0.08	0.286/ 0.26	0.088/ 0.08	0.273/ 0.24	0.078/ 0.07
2	0.303/ 0.27	0.096/ 0.09	0.289/ 0.26	0.090/ 0.08	0.280/ 0.25	0.080/ 0.07
3	0.311/ 0.28	0.099/ 0.09	0.293/ 0.26	0.098/ 0.09	0.286/ 0.26	0.086/ 0.08
4	0.318/ 0.29	0.102/ 0.09	0.298/ 0.27	0.100/ 0.09	0.295/ 0.27	0.090/ 0.08
5	0.328/ 0.29	0.111/ 0.10	0.309/ 0.28	0.110/ 0.10	0.302/ 0.27	0.100/ 0.09

shape of the polarisation curves the kinetics parameters (ϵ_{st} , ϵ_{cor} and i_{cor}) of the corrosion process were calculated.

The corrosion final compounds, for every value of water concentration, were insoluble in the system. They were analysed by X-ray diffraction on a HZG 4C Karl Zeiss Jena diffractometer using Co(K_{α}) radiation, by IR spectroscopy on a SPECORD M82. The chemical composition (C, H, O and Fe) of the final compounds were also determined.

Results and Discussions

The pH-metric study of the system ethylene-glycol – 10 % methanol – 5 % organic acid shows that the influence of water on acid dissociation is significant. The initial value of pH in anhydrous medium is 2.95 for the succinic acid system and 3.12 for the adipic system respectively. If we add water until the system contains 5 % water concentration, the pH- value decreases to 2.83 and 2.94.

In Table 2, the experimental data for weight losses expressed by K and P figures are presented. From these values, resulted that the corrosion rate increases with the increase of water concentration without reaching an optimal value of it in accomplishing the passive layer. Even at molar ratio water/acid of 6.53/1 for succinic acid and 8.10/1 for adipic acid, the passive layer is not obtained.

In corrosive medium of inorganic acids the ratio water/acid necessary for obtaining the passive layer is 4/1 [5,6]. In organic medium, because of the polar character of the solvent molecules of ethylene glycol and methanol is possible that water is stronger

Table 3 The values of the kinetic parameters of the corrosion in the system methanol- 10 % ethylene glycol- 5 % organic dicarboxylic acids

Type of steels	ϵ_{st} , mV		ϵ_{cor} , mV		i_{cor} , $\mu A/cm^2$	
	Succinic acid	Adipic acid	Succinic acid	Adipic acid	Succinic acid	Adipic acid
OL 37	-558	-500	-570	-525	12.38	7.63
OL 50	-520	-491	-550	-520	10.86	7.47
OL 60	-506	-481	-540	-510	9.53	7.35

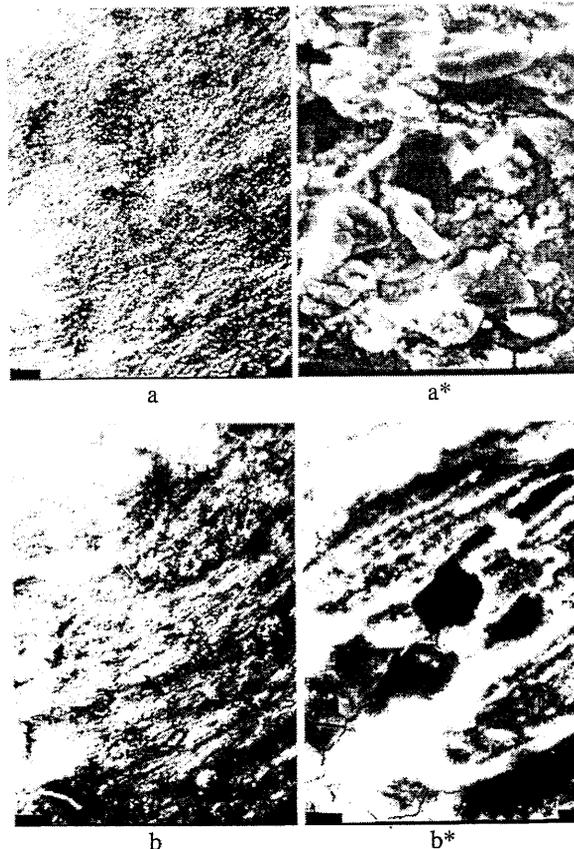


Fig.1 The metallic surface of OL 60 (a, a*: succinic acid; b, b*: adipic acid; a, b: 60 x; a*, b*: 1200 x)

bonded through hydrogen bridges and so it does not participate in passive oxy-hydroxylic layer formation.

From experimental data resulted also that the steel with the best behaviour in corrosive medium is OL 60, steel that presents the higher carbon concentration and that the succinic acid is more corrosive than the adipic acid, but the differences are not significant.

The metallic surface shown in Fig.1 presents different aspects for the two systems. It is observed that the succinic acid determines a pitting corrosion being different from the generalized corrosion determined by the adipic acid. In the second type of corrosion, the metal is covered with a layer of corrosion compound but this is not uniform permitting the access of the corrosive agent to the metallic surface.

The polarization curves were plotted for 5 % water concentration (Fig.2) and the values of the kinetic

Table 4 The chemical composition of the corrosion products in the system methanol- 10 % ethylene glycol- 5 % organic dicarboxylic acids

%	OL 37		OL 50		OL 60	
	Succinic acid	Adipic acid	Succinic acid	Adipic acid	Succinic acid	Adipic acid
C	28.37	37.73	29.05	37.83	29.17	38.25
H	3.56	4.79	3.16	4.98	3.48	5.14
O	38.45	33.27	38.18	33.03	39.06	34.05
Fe	29.32	24.21	29.61	23.36	28.29	22.56

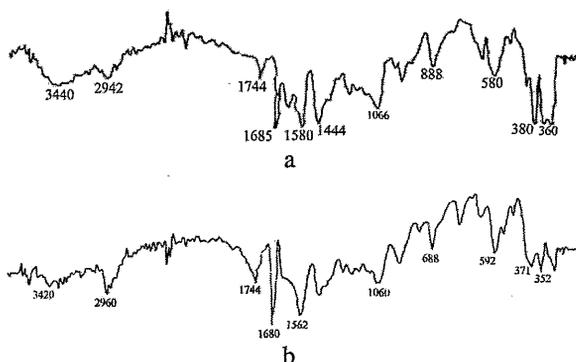


Fig.3 The IR spectra of the corrosion compounds derived from a: succinic acid and b: adipic acid

parameters determined from these curves are presented in Table 3. It is also observed that in this case, the succinic acid is more corrosive than the adipic acid and the steel with the best behaviour in the corrosive medium is also OL 60.

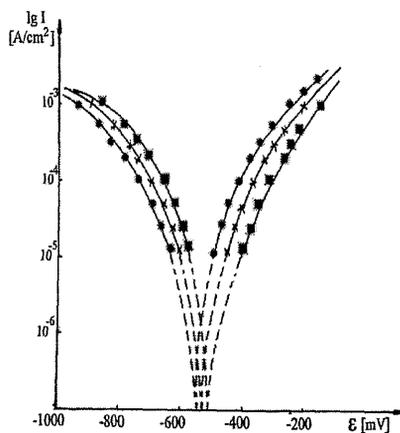
In order to establish a corrosion mechanism, the corrosion compounds were analysed. These were insoluble in the studied systems and presented a red colour.

The X-ray diffraction spectra do not show the existence of crystalline compounds in any of the obtained products at any water concentration.

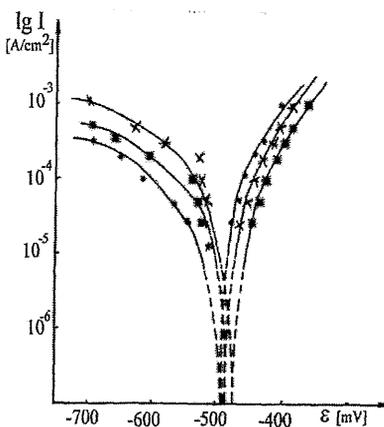
The I.R. spectra are identical for all systems at any water concentration, meaning that they present absorption maximum points at the same wave numbers.

The I.R. spectra of the corrosion compounds at 5 % water concentration for the two analysed systems are presented in Fig.3. These show primarily the displacement of the absorption frequency of the group COO^- of the two acids from 1700 to 1685 cm^{-1} for succinic acid and from 1695 to 1680 cm^{-1} for adipic acid due to a stronger bonding of oxygen.

The bond Fe-O is clearly showed by the two peaks that appear in the I.R. spectra. These are situated at 380 and 360 cm^{-1} in the I.R. spectra of the compound with succinic acid and at 371 and 352 cm^{-1} in the spectra of the product with adipic acid. The absorption frequency of this bond is displaced to smaller wave numbers in case of adipic acid because of the greater organic chain determining also stronger covalent and coordinative bonding between Fe and oxygen. Also, the displacement of the absorption band characteristic for the alcoholic group OH from the value 1080 cm^{-1} to 1066 cm^{-1} and



a



b

Fig.2 The polarisation curves (a: succinic acid; b: adipic acid;

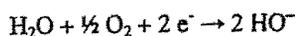
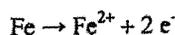
● OL 37; x OL 50; ■ OL 60)

1060 cm^{-1} respectively, shows that the two solvents participate to the coordination bond in the obtained compound. The OH group from water presents two vibration frequencies at 3440 and 2942 cm^{-1} and 3420 and 2960 cm^{-1} respectively, fact that is explained by the existence of water bonded in two different ways: a group OH is coordinative bonded and the other in bridge linkage.

In both I.R. spectra is a well-defined peak at 1744 cm^{-1} , characteristic to the ester type bond. The other peaks from the I.R. spectra are characteristic to the C—H and C—C bonds.[14,15].

The chemical element analysis of the corrosion compounds is presented in Table 4. The analysis corresponds to a compound in which the ratio Fe/succinic or adipic rest is 1/1 with a small surplus of oxygen and hydrogen. This ratio can be explained only in polymer compounds.

From the presented data, the following corrosion mechanism is assigned:



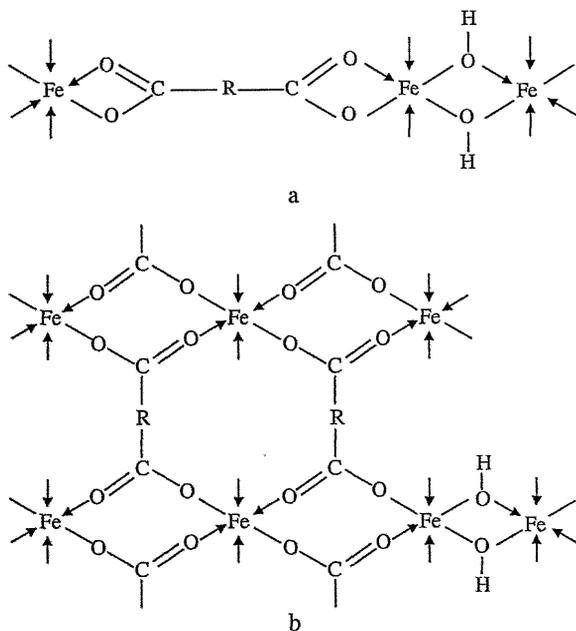
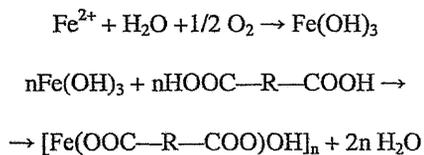


Fig.4 The proposed structures for the polymer compounds; a: linear; b: cyclic



The structure of the resulted compound with R derived from succinic or adipic acid with Fe(III) is presented in Fig.4. The structure is in both linear and polymer forms. The compounds of Fe(III) with succinic or adipic acid are not presented in the literature.

The hexacoordination of Fe is accomplished through both water molecules and the solvent ones. Also, the polymer chain is extended through ether type bonds.

Conclusions

- All steel types are corroded in the studied medium
- The best behaviour is presented by the steel with the highest carbon concentration (0.4 %). That is due to the existence in the steel structure of the solid Fe—C solution that determines a superior stability of the material [16].
- Water is not used in the passive layer formation even if it is present in molar rates higher than 4/1 (when the system contain 5 % water the molar rate water/acid has the value 6.53/1 for succinic acid and 8.10/1 for adipic acid). The fact that water does not

participate in anticorrosive protection can be justified by the existence of two groups COO^- in the structure of the acid that requires a higher quantity of water in order to accomplish the oxyhydroxilic passive layer formation, using the dissolved O_2 . The water molecule is possible to be stronger bonded through hydrogen bridges of the organic solvents so it does not participate in passive oxy-hydroxylic layer formation.

- The corrosion mechanism is a complexing one with formation of insoluble compounds non-adherent on the surface of the corroded metal. These compounds presented an amorphous polymer structure.
- Remarkable is the fact that the succinic acid determines a pitting corrosion process.

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