

Electrochemical Evidences of the Protection Efficiency of Furfural on the Corrosion Processes of Low Carbon Steel in Ethanolic Medium.

Reinaldo Simões Gonçalves* and Winston Xaubet de Olivera

Departamento de Química, Universidade Federal de Santa Maria, C.P. 5061, 97119 Santa Maria, RS, Brasil.

Received: april 27, 1992.

As melhores condições que confirmam o furfural como inibidor de corrosão de aço com baixo teor de carbono, em meio etanólico, são discutidas. Mesmo em ácido acético 0,1 M em etanol a presença de furfural reduz em 90% a velocidade de corrosão do metal.

In this paper is presented the best conditions that confirms the furfural as a corrosion inhibitor of the low carbon steel in ethanolic medium. Even in an aggressive 0.1 M acetic acid ethanolic solution, the presence of furfural decreases 90% the corrosion rate of the metal.

Key words: inhibitor; furfural; ethanol.

Introduction

The corrosion processes of low-carbon steel in ethanolic medium depends on water and sulphate contents and, pH of the solution¹. Some authors²⁻⁹, confirms that chloride ions can promote the processes. The addition of organic inhibitors in the aggressive ethanolic solutions can decrease the corrosion rate of the metal, as was observed in aqueous solutions⁴.

It is accepted that the organic molecule inhibits corrosion by adsorbing at the metal-solution interface⁵. However, the electrochemical phenomena that involve adsorption and charge transfer steps at electrode solution interfaces may be largely dependent on the structuring of the solvent. In aqueous solutions, it was confirmed the adsorption process of furfural on low-carbon steel⁶.

This work was directed towards the establishment of conditions leading to the maximum coverage of the electrode (low-carbon steel), in the absence and presence of furfural (C₅H₄O₂) in ethanolic medium. Potentiodynamic I(E) profiles were used as electrochemical method to confirm the adsorption process. To obtain comparative performance data, standard weight-loss were made in different conditions, in the absence and presence of pure furfural.

The parameters that were studied: a) furfural concentration; b) acetic acid concentration; c) adsorption potentials E_{ads} and d) oxygen concentration.

Experimental

Electrochemical methods and weight loss tests: the electrochemical experiments were carried out in a three-electrode electrochemical cell with a platinum counterelectrode and a Ag/AgCl electrode as reference. All potentials are reported with respect to it. The working

electrode was a low carbon steel (C,0.08 wt%). The samples were cut from the same sheet in a rectangular form (2.0 x 2.5 x 0.1 cm thickness). After mechanical polishing with emery papers and alumina, the specimen edges were covered with a epoxy glue. To calculate the current density, the operating surface was measured with a sliding caliper.

The ethanol solutions were prepared from distilled ethanol, QEEL hydrochloric acid (p.a.) and, Merck acetic acid (p.a.). The supporting electrolyte was a Reagen lithium sulfate (p.a.). Before each experiments, low pressure distillations were necessary in order to maintain the purity level of Merck furfural (p.a.). Distilled water was added in some solutions. The ethanolic solutions were de-oxygenated by bubbling pure N₂ through the solution. Some tests were made in aerated solution.

The electronic arrangement consisted of a PAR 173 potentiostat with a 376 logarithm current converter, a PAR 175 universal programmer, and a PAR RE0089 X-Y recorder.

The weight loss tests were made with disk samples of the metal. The coupons were cleaned with ethanolic 0.5 M acetic acid, distilled ethanol, acetone in this sequence, and dried. This treatment was carried out immediately before and after making the test. The corrosion rates were also calculated on the basis of the apparent surface area. The immersion time for the weight losses at 25°C in aerated conditions were 5, 15 and 30 days. All experiments were made in triplicate.

Experimental

Weight loss tests: Table 1 shows the protection efficiency of furfural on the corrosion processes of low-carbon steel (ABNT 1008) in distilled aerated ethanol at 25°C. These values are related with weight loss in absence and presence of the inhibitor and in static conditions. The

protection effect of the compound increases with the furfural concentration up to 1.0 mM. At more concentrated solutions, the inhibition efficiency decreases. This fact may be related with the dissolution of the metal by complexation reactions with the dissolution of the metal by complexation reactions with the inhibitor⁷. The process of inhibitor film formation is not an instantaneous one. This effect was also observed in aqueous solutions with another compound⁴.

Table 1. Protection efficiency of furfural on low-carbon Steel (ABNT 1008) In distilled aerated ethanol at 25 °C, in static conditions.

Time/days	C _F =Zero	C _F =0.3mM	C _F =1.0mM	C _F =5.0mM	C _F =10mM
5	0.00%	9.72%	35.4%	—	11.8%
15	0.00%	13.2%	47.7%	13.7%	39.3%
30	0.00%	13.2%	47.70%	13.7%	32.9%

The protection efficiency of furfural on this metal increases in an 0.1 M acetic acid aerated ethanolic solution as is shown in Table 2. This acid solution is more aggressive than distilled ethanol. However, the inhibitor effect of the furfural increases even in this medium. It was confirmed that 1.0 mM furfural concentration is sufficient to decrease the corrosion rate of the low-carbon steel in these conditions. These data confirm the time-dependence of the protection efficiency of furfural on this metal. At short immersion-time the inhibition of the corrosion processes was not so efficient as at high immersion-time.

Table 2. Protection efficiency of furfural on low-carbon Steel (ABNT 1008) In 0.1 M acetic acid aerated ethanolic solution at 25 °C and, in static conditions.

Time/days	C _F =Zero	C _F =0.3mM	C _F =1.0mM	C _F =5.0mM	C _F =10mM
5	0.00%	71.4%	81.3%	73.5%	74.2%
15	0.00%	87.5%	90.0%	87.7%	88.2%
30	0.00%	82.5%	86.3%	86.8%	89.5%

Cyclic voltametric studies.

The potentiodynamic I(E) profiles were recorded after pre-activation of the electrode in the aggressive solution. This process was the same applied in another medium⁴. The main information obtained from the difference between the voltammogram recorded with and without furfural in ethanolic solution is related to the current density variation in the potential range.

The reproducibility of the data with respect to this method is shown in Fig. 1, where the current values obtained from the voltammograms vs the geometrical surface of different electrodes in contact with the aggressive solution are plotted. The current values change linearly with the geometrical surface of the electrode.

The dependence of the kinetics of electrode processes on the adsorption of the furfural, and the dependence of adsorption on the potential, E_{ads}, is shown in Fig. 2. The I(E)

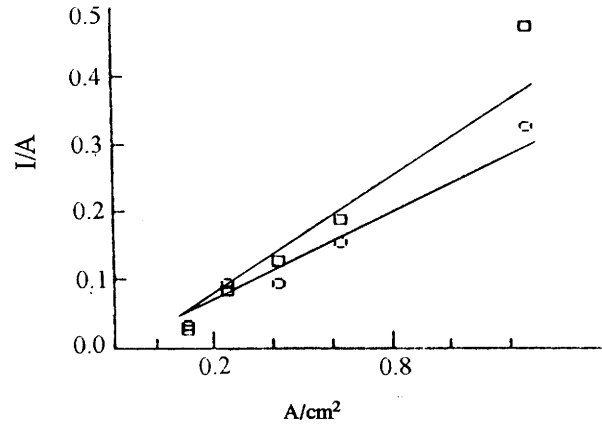


Figure 1. Linear correlation between the geometrical surface area of the working electrode and the current in deaerated ethanolic solution with 0.1 M acetic acid, 0.235 M Li₂SO₄ and 25% (v/v) of distilled water, at 25 °C. a) Current values at -0.88V; b) current values at -0.45V.

curves in absence and presence of furfural were made at different adsorption potentials. The current related with the anodic and cathodic corrosion processes decreases in the presence of furfural. The adsorption potential, E_{ads}, where the minimum anodic and cathodic density currents were observed in this medium was -1.45V.

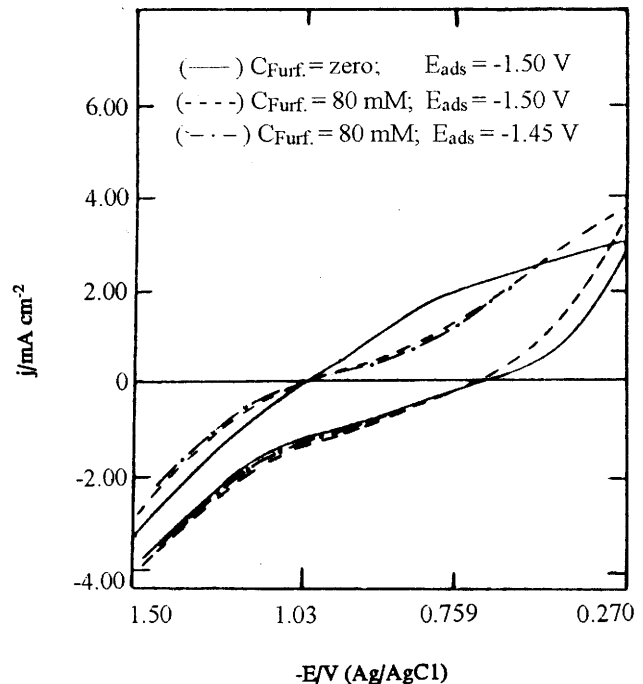


Figure 2. I(E) profiles at different adsorption potentials, E_{ads}, in deaerated 0.01N HCl ethanolic solution with 25% (V/V) distilled water, 0.0235M Li₂SO₄, v = 0.5 V/s t_{ads} = 60s and at 25 °C.

Fig. 3 shows the effect of furfural concentration on the I(E) curves in 0.01 N HCl ethanolic solution. The potential adsorption was fixed in -1.45 V during t_{ads} = 60 s. As the furfural concentration increases, the cathodic and anodic current densities decrease proportionally. This fact con-

firmes that both processes involved in the corrosion of low-carbon steel in ethanodic medium were influenced by presence of furfural. This effect was also observed in aqueous solutions⁶.

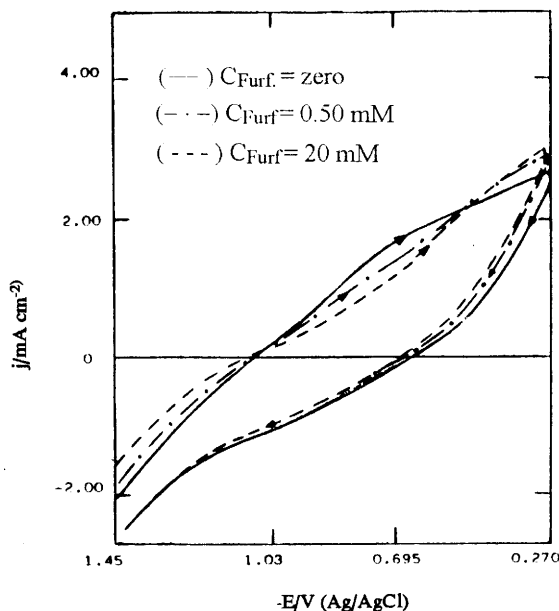


Figure 3. The effect of furfural concentration on the $I(E)$ curves at 25 °C, $v = 0.5$ V/s, $t_{\text{ads}} = 60$ s, in deaerated 0.01N HCl ethanolic solution with 25% (v/v) distilled water

The effect of oxygen concentration on the $I(E)$ curves in 0.01 N HCl ethanolic solution is shown in Fig. 4. In aerated solutions, only the anodic current related with the corrosion processes of the metal in this medium, is affected by the presence of furfural. This fact may be related with the oxygen influence on the film formation on metallic surface.

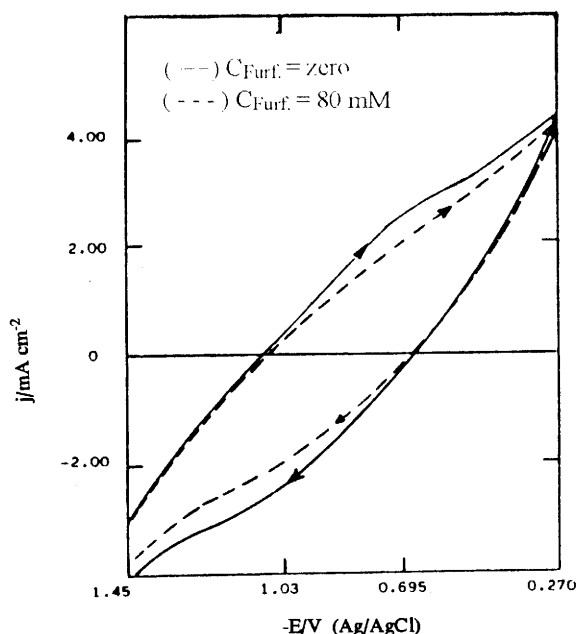


Figure 4. The effect of oxygen presence on the $I(E)$ curves at 25 °C, $v = 0.5$ V/s, $t_{\text{ads}} = 60$ s in aerated 0.01N HCl ethanolic solution with 25% (v/v) distilled water and 0.0235M Li_2SO_4 .

Conclusion

The protection efficiency of furfural on low carbon steel in ethanolic solutions depends on the inhibitor concentration. Weight loss tests confirm that 1.0 mM furfural concentration is the best condition for an effective inhibition of the corrosion processes. Even in an aggressive 0.1M acetic acid ethanolic solution, the presence of furfural decreases 90% of the corrosion rate of the metal.

The process of film formation on the metallic surface is not an instantaneous one. It depends on the potential applied on the working electrode (low carbon steel). In ethanolic de-oxygenated 0.01N HCl solution, the E_{ads} was -1.45 V.

Both anodic and cathodic density currents decrease with furfural concentration increases. In aerated ethanolic solution, only the anodic current density decreases in the presence of the inhibitor.

This may be related with the oxygen influence on the film formation on the metallic surface.

Acknowledgments

This work was carried out with financial support from FAPERGS (Fundação de Amparo a Pesquisa do Estado do Rio Grande do Sul). The authors express their thanks to CNPq and GTZ/Germany.

References

1. E. Cavalcanti, V.G. Wanderley, T.R.V. Miranda and L. Uller, *Electrochimica Acta* **32**, 935 (1987).
2. C.L. Nogueira and M.A.G. Cechini, 11° SENACOR - ABRACO, pp 225 - 239, Rio de Janeiro (1984).
3. N. Carbonel and L. Sathler, 9° SENACOR - ABRACO, pp 184 - 199, Rio de Janeiro (1982).
4. A. Spinelli and R.S. Gonçalves, *Corrosion Science* **30**, 1235 (1990).
5. H. Fischer, *Werkstoffe Korros* **23**, 445 (1972).
6. R.S. Gonçalves; P. C. do Nascimento and D.B. do Nascimento, *An. V. Simp. Bras. Eletrop. Eletroanal.*, p. 237, São Paulo (1986).
7. I.N. Putilova, S.A. Balezin and V.P. Barannik, *Metallic Corrosion Inhibitors* (Pergamon Press, New York 1960).