

Performance of corrosion inhibitors based on n-butylamine in protection of carbon steel in hydrochloric acid solution

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Abstract:- Corrosion inhibitors are chemical substances that, when added in small concentration to an environment prevent or impede the development of corrosion reactions. They are used in various segments of the oil industry, showing great efficiency in internal protection against the corrosion of pipelines, gas pipelines and boilers, in the area of refining, production of petroleum, water injection, in acidification, secondary recovery and drilling fluids. To evaluate the performance of substances with the potential to inhibit the process of corrosion in acidic solutions, and to measure the loss of mass, carbon steel coupons were manufactured and immersed in hydrochloric acid solutions 10 and 15 % (by mass), in the range of 40 to 60 °C and using n-butylamine solutions as corrosion inhibitors. Gravimetric laboratory tests show efficiencies of the addition of n-butylamine (1.5 g/L) in anti-corrosion protection for carbon steel coupons immersed in hydrochloric acid solution (10 and 15 %) were of the order of 50%.

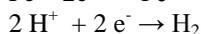
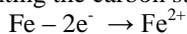
Keywords: - Corrosion, Corrosion inhibitors, n-butylamine, acidification, hydrochloric acid.

I. INTRODUCTION

The first injection of hydrochloric acid in order to stimulate the productivity of oil well occurred in 1894, near an oil refinery in Lima, Ohio (USA). The process consisted essentially in the injection of hydrochloric acid into the pipe to remove mainly calcareous minerals adhering to the metallic surface [1].

Since that time, the success and importance of this operation in the oil industry can be evaluated by the development of these techniques in onshore and offshore operations using various types of injection equipment installed in specially adapted trucks or vessels and finally by the annual consumption of hydrochloric acid for this purpose. In Brazil, although hydrochloric acid is used in other industries, about 10% of the annual production of acid is destined for the oil industry.

Various types of organic corrosion inhibitors have been utilized, predominantly, in acid solutions (acidification operations in petroleum production) in view of the high rate of corrosion shown by carbon steel in such media. The internal protection of carbon steel pipes pumping hydrochloric acid solutions is generally done by adding corrosion inhibitors that can form a film that is adsorbed or chemisorbed on the surface of metallic parts, preventing or retarding the reactions of dissolution of steel. The anodic and cathodic reactions representing the carbon steel etches are, respectively, presented below:



Failures in these operations are, for the most part, forgotten, unpublished and/or computed to the restoration and maintenance of wells. Generally, these are due to an intense acid attack that is corrosive to pipes and injection equipment due to the lack of any protection exercised by a corrosion inhibitor.

Commercial formulations for use in inhibiting acidification consist of a mixture of several compatible substances, which between them usually have the following characteristics: the ability to form a film that is adsorbed or chemisorbed on the metal surface; the ability to disperse or prevent contact of the aqueous medium with the metal surface; the ability to disperse compounds formed by reaction with acid corrosion products; antifoaming properties and compatibility with other components such as dispersants, complexing agents, biocides, etc. [2,3].

The performance of commercially formulated corrosion inhibitors for the protection of carbon steel in acidic solutions is more efficient than the chemical substance itself. However, to evaluate the corrosion efficiency, it is important to note that the performance depends on several factors such as: concentration, molecular weight of the substance, temperature, pressure, velocity of the fluid, levels of contaminants, etc. [4].

This paper presents the results of gravimetric tests conducted from carbon steel coupons immersed in hydrochloric acid and additions of n-butylamine.

II. MATERIALS AND METHODS

In the gravimetric tests (weight loss) a plate of carbon steel with the following composition was used: 0.12 % carbon; 0.25 % Mn, 0.030 % Si, 0.011 % S and 0.009 P%. From this steel plate coupons were made with the following dimensions: 45 mm x 15 mm x 10 mm. The metal surface was prepared with grade 100 sandpaper until grade 250. They were washed with water and alcohol and dried with hot air, then weighed to the nearest 0.0001 g.

As the corrosive medium, 10 % and 15 (% mass) hydrochloric acid (HCl) solution of high purity and deaerated with a continuous flow of nitrogen was used. For acidic solutions, additions of n-butylamine as corrosion inhibitor were used. Concentrations were fixed at 0.5, 1.0 and 1.5 g/L. For the thermostatic bath, temperatures were set at 40 °C and 60 °C with an accuracy of 0.1°C. The times of exposure to the corrosive medium were set at 1 h and 3 h. Finally, the agitation coupon was fixed in a mechanical stirrer operating at 100 rpm.

The test consisted of placing exactly 300 mL of hydrochloric acid deaerated in a 500 mL glass container equipped with a condenser and mechanical agitator, as shown in Figure 1. The function of the condenser is to avoid losing hydrochloric acid solution and allow the evolution of hydrogen (H₂) resulting from acid attack. Then the coupons were introduced into the solution with a speed of 100 rpm, and at the precise moment of contact of the metal surface with the acidic solution the time controller was actuated.

Upon completion of the test the system shuts down and the coupons are quickly removed from the corrosive medium, then washed with water, alcohol and dried with hot air. The coupons are then weighed again to the nearest 0.0001 g.

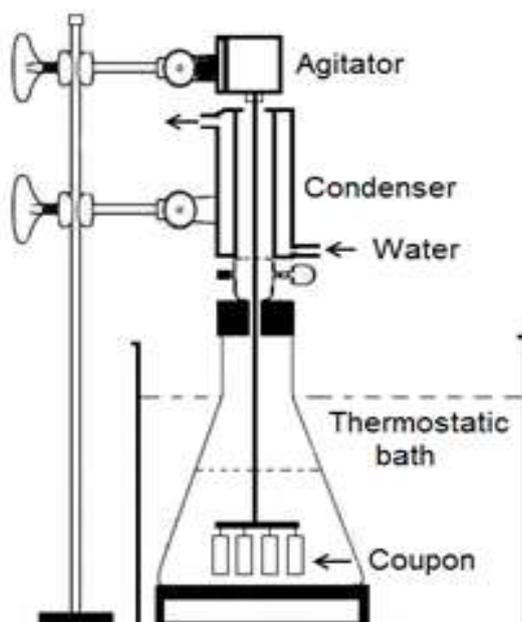


Figure 1 - Corrosion test schema

The corrosion rate (CR) and the efficiency of each corrosion inhibitor (E %) were defined by the following expressions:

$$\text{Corrosion rate} = CR = (W_o - W_f) / S.t \quad (\text{mg/cm}^2.\text{h})$$

$$\text{Efficiency} = E \% = 100 (W_o - W_i) / W_o$$

where:

W_o and W_i are the weight loss in the absence and presence of inhibitor;

S = area (cm²);

t = exposure time, h.

III. RESULTS AND DISCUSSION

The results of the laboratory tests referring to an average of four (4) carbon steel coupons immersed in hydrochloric acid solutions with additions of corrosion inhibitor (n-butylamine) are shown in Tables 1 and 2 and in the graphs presented in Figures 2 to 5.

Table 1 - Results of tests of weight loss of carbon steel coupons in 10 % and 15 % solution of hydrochloric acid at 40 °C and 60 ° C with addition of n-butylamine.

Corrosion inhibitor concentration, n-butylamine, g/L	Weight loss, mg/cm ²							
	Hydrochloric acid 10 %				Hydrochloric acid, 15 %			
	40 °C		60 °C		40 °C		60 °C	
	1 h	3 h	1 h	3 h	1 h	3 h	1 h	3 h
0	41.8	86.1	53.5	119.8	48.1	99.8	55.8	140.6
0.5	28.1	57.2	36.5	81.8	35.2	73.2	43.2	109.7
1.0	22.8	45.6	31.9	75.6	28.2	57.2	34.2	85.3
1.5	20.1	41.2	29.7	61.1	24.7	49.1	32.1	79.1

Table 2 - Efficiency of n-butylamine-based inhibitor in hydrochloric acid solutions 10 and 15% (by mass) at temperatures of 40°C and 60°C.

Corrosion inhibitor concentration, n-butylamine, g/L	Efficiency (%)							
	Hydrochloric acid 10 %				Hydrochloric acid 15 %			
	40 °C		60 °C		40 °C		60 °C	
	1 h	3 h	1 h	3 h	1 h	3 h	1 h	3 h
0.5	32.7	33.6	31.8	31.7	26.8	26.7	22.6	21.9
1.0	45.4	47.0	40.3	36.9	41.3	42.6	38.7	39.3
1.5	51.9	52.1	44.5	49.0	48.6	50.8	42.4	43.7

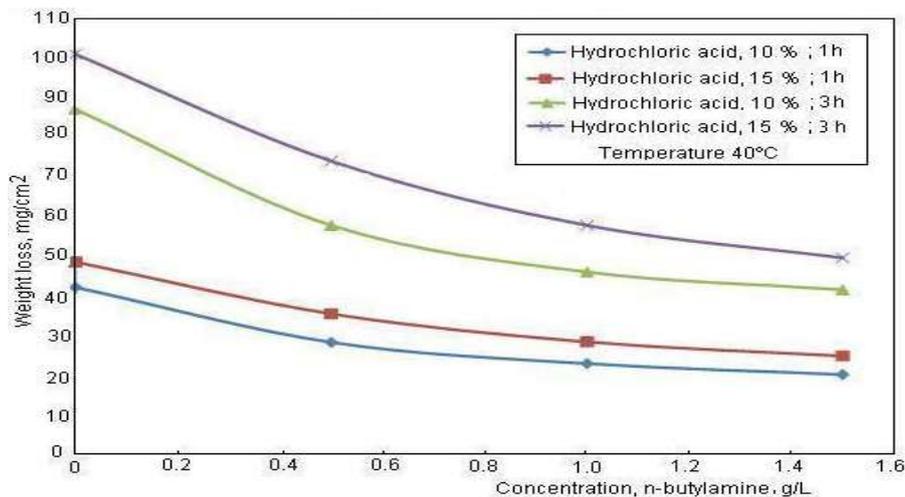


Figure 2 - Rate of corrosion of carbon steel in hydrochloric acid (10 % and 15 % mass) With n-butylamine at 40 °C

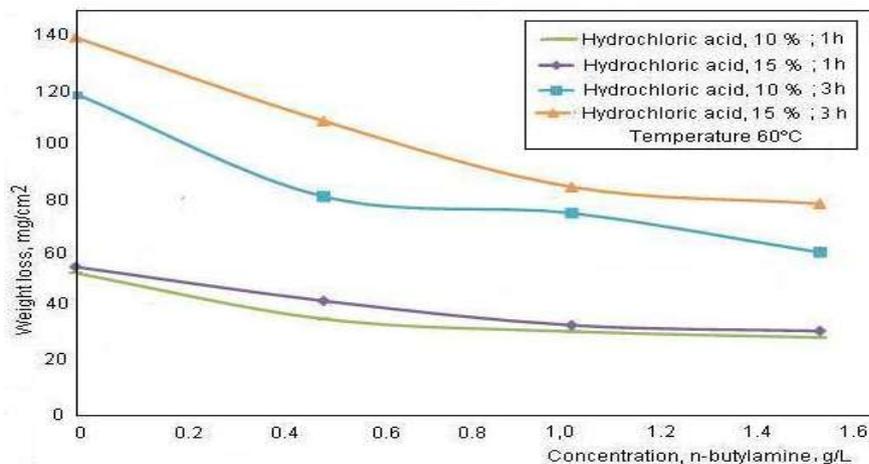


Figure 3 - Rate of corrosion of carbon steel in hydrochloric acid (10 % and 15 % mass) With n-butylamine at 60 °C

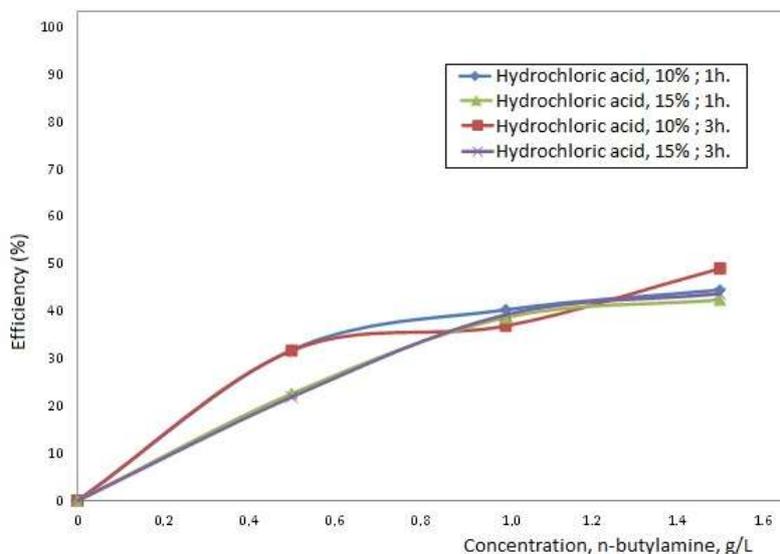


Figure 4 - Evaluation of efficiency of anticorrosive protection of carbon steel coupons in Hydrochloric acid (10 % and 15 % mass) with n-butylamine at 40 °C

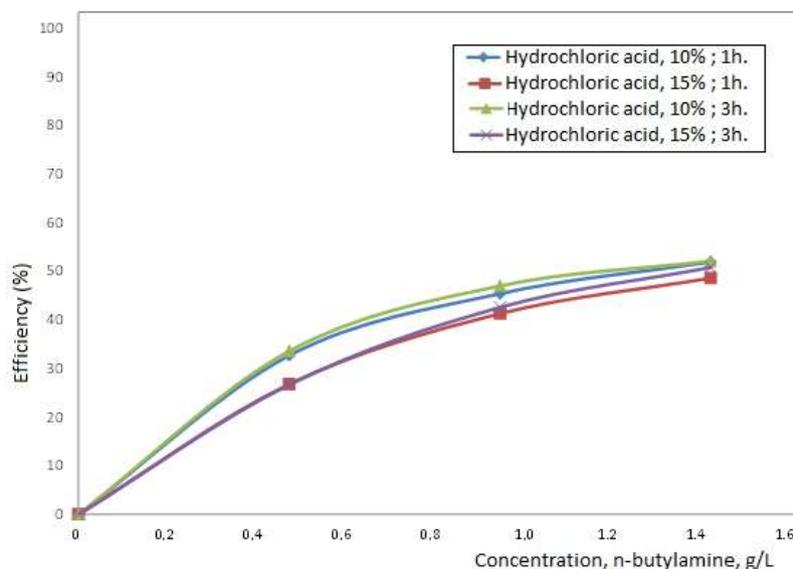


Figure 5 - Evaluation of efficiency of anticorrosive protection of carbon steel coupons in Hydrochloric acid (10 % and 15 % mass) with n-butylamine at 60 °C

Gravimetric testing performed with the carbon steel coupons immersed in solution of hydrochloric acid at concentrations of 10 and 15 % (by mass) show that the rise in temperature favours the increased rate of corrosion. The additions of n-butylamine-based corrosion inhibitors show reduced (less than 53 %) efficiency in corrosion protection, particularly with concentrations higher than 1.5 g/L.

The addition of an organic inhibitor type system (n-butylamine) in the hydrochloric acid can lead to partial or total reaction even with the H^+ ions dissociated in acidic solution, having spontaneously captured the positive charges by the inhibitor molecules, a process called protonation [4, 5, 6].

Thus there is an intense competition between the H^+ ions and protonated inhibitor molecules moving into areas where they accumulate cathode electrons. Although the ion mobility of H^+ ions is much greater (smaller ion) than the protonated inhibitor molecules, there is a stable inhibitor adsorption on the metallic surface, forming a barrier that prevents migration of H^+ ions to capture the electrons, thus preventing the formation of atomic hydrogen (H) and the detachment of molecular hydrogen (H_2) [4].

The barrier formation by the inhibitor molecules on the metal surface will be a function of the concentration of non-oxidizing acid, the concentration of the inhibitor, the temperature and the adsorption capacity of the inhibitor molecules [4, 7].

IV. CONCLUSION

On the basis of laboratory tests it can be concluded that the addition of n-butylamine (at concentrations of 0.5 to 1.5 g/L) in hydrochloric acid solution (10 to 15 %) leads to corrosion rates ranging from 28.1 mg/cm².h to 20.1 mg/cm².h, corresponding to a maximum corrosion protection efficiency of 52.1 %.

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