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Effects of Thiourea on the Corrosion of Low Carbon Steel in Hydrochloric Acid Solution

I. D. Sulliman

Department of Chemistry, College of Education, Ibn Al-Haitham, Baghdad University

Abstract

The corrosion rate of low carbon steel in 4M hydrochloric acid with and without presence of thiourea has been studied by gravimetric and gasometric methods over the temperature range 303-333 K.

The percentage protection of steel increases with the decrease of thiourea concentrations at various temperature range 303-333 K and approaching highest protection (86.82%) at 303K by using 1×10^{-4} M of thiourea. The high concentration of thiourea (1×10^{-3} M), enhances the corrosion rates and act as depolariser for the hydrogen evolution reaction, with H_2S being a product of the chemical depolarisation stage. The H_2S is considered to be adsorbed in the S^{-2}, HS^{-} state, forming activated sites where anodic dissolution is thereby enhanced.

The results were discussed on basis of adsorption of dissociated thiourea molecules on steel surface. The energies of activation have been calculated for the corrosion process of the carbon steel in acid from corrosion rates in the absence and the presence of thiourea.

Introduction

Acid solutions are widely used in industry (1-3), the most important fields of application being acid picking, industrial acid cleaning, acid descaling and oil well acidizing. Furthermore, acids are also used in numerous manufacturing processes in different industries. Due to general aggressivity of acid solutions the practice of inhibition is commonly used to reduce corrosive attack on metallic materials (4-6). However, the methods of corrosion inhibition must be evaluated according to the parameters of the particular corrosion system, as preventive measures designed for application in an environment may fail for the same metal under different conditions (7).

The present work has therefore been planned to investigate the corrosion behaviour of a low carbon steel specimen in 4M HCl over the temperature range 303-333 K. The research plan also involved the use of thiourea as an inhibitor for the acid corrosion of steel. The effect of thiourea on the corrosion rate, protection efficiency has been estimated using both weight loss and the volume of H_2 gas evolved measurements (8-10).

Experimental Method

The carbon steel specimen (obtained from ministry of industry) had the following composition as revealed by emission spectroscopic analysis:

Element	C	Mn	Si	P	S
%	1.4	1	0.3	0.05	0.05

The test pieces, (19×15.5×3) mm were cleaned at 350 K^o in nitric acid/hydrochloric acid solution, then rinsed with distilled water before being immersed in the corrosive medium. Thiourea (Analar grade) was obtained from Fluka, solutions used were prepared from Analar HCl solution using distilled water. The temperature was adjusted electrically to ±0.1 ^oC.

Gasometric test included the immersion of the low carbon steel pieces in the corrosion cell (11), which were connected to the gas collector over a salt solution which was acidified with H_2SO_4, such a solution has very little solubility effect on the collected gas. The volume of gas was always measured at atmospheric pressure by means of the pressure reserviour bulb. The hydrogen evolved was measured at a constant interval of time. Data are plotted for volume of H_2 gas evolved against time, then the rate of corrosion derived from the slopes of the straight lines.

For weight loss measurements, samples were completely immersed in 80 ml per specimen of the corrodent in conical flasks. They were exposed for different time intervals up to 4 hours and their weight losses were determined, using sensitive ($\pm 10^{-4}$ gm) balance type Mettler HL 32 from Switzerland. The loss in weight increased linearity with time.

Results and Discussion

Values of the calculated corrosion rates using the two ways above-cited give similar values of protection efficiency (%p), which calculated using the equations (12, 13):

$$P = 100(W_0 - W)/W_0 \quad [1]$$

and

$$P = 100(V_0 - V)/V_0 \quad [2]$$

where; W_0, V_0 are the rate of weight losses, and rate of hydrogen evolution in the absence of thiourea and W, V are the presence of thiourea.

The variation of corrosion rate of carbon steel in 4M HCl with thiourea concentration at various temperatures are shown in Fig.(1).

Clearly, at a constant temperature the corrosion rate decreases as the concentration of the thiourea decreases. The concentration (1×10^{-3} M) of thiourea inhibited the corrosion rate less then the other concentrations.

Fig.(2) shows the variation of the protection efficiency (%p) of steel with for various concentrations of thiourea at the temperature range (303-333 K).

The maximum efficient concentration of thiourea was (1×10^{-5} M) at the three temperatures (303-323).

Fig.(3) shows the minimum efficient concentrate of thiourea was (1×10^{-3} M) at four temperatures. An increase in temperature from 303 to 323 K causes a significant decrease in the protection efficiency for the same inhibitor concentration (1×10^{-5}, 1×10^{-4}, 5×10^{-4}) M, while the thiourea concentration 1×10^{-3} M causes a corrosion stimulation, which increases with temperature attaining a maximum stimulation at 313 K, which followed with a decrease in the corrosion stimulation with the temperature increase to 313 and 333 K.

Fig.(4) shows an Arrhenius plot of the corrosion process of low carbon steel in 4M HCl. The results fit a satisfactory straight line which conform to an Arrhenius equation (14):

$$r = A\exp(-E_a/RT) \qquad [3]$$

where; r is the rate of corrosion, E_a is the energy of activation and A is the pre-exponential factor.

E_a values derived from the slopes of the lines in the Arrhenius plots Fig.(4), were plotted against thiourea concentrations to establish Fig.(5). There was an initial sharp increase at thiourea addition of 1×10^{-5} M decreasing, thereafter, steadily with increasing thiourea concentration to 1×10^{-3} M. Thus, the presence of thiourea in HCl medium probably alters the energy barrier for the metal corrosion through enhancing the energy of activation resulting in the consequent decrease of the surface tendency for corrosion when it used with concentration bellow 1×10^{-3} M.

It is known that many of the organic inhibitors function via an adsorption mechanism (15). Under such conditions the degree of coverage equals the protection efficiency, thus according to the Langmiur isotherm. The protection imparted by thiourea occurs via an adsorption mechanism.

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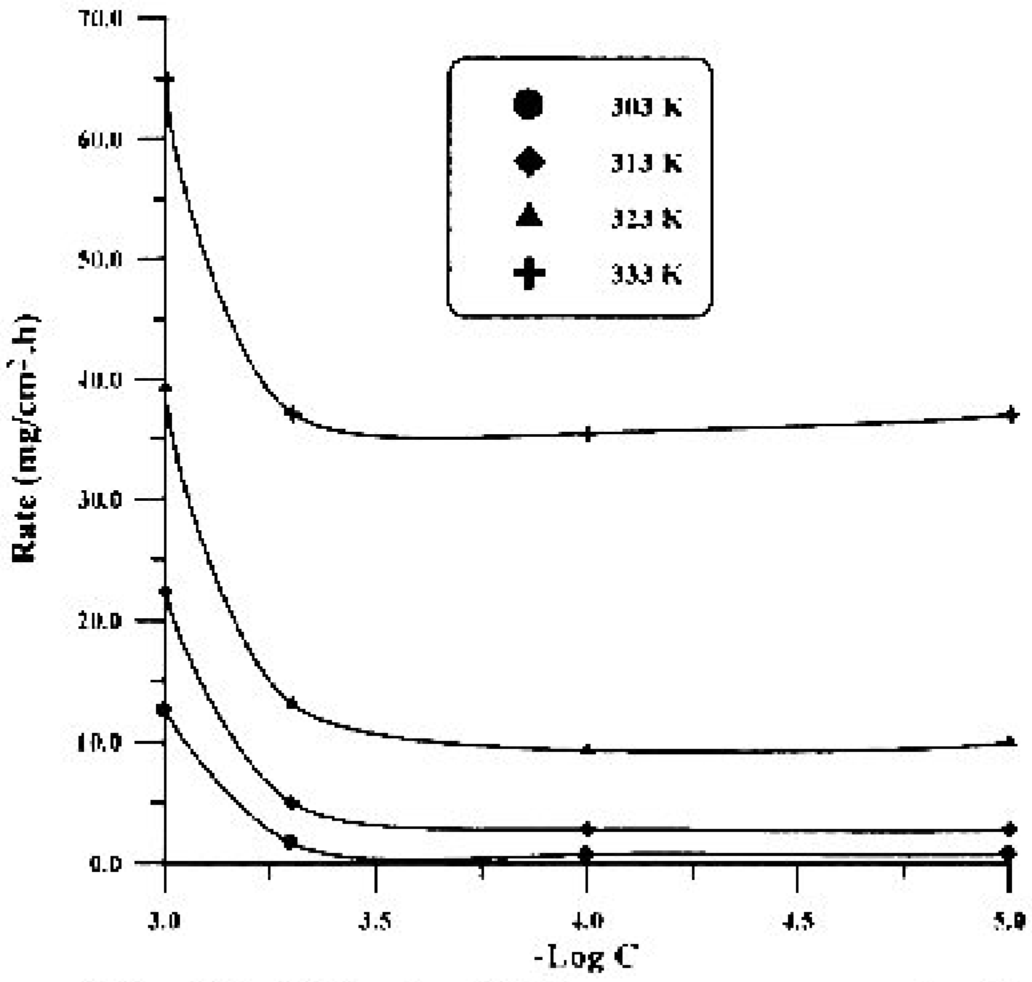

Fig.(1) Effect of thiourea concentration on the corrosion rate of carbon steel in 4M HCl at the temperature range (303-333) K

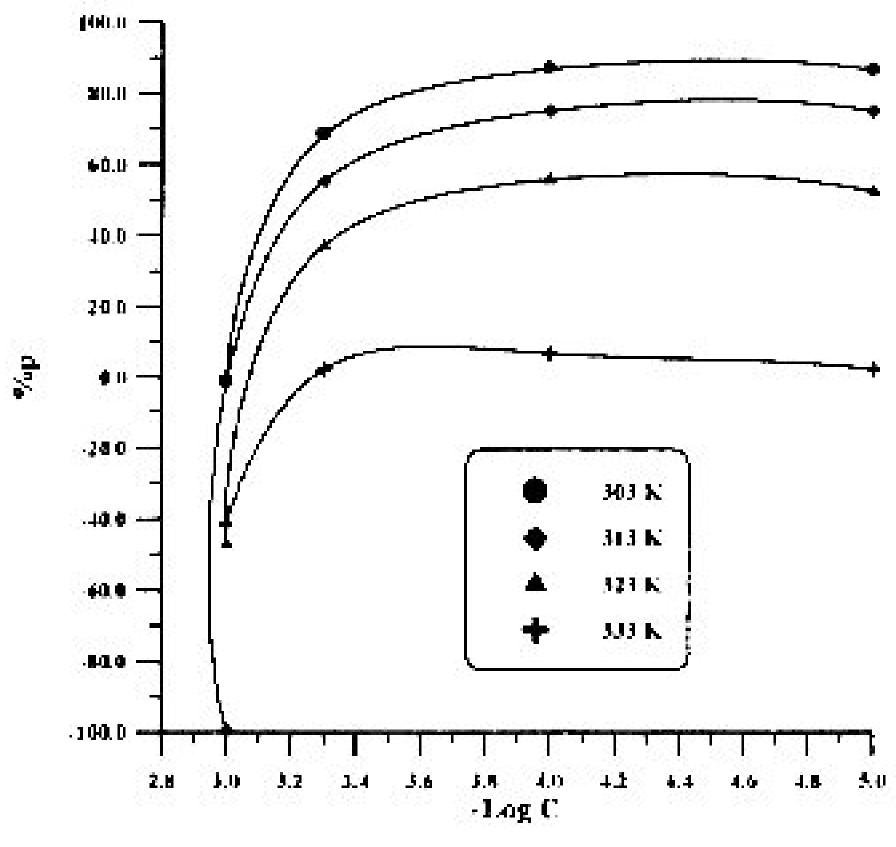

Fig.(2) Effect of thiourea concentration on the protection efficiency of low carbon steel in 4M HCl at four temperature range(303-333) K

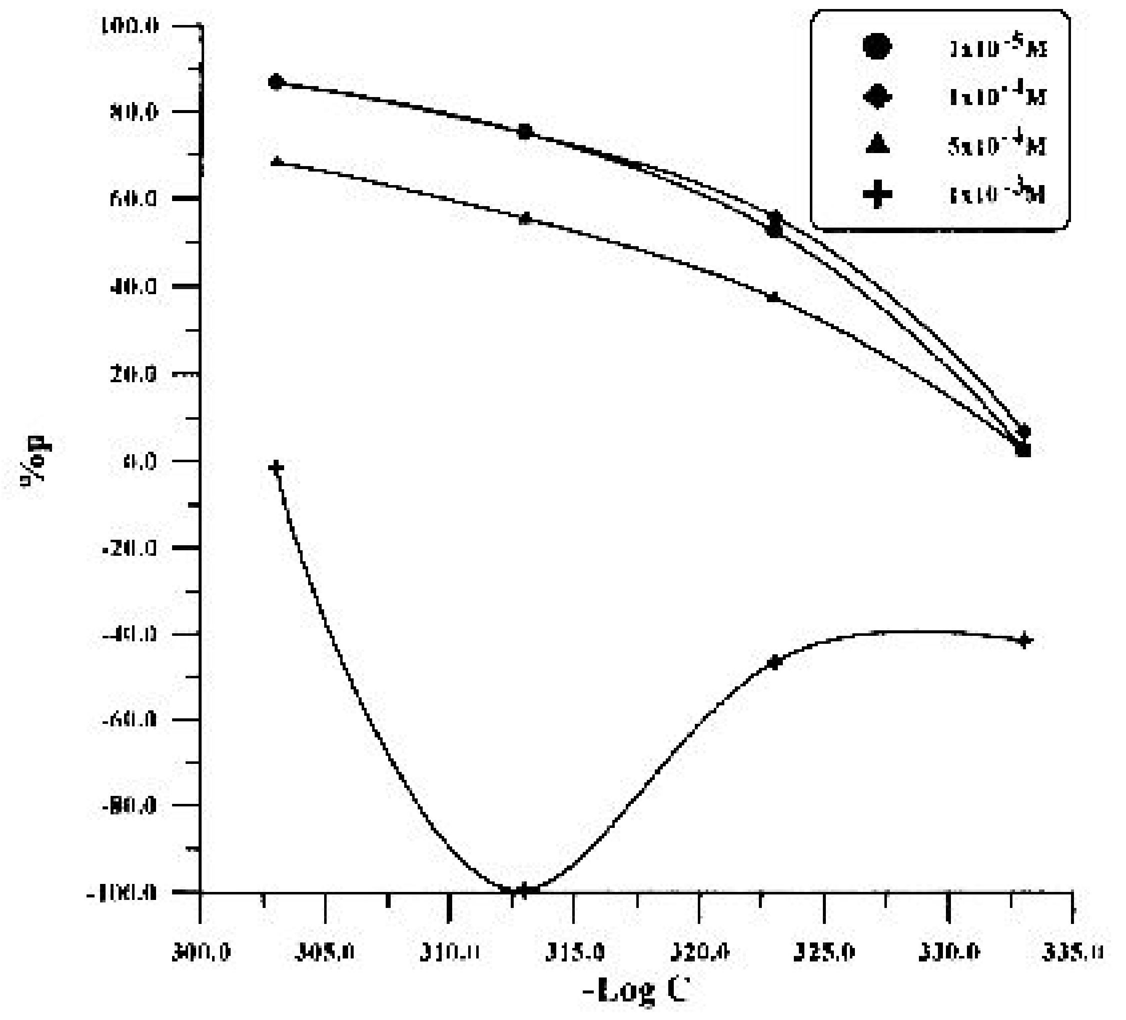

Fig.(3) Effect of temperature on the protection efficiency of thiourea at different concentrations

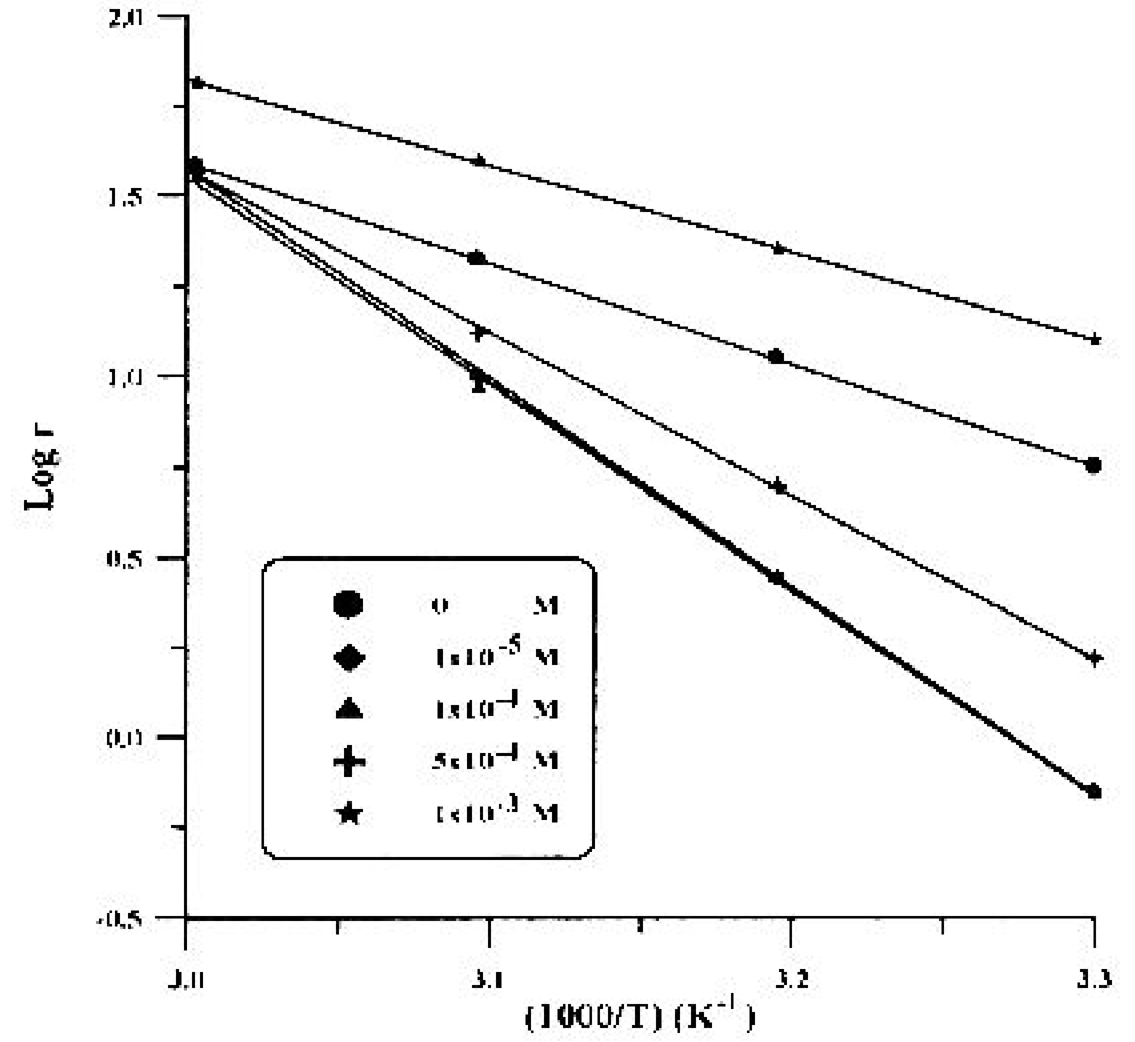

Fig.(4) Arrhenius plot of the corrosion rate of low carbon steel in 4M HCl in presence and absence of thiourea

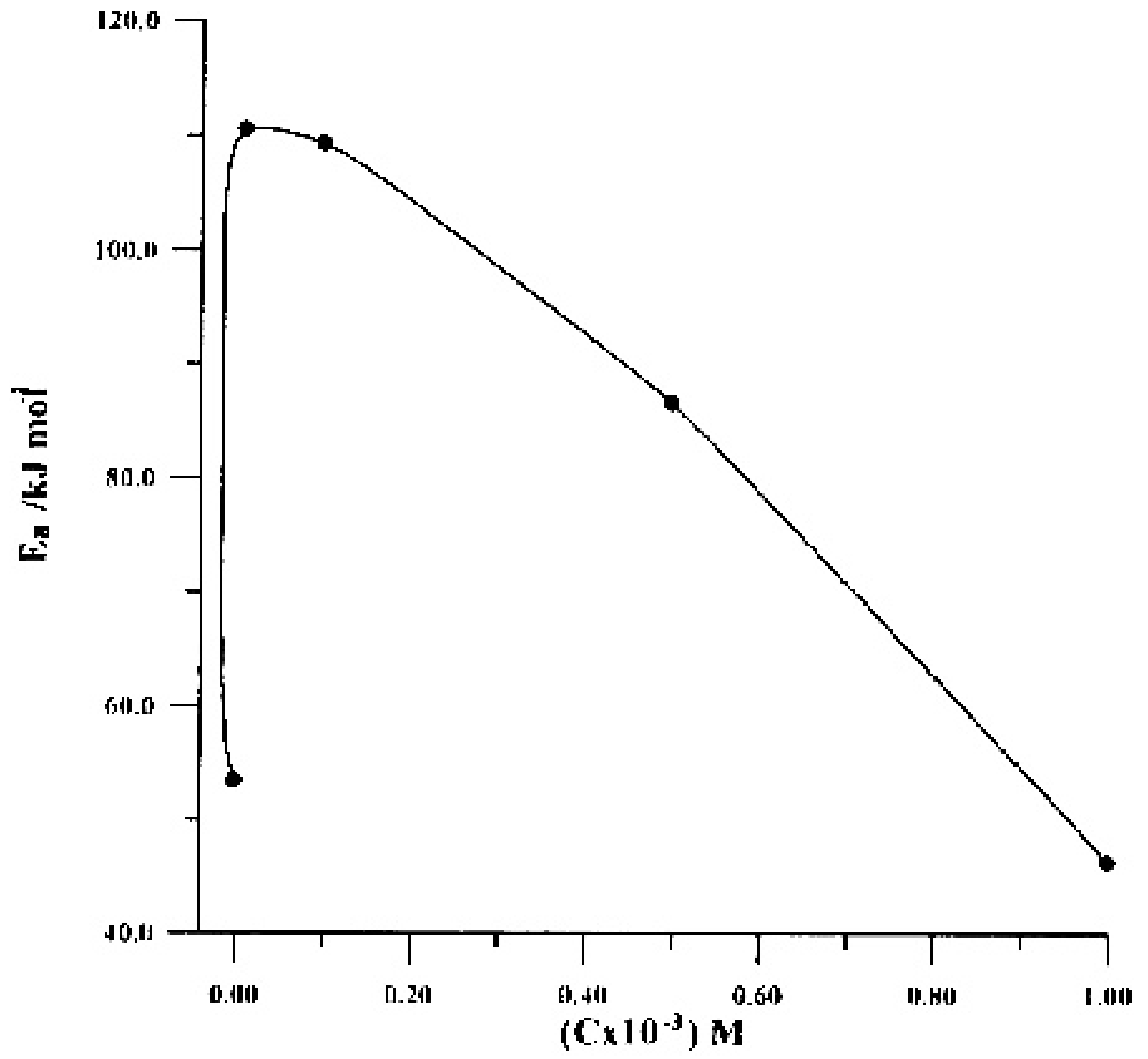

Fig.(5) Values the energy of activation (E_a) for the corrosion of low carbon steel in 4M HCl as a function of thiourea concentration.

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تأثير الثايويوريا على تآكل حديد الصلب واطئ الكاربون في محلول حامض الهيدروكلوريك

إنتظار داود سليمان

قسم الكيمياء،كلية التربية، أبن الهيثم، جامعة بغداد

الخلاصة

تمت دراسة سرعة تآكل حديد الصلب واطئ الكاربون في محلول حامض الهيدروكلوريك 4 مولاري بغياب ووجود مادة الثايويوريا وبطريقتين، قياس فرق الوزن وطريقة قياس حجم الغاز المتحرر وبمدى من درجات الحرارة (303-333) كلفن.

لقد حصلت حماية لحديد الصلب بسبب أضافة الثايويوريا، وهذه الحماية تزداد كلما قل تركيز الثايويوريا في المدى الحراري أعلاه، ووصلت أعى نسبة حماية الى 86.82% عند درجة حرارة 303 كلفن بأستخدام تركيز الثايويوريا (1×10^{-4} مولاري).

وبأستخدام تراكيز عالية من الثايويوريا حوالي (1×10^{-3} مولاري) فأكثر تحدث زيادة في سرعة التآكل حيث تعمل الزيادة من الثايويوريا كمادة محفزة للتآكل لزيادة تفاعلات الاختزال الخاصة بتحرر غاز الهيدروجين وأختزال الثايويوريا يولد جزيئات من H_2S والذي سوف يمتز بصيغة S^{-2}، HS^- على السطح مولداً مواقع فعالة وبالتالي تتحفز التفاعلات المصعدية المتمثلة بذوبان السطح.

تم تفسير النتائج أعتماداً على أمتزاز جزيئات الثايويوريا المتفككة على السطح وعلى قيم طاقة التنشيط لعملية التآكل وذلك من قياسات سرعة التأكل بوجود وبغياب الثايويوريا في الدرجات الحرارية المختلفة.