

## PROTONATION OF THIOUREA IN ACID SOLUTIONS

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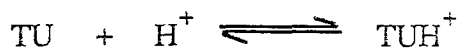
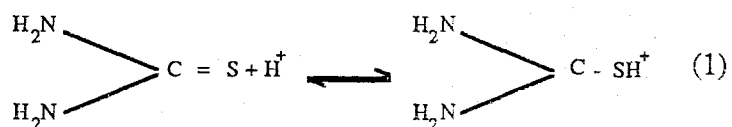
### ABSTRACT

UV Spectroscopy is applied here for the determination of the protonation constant of thiourea. The spectrum shows two peaks at 208 and 238 nm. The UV absorbance of the two peaks changes by changing pH ( or acidity function  $H_0$  for strongly acid solutions).

The ionization constant is determined from a plot of a function of absorbance against  $H_0$ . A value of 0.105 for the protonation constant is obtained.

### INTRODUCTION

Thiourea (T.U.) is known as a corrosion inhibitor for many metals. It shows an interesting pattern of concentration dependence. At low concentration it shifts both the cathodic and anodic polarization curves to higher values with the consequence of decreasing the corrosion current  $I_{COR}$  [1]. At higher concentration (> 5 mM), TU reverses its effect and increases  $I_{COR}$  [2]. Several authors explained this peculiarity by the fact that TU is protonated in aqueous solutions according to [1] :



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The protonated form is said to facilitate the hydrogen evolution reaction and accordingly increases the corrosion rate. A value of 0.1 for the protonation constant is given in the literature [3, 4] and used by many authors (see e.g. ref.5). Reference[3] lists the value of 0.1 based on kinetic methods. This paper reports on the determination of the protonation constant of TU using UV spectrophotometry. It was found necessary to supplement the already published value with another technique.

## EXPERIMENTAL

Ultraviolet spectrophotometer model (PIN 204) Shimadzu (Kyoto - japan) was used. Thiourea specimens were used as received. Conductivity water was used to prepare the solutions of sulphuric acid. The temperature was adjusted to  $25 \pm 0.1^\circ\text{C}$ . The UV spectrophotometer was adjusted at a slit width of 1.0 nm, and the wavelength scan range was 190 - 400 nm.

## RESULTS AND DISCUSSION

Ultraviolet spectra for solutions of 0.1 mM TU in various concentrations of  $\text{H}_2\text{SO}_4$  were measured. Fig. (1) shows the UV spectra of three samples of these solutions (pure  $\text{H}_2\text{O}$ , 1.5 M and 4.5 M  $\text{H}_2\text{SO}_4$ ). The spectra show two absorption peaks in the UV range: at 238 and 208 nm (at 1.5 M acid). The substance is supposed to be negligibly protonated in pure  $\text{H}_2\text{O}$  while it is nearly completely protonated at the highest concentration of the acid used (4.5 M  $\text{H}_2\text{SO}_4$ ).

According to equation (1). The ionization constant  $K_a$  is expressed as

$$K_a = \frac{[TU][H^+]}{[TUH^+]} \quad (2)$$

where [TU], [H<sup>+</sup>] and [TUH<sup>+</sup>] refer to the concentrations of the molecular form, H<sup>+</sup> and the protonated form respectively.

The principle of the method is based on measuring the extinction coefficient (molar absorptivity) as follows [3]:

$$pK_a = pH + \log \frac{\epsilon_I - \epsilon}{\epsilon - \epsilon_M} \quad (3)$$

Where  $\epsilon_I$  is the absorptivity (extinction coefficient) of the ion at the analytical wavelength  $\epsilon_M$  is the absorptivity of the molecule at the same wavelength, and  $\epsilon_N$  is the absorptivity of the mixture of the ions and molecules at the same wavelength.  $\epsilon$  changes with pH.

Provided that the same cell - thickness and concentrations are used, equation (3) may be written in terms of optical absorbance  $A$  instead of absorptivity :

$$pK_a = pH + \log \frac{A_{\max} - A}{A - A_{\min}} \quad (4)$$

Where  $A_{\max}$  is the maximum absorbance at 238 nm,  $A_{\min}$  is the same variable at minimum, and  $A$  is the value of the absorbance for ions and molecules.

For the determination of  $pK_a$  values of very weak bases, the acidity function  $H_O$  replaces the ordinary pH. The  $H_O$  scale is constructed by measuring the ratio

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(BH<sup>+</sup>/B) for an indicator of known pK<sub>a</sub> value (e.g. p-nitroaniline) in solutions of increasing acidity [3]. Replacing H<sub>0</sub> in equation (4) :

$$pK_a = H_0 + \log \frac{A_{\max} - A}{A - A_{\min}} \quad (5)$$

which is the equation used here for determination of pK<sub>a</sub> of TU. This equation (5) predicts a straight line relationship between the second term and H<sub>0</sub>. Such a relationship should have a value of intercept at zero H<sub>0</sub> corresponding to pK<sub>a</sub>.

Table (1) : Ultraviolet absorbance for 0.1 mM Tu in different concentrations of H<sub>2</sub>SO<sub>4</sub> at the analytical wavelength 238 nm.

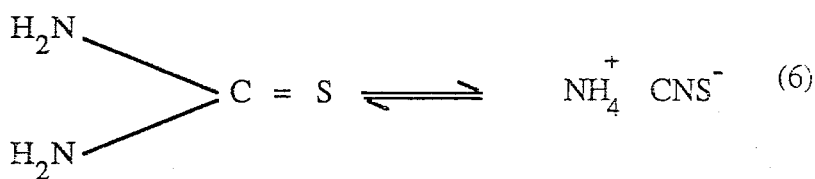
[H <sub>2</sub> SO <sub>4</sub> ] (moles / L)	H <sub>0</sub>	A
0.000	-	1.28
0.375	+0.26	1.21
0.750	-0.07	1.15
1.000	-0.26	1.11
1.500	-0.56	1.00
2.500	-1.12	0.70
3.500	-1.62	0.43
4.500	-2.06	≈ 0.23

values are taken from reference (6).

In Table (1), values of the molar concentration, acidity function  $H_0$  for  $H_2SO_4$  are given together with the absorbance at 238 nm.  $H_0$  is taken from reference[6]. Fig. (2) is the representation of equation (5) applied to the results obtained for TU in  $H_2SO_4$ . The value  $pK_a$  for TU can be deduced from Fig. (2) at a value of zero for the term  $\log [A_{max} - A] / (A - A_{min})$ . The value obtained here for  $pK_a$  of TU is -0.98. This corresponds to a value of 0.105 for the protonation constant of TU, which is in excellent agreement with the published value using kinetic methods[3].

Many authors explained the concentration behaviour of TU, as a corrosion inhibitor for iron and steel, as a result of its protonation (see e.g. ref.[1]). One argument against this approach lies in the fact that theiosemicarbazide, which is a more protonated TU derivative, does not, however, have concentration effect found with TU [7].

In another publication, we proposed a scheme for the concentration effect observed in the case of TU. It was found out that it decomposes in acid solution producing a small concentration of thiocyanate.



Actually  $CNS^-$  ions were detected and determined in acid solutions of TU using a simple spectrophotometric method ( $Fe^{3+}$  - Thiocyanate complex in the visible range at 456 nm) [7]. It was further proved that the addition of small concentrations of  $CNS^-$  (0.01 - 1 mM) to acid solutions of TU, increased the corrosion rate of mild

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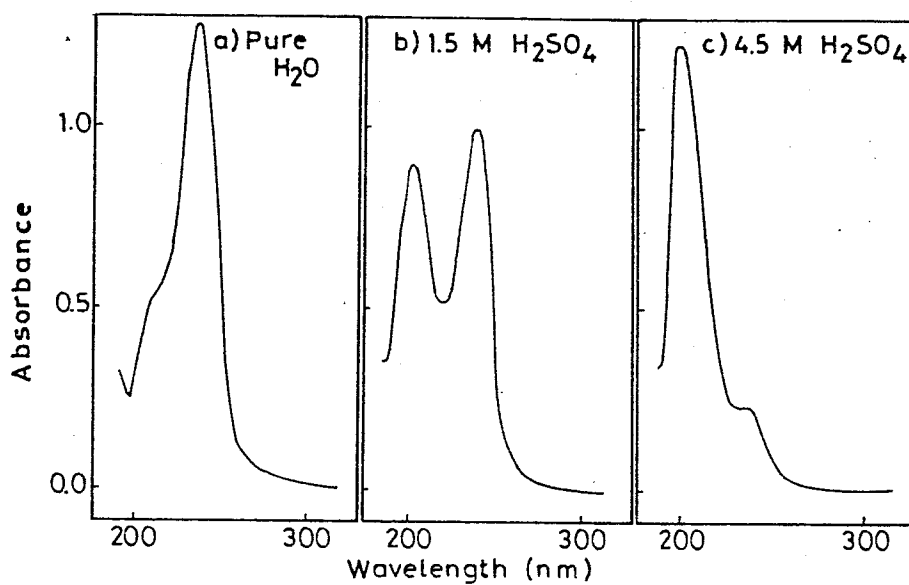


Fig.(1): Ultraviolet spectra for 0.1 mM thiourea in different concentrations of H<sub>2</sub>SO<sub>4</sub>.

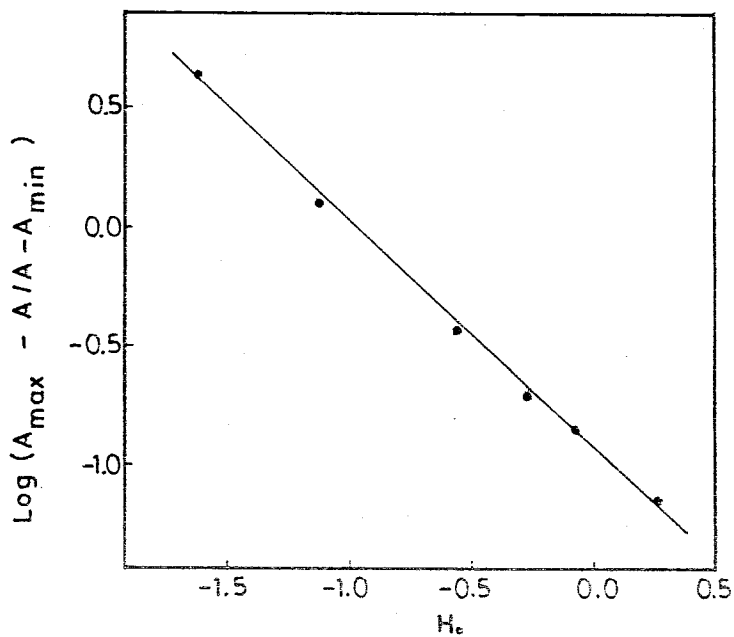


Fig.(2): H<sub>0</sub> -  $\log (A_{\max} - A / A - A_{\min})$  relationship for pK<sub>a</sub> determination of thiourea [equation (5)].

steel (relative to TU alone) [7]. It is feasible to assume that  $\text{CNS}^-$  ions have an antagonistic effect on the inhibiting action of TU probably as a result of a competitive surface adsorption process. A similar conclusion was found by Ammar *et al.* [8].

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تقدير ثابت التآين لمركب الثيوبوريا

محمد وحيد خليل

فى هذا البحث أستخدمت طريقة الأشعة فوق بنفسيجيه فى تقدير ثابت التآين للثيوبوريا. وقد وجد أن الطيف فوق بنفسجى يحتوى على قمتين عند ٢٠٨ و٢٣٨ ن م وقد وجد أيضا أن الامتصاص فوق بنفسجى للقتين يتغير بتغير الحمضية ( أو دالة الحموضه  $H_0$  فى حالة الاحماض القويه). وقد عين ثابت التآين من علاقة خطيه بين دالة الامتصاص و  $H_0$  وكانت قيمة ثابت الهدرجه ( وهو مقلوب ثابت التآين) ١٠٥ ر.