



Effects of ethanolamine and ethylamine on the entropy content of the corrosion of mild steel in 1mol/l HCl solution

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ABSTRACT

The acid corrosion of mild steel in the absence and presence of ethanolamine and ethylamine was investigated by weight loss method at room temperature (298K). The inhibition efficiency was found to increase with increase in inhibitor concentration. The entropy content of the aggressive medium (-279.31J/K/mol) reduced to -296.60J/K/mol on addition of 1.5ml of ethylamine and -288.98J/K/mol on addition of 1.5ml of ethanolamine. The mechanism of inhibition was attributed to the molecular structure of the compounds. © 2013 Trade Science Inc. - INDIA

KEYWORDS

Mild steel;
Hydrochloric acid;
Corrosion inhibitors;
Ethylamine;
Ethanolamine.

INTRODUCTION

Every metal has the natural tendency to revert to its original form—the ore—from which it was initially extracted^[1]. This process is always initiated and propagated by the aggressive environment for which the metal is exposed to. Dry conditions would eliminate much corrosion; so too would protective coatings, but these are often not durable^[2]. The inhibition of such dissolution may be achieved with organic compounds containing π -electrons and/or heteroatoms (N, S, etc) which can adsorb on the metal surface hindering attacks from aggressive species in the environment^[3-6]. By definition, a corrosion inhibitor is a chemical compound or substance that, when added in small concentration to an environment, effectively decreases the corrosion rate^[7]. Since aggressive acid solutions are widely used for industrial purposes, inhibitors are commonly used to reduce the corrosion attack on metallic materials^[8]. It

has been proven that the use of inhibitors is one of the most practical methods for protection of materials against corrosion, especially in acidic media^[9,10].

The extensive use of mild steel in most industrial sector is fundamentally because of its low cost and availability^[11]. However, mild steel is very susceptible to corrosion. This has triggered efforts towards enhancing corrosion resistance of the metal.

Surveys of available literature reveal that nitrogen-containing organic compounds have been used as corrosion inhibitors for several metals in different media^[12-22]. Ethanolamines and ethylamines have specifically been studied separately as corrosion inhibitors for some metals like copper, zinc, mild steel and carbon steel^[23-26]. However, a comparative study of the inhibitory effect of the two compounds with the view of revealing the complementary effect of the functional groups on each other as well as the adsorption entropy content has not been reported.

It is well known that a particular inhibitor which gives a very high efficiency for a particular metal in a specific medium may not work with the same efficiency for other metals in the same or similar medium^[27]. Thus, in our recent work^[28], we compared the action of ethanolamine and ethylamine as corrosion inhibitors for galvanized steel in saline medium. This investigation is part of an intensive project carried out and still going on in our laboratory to study the corrosion of metallic surfaces in various media and their inhibition by some organic compounds. As part of the series, the aim of this present work is to investigate the effect of ethanolamine and ethylamine on the entropy content of the corrosion of mild steel in 1 mol/l HCl at room temperature (25°C) using the weight loss method.

EXPERIMENTAL

Materials

The sheets of commercially available mild steel used for this study were obtained and identified locally. Each sheet was 0.07 cm in thickness. The sheets were mechanically press cut into 4 cm by 4 cm coupons. The specimens were polished to remove adhering impurities using emery papers, degreased with acetone, washed in distilled water and air-dried before use^[29-31]. The concentration of the reagents were prepared by dilution method^[32,33].

Weight loss measurements

The specimens were immersed in five 200 ml beakers (in two sets) and that of the blank (1 mol/l HCl). The sets contained 1 mol/l in each and a corresponding 0.1236 mol/l, 0.2472 mol/l, 0.3708 mol/l, 0.4944 mol/l and 0.6180 mol/l of ethanolamine respectively. The second sets contained 0.1136 mol/l, 0.2272 mol/l, 0.3409 mol/l, 0.4545 mol/l and 0.5681 mol/l ethylamine respectively. The inhibitor solutions were prepared from the stock solution following uniform trend of volumes corresponding to their calculated concentrations given above viz: 1.5 ml, 3.0 ml, 4.5 ml, 6.0 ml and 7.5 ml. The mild steel coupons were suspended into the experimental solution with the help of glass hooks. The initial weights of the specimens were noted. The variation in weight loss was monitored at 1 hour interval progressively for 5 hours. After every hour the specimens were removed,

polished with emery papers, washed in distilled water, degreased with acetone, air-dried and final weights noted. From the initial and final weights of the specimen, the loss of weights was calculated and inhibitor efficiency (%IE) was calculated using equation 1 below^[34,35]:

$$IE (\%) = \frac{W_o - W_1}{W_o} \times 100 \quad (1)$$

where W_o is the weight loss without inhibitor and W_1 is the weight loss with inhibitor.

The corrosion rate of mild steel was calculated (in mp/y – millimetre penetration per year) using the equation^[36]:

$$CR = \frac{534W}{DAT} \quad (2)$$

where W = weight loss (g); D = density of mild steel (7.85 g/cm³); T = exposure time (h); A = area of metal in cm².

RESULTS AND DISCUSSION

Weight loss measurements

The corrosion of mild steel in 1 mol/l HCl solution in the absence and presence of inhibitors was studied by weight loss method at room temperature. The results obtained show that ethanolamine and ethylamine acted as corrosion inhibitors for mild steel in the acid medium. It can be seen from TABLE 1 that the corrosion rate reduces with increase in concentration of the inhibitors. This may be due to an increase of the surface coverage of the metal by the additive molecules. The data also show that the inhibitor efficiency increases with increase in the inhibitors concentration. It is clear from the results that ethylamine is a more efficient inhibitor than ethanolamine in the conditions under consideration. Figures 1 and 2 show the variation in weight loss with time in the absence and presence of the inhibitors. From the figure it is seen that irrespective of the amounts of inhibitor ethylamine performed better than ethanolamine.

Application of absolute reaction rate theory

The theory of absolute reaction rates, frequently also called the transition-state theory, is based on statistical mechanics and represents an alternative approach to reaction kinetics. This Theory postulates

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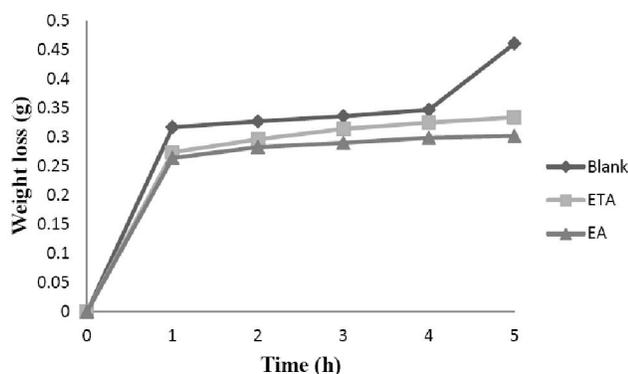


Figure 1 : Variation of weight loss of mild steel without and with 1.5ml of the inhibitors (EA and ETA) in 1mol/l HCl

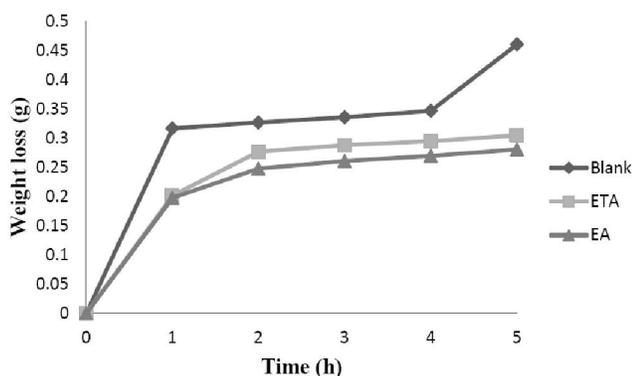


Figure 2 : Variation of weight loss of mild steel without and with 7.5ml of the inhibitors (EA and ETA) in 1mol/l HCl

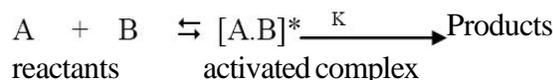
TABLE 1 : Calculated values of corrosion rate, CR and inhibition efficiency (%IE), equilibrium constant (k), adsorption enthalpy (ΔH), and adsorption entropy (ΔS) for the corrosion of mild steel in 1mol/l HCl with ethanolamine (ETA) and ethylamine as inhibitors

System	Concentration (mol/l)	K	ΔH^* (J/K/mol)	ΔS^* (J/K/mol)	CR (mp/y)	% IE
Blank (HCl)	1.00	0.016		-279.31	0.026	-
	0.1236	0.005		-288.98	0.025	3.90
	0.2472	0.007		-286.16	0.024	6.07
HO-CH ₂ -CH ₂ -NH ₂	0.3708	0.012		-281.70	0.022	15.40
	0.4944	0.014		-280.42	0.020	21.10
	0.6180	0.014	-7.40	-280.40	0.019	27.86
	0.1136	0.002		-296.60	0.020	10.66
	0.2272	0.005		-288.18	0.018	12.39
CH ₃ -CH ₂ -CH ₂ -NH ₂	0.3409	0.009		-284.09	0.017	20.71
	0.4545	0.009		-284.09	0.016	22.99
	0.5681	0.012		-281.70	0.014	29.29

that molecules before undergoing reaction must form

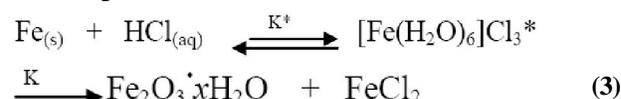
an activated complex in equilibrium with the reactants, and that the rate of any reaction is given by the rate of decomposition of the complex to form the reaction products.

For a reaction between a molecule of A and one of B, the postulated steps can be represented by the scheme



The activated complex has certain properties of an ordinary molecule and possesses temporary stability.

Following the above theory, the corrosion mechanism is postulated with the scheme



Following the above ideas, Eyring^[28] showed that the rate constant k of any reaction irrespective of the order or molecularity is given by the expression

$$k = \frac{RT}{Nh} K^* \quad (4)$$

where R is the gas constant; N , Avogadro's number; h , Plank's constant; T , the absolute temperature; and K^* , the equilibrium constant for the reaction of the activated complex from the reactants.

We resort to thermodynamics and write for K^*

$$\ln K^* = \frac{-\Delta G^*}{RT} \quad (5)$$

$$\ln K^* = \frac{(\Delta H^* - \Delta TS^*)}{RT} \quad (6)$$

where ΔG^* , ΔH^* and ΔS^* are respectively the free energy, enthalpy and entropy of activation.

Introducing equation (6) into equation (4) we obtain for k

$$k = \frac{RT}{Nh} \exp\left(\frac{\Delta S^*}{R}\right) \exp\left(\frac{-\Delta H^*}{RT}\right) \quad (7)$$

$$\ln k = \ln\left(\frac{RT}{Nh}\right) + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad (8)$$

Consequently when k and ΔH^* of a reaction are known at a given temperature, ΔS^* may be found.

$R = 8.314 \text{ J K}^{-1} \text{ mol}^{-1}$; $N = 6.023 \times 10^{23} \text{ mol}^{-1}$; $h = 6.626 \times 10^{-34} \text{ Js}$

$$\therefore \text{Slope} = \frac{-k}{2.303}$$

The equilibrium constant of the reaction in the Eyring-type equation (eqn.8) has been extrapolated from the slope of the straight line of the natural logarithm of the concentration of mild steel (calculated from molar mass-weight of substance relation) and time as shown in Figure 3 and 4 and TABLE 1.

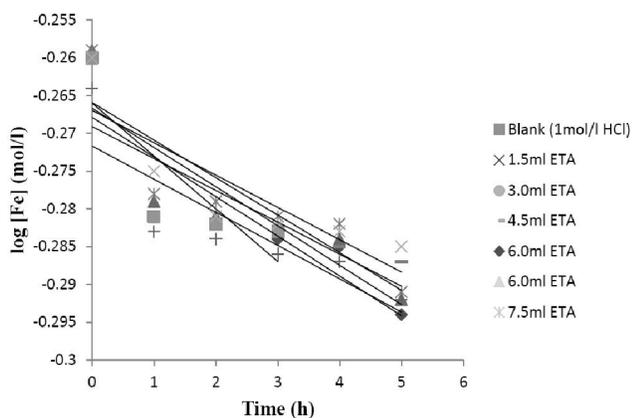


Figure 3: Plot of $\log [Fe]$ (mol/l) versus time (hours) for mild steel corrosion in 1mol/l HCl (Blank) with different concentration of ethanolamine (ETA)

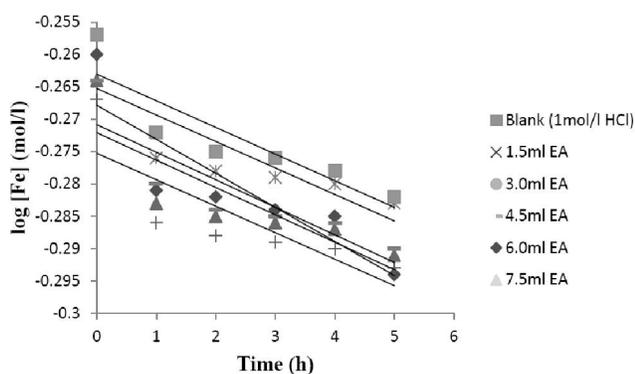


Figure 4: Plot of $\log [Fe]$ (mol/l) versus time (hours) for mild steel corrosion in 1mol/l HCl (Blank) with different concentration of ethylamine (EA)

From equation 3, the enthalpy of the reaction was evaluated from standard tables to be -7.4J/K/mol since the experiment was carried out at room temperature. Hence, the entropy of the reaction at different concentrations of the inhibitors was calculated from k and ΔH^* .

It can be seen from TABLE 1 that the values of entropy (ΔS^*) in the presence of inhibitors are negative and larger than in the absent of inhibitors. This means that the aggressive ions were in a more ordered state than at the blank^[37]. The decrease in the solvent entropy is as a result of desorption of water/aggressive ions that were adsorbed on the surface of the metal which were followed by adsorption of the inhibitors on

the surface of the metal^[38].

The solution which had the aggressive ions in the most ordered state was obtained with about 0.1136mol/l of ethylamine as inhibitor with ΔS^* value of -296.60K/J/mol with a corresponding inhibitory efficiency of 10.66% whereas 0.1236mol/l of ethanolamine gave -288.98J/K/mol of entropy corresponding to 3.90% efficiency. This anomalous, as being reported by *Noor et al*^[8], indicates that the retardation of reaction (metal dissolution) by the compounds is being effected without changing the mechanism. It can be said that the inhibitors may possess better inhibitory effect specifically for acid corrosion of mild steel at higher concentrations.

MECHANISM OF CORROSION INHIBITION

The inhibition of corrosion can be explained on the basis of the concept of adsorption of the inhibitors on the corroding metal surface^[39,40]. The inhibitive action of ethanolamine and ethylamine has been attributed to the strong adsorption on the metal surface using the lone pairs of electron available on the heteroatoms^[28].

The compounds acted as corrosion inhibitors for mild steel though with low efficiencies. Furthermore, a comparison of the inhibitors efficiency revealed that ethylamine performed better than ethanolamine. *Akpan et al.*^[28] reported that the $-\text{OH}$ group, being more electronegative, exerts electron-withdrawing inductive effect on the carbon chain which destabilizes the C-N bond and thereby causing a possible desorption of the main adsorption centre, the $-\text{NH}_2$ group^[23], from the metal surface. In addition, confirmation of $-\text{NH}_2$ as the main adsorption centre has been confirmed by studies reported by *Khalifa et al*^[25]. Another study of ethanolamines has shown that an increase in the number of $-\text{OH}$ groups in an ethanol amine reduces the corrosion inhibition efficiency^[26].

CONCLUSION

Ethanolamine and ethylamine significantly reduced the corrosion rate of mild steel in 1mol/l HCl at high concentrations. The entropy content of the aggressive ions was found to have reduced on the introduction of

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the inhibitors into the corrodent medium. The behaviour of the inhibitors indicates the action of their molecular structure.

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