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Effect of Ethanolamine and Ethylamine on the Entropy Content of the Corrosion of Mild Steel in Tetraoxosulphate (VI) acid Solution

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Abstract

The influence of ethanolamine and ethylamine on the corrosion behaviour of mild steel in 1M H_2SO_4 solution was investigated at room temperature (25^{o}C) by weight loss method. Results obtained show that the compounds are better inhibitors at low concentrations (<0.3M). From the decreasing weights of the metal over time, the concentrations of the metal was evaluated and plots of logarithm of the concentration of metal versus time as well as *Erying*-type equations facilitated the access of thermodynamic parameters such as equilibrium constant (k), enthalpy (ΔH^*) and entropy (ΔS^*) of the corrosion process. The entropy of the aggressive ions was found to have reduced on introduction of the inhibitors into the corrodent medium. Attempt to correlate the molecular structures of the inhibitors to the mechanism of inhibition was made.

Keywords: corrosion inhibition, mild steel, ethanolamine, ethylamine

1. Introduction

The development of corrosion inhibitors is of growing interest in the field of industrial chemistry, as corrosion poses serious threats to the service lifetime of metals as well as alloys used in the industry (Mabrouk *et al.* 2011). Mild steel is extensively used in industry especially for structural applications, but its susceptibility to rusting in humid air and its high dissolution rate in acidic media are the major obstacles for its use (Sachin *et al.* 2009). Therefore, efforts toward the enhancement of the corrosion resistance of the alloy have become a continuous idea (Popoola *et al.* 2012).

It is well known that a particular inhibitor which gives a very high efficiency for a particular metal or alloy in a specific medium may not work with the same efficiency for other metals in the same or similar medium (Joseph *et al*. 2010). Hence, the inhibition efficiency strongly depends on the structure and chemical properties of the inhibitors under the particular experimental condition (Desai & Kapopara 2009).

Nitrogen containing organic compounds have been studied as corrosion inhibitors for mild steel in acidic media (Chitra *et al.* 2010; Loto *et al.* 2012; Mistry *et al.* 2011; Achary *et al.* 2008; Kumar & Karthieyan 2012; Quaraishi & Sardar 2004; Mobin *et al.* 2011). Other experimental studies have also been carried out separately on the use of ethanolamines and alkylamines as corrosion inhibitors (Singh *et al.* 2008; Ashassi-Sorkhabi & Nabavi-Amri 2000; Khalifa *et al.* 2010; Vashi *et al*. 2010; Vashi & Bhajiwala 2010).

Contrary to previous studies, the present work is focused on a comparative investigation of ethanolamine and ethylamine as corrosion inhibitors for mild steel in 1M sulphuric acid solution.

2. Experimental

Hitherto, various kinetic and thermodynamic parameters have been monitored in corrosion of metals via weight loss trends, gasometric methods, thermometric methods, etc. However, the experimental model developed for this study was implemented using the weight loss technique. The weight loss method of monitoring corrosion rate is useful because of its simple application and reliability (Niamen *et al.* 2012).

2.1. Materials

Commercially available grade of mild steel sheets (purity 98%) of 0.10cm in thickness used in this study were identified and obtained locally. The sheets were mechanically pressed cut into 3cm by 3cm coupons with small hole of about 5mm diameter near the upper edge to help hold them with glass hooks. The coupons were polished to remove unwanted adhering impurities using emery papers, degreased with acetone, washed in double distilled water and dried in a desiccator before use (Umoren *et al.* 2008b). The concentrations of the hydrochloric acid, ethanolamine and ethylamine solutions were prepared by dilution method (Zhang & Hua 2009). The chemicals used were analytical grade without further purification (Ebenso *et al.* 2004).

2.2. Weight loss measurements

The specimens were immersed in eleven 250ml beakers out of which one was labelled “BLANK” containing 1M of sulphuric (H_2SO_4) acid (corrodent). The next sets of five beakers were labelled A-E containing 1M H_2SO_4 and a corresponding 1.5ml, 3.0ml, 4.5ml, 6.0ml and 7.0ml of ethanolamine (ETA) as inhibitor. The remaining five beakers were labelled F-J and contained 1M H_2SO_4 and a corresponding 1.5ml, 3.0ml, 4.5ml, 6.0ml and 7.0ml of ethylamine (EA) as inhibitor. The initial weights of the coupons were noted. The variation in weight loss was monitored at 1hour interval progressively for 5hours. After every hour the specimens were removed, polished with emery papers, washed in double distilled water, degreased with acetone, dried and final weights noted. From the initial and final weights of the specimens, the loss of weights was calculated and the efficiency of inhibitor (%IE) was calculated using the equation below (Kumar 2008):

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

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 (Umoren *et al.* 2008a):

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

where W = weight loss (g); D = density of mild steel (7.85g/cm^3); T = exposure time (h); A = area of metal in cm^2.

3. Results and Discussions

3.1. Weight loss measurements

The effect of introduction of ethanolamine and ethylamine at different concentrations on the corrosion of mild steel in 1M H_2SO_4 was studied at room temperature (25°C). The results obtained show that the corrosion rate significantly reduced on the addition of the inhibitors as shown in Table 1. The compounds achieved maximum corrosion inhibition efficiency at low concentrations as indicated on the trends of percentage inhibition efficiency (%IE) values in Table 1.

It is also observed that ethylamine inhibited corrosion more efficiently than ethanolamine at the concentration considered as indicated in Figure 1. The maximum inhibitory action of these compounds at low concentration are consistent with the findings of *Mabrouk et al.* (2011); that in such a solution the concentration of the inhibitor is sufficient to cover almost completely the metal surface and the rate of adsorption becomes slower, compared to that at lower concentrations.

3.2. Application of Absolute Reaction Rate Theory

The theory of absolute reaction rates (frequently also called the transition-state theory), as stated by Sharma & Sharma (1999), is based on statistical mechanics and represents an alternative approach to reaction kinetics. This theory postulates 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

$$A + B \leftrightarrows [A.B]^* \xrightarrow{K} \text{Products}$$

reactants activated complex

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

$$Fe_{(s)} + H_2SO_{4(aq)} \xrightleftharpoons{K^*} [Fe(H_2O)_x]SO_4^* \xrightarrow{K} FeSO_4 \cdot xH_2O + FeSO_4 \qquad (3)$$

Following the above ideas, Eyring, according to Sharma & Sharma (1999), showed that the rate constant, k, of any reaction irrespective of the order or molecularity is given by the expression

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

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*

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

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

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 = 8.314JK^{-1}mol^{-1} ; N = 6.023 x10^{23}mol^{-1} ; h = 6.626 x10^{-34}Js

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

The equilibrium constant (k) 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 2 and 3 and Table 1.

The enthalpy of the reaction obtained as -2095.3J/K/mol was evaluated from tables since the reaction was carried out at constant 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 medium and that the activated complex at the rate determining step represents an association rather than a dissociation step (Saliyan & Adhikari 2009). However, the value of ΔS* decreases gradually with increasing inhibitor concentration in all cases. 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 (Emranuzzaman *et al.* 2004).

The solution which had the aggressive ions in the most ordered state was obtained with about 0.12M of ethylamine as inhibitor with ΔS* value of -288.90K/J/mol and a corresponding highest corrosion efficiency of 96.01%.

3.3. 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 (Shylesha *et al.* 2011). The inhibitive action of ethanolamine and ethylamine may be attributed to the strong adsorption on the metal surface using the lone pairs of electron available on the heteroatoms.

The compounds acted as corrosion inhibitors for mild steel in 1M H_2SO_4. Furthermore, a comparison of the inhibitors' efficiency (%IE) revealed that ethylamine performed better than ethanolamine. It may be possible that the –OH group, being more electronegative than all the organic functional groups present, exerts electron-withdrawing inductive effect on the carbon chain and consequently destabilize the C-N-Fe bonds thereby causing a possible desorption of the main adsorption centre, the $-NH_2$ group, from the metal surface. In addition, confirmation of $-NH_2$ as the main adsorption centre has been confirmed by studies reported by Khalifa *et al.* (2010). Another study of ethanolamines has shown that an increase in the number of –OH groups in an ethanol amine reduces the corrosion inhibition efficiency (Vashi *et al.* 2010).

4. Conclusion

Ethanolamine and ethylamine significantly reduced the corrosion rate of mild steel in 1M solution of sulphuric acid at low concentrations. The entropy content of the aggressive ions was found to have reduced on the introduction of the inhibitors into the corrodent medium. The behaviour of the inhibitors indicates the action of their molecular structure.

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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 1M H_2SO_4 with ethanolamine (ETA) and ethylamine as inhibitors at room temperature (298K)

System	Concentration (M)	K	ΔH* (J/K/mol)	ΔS* (J/K/mol)	CR (mp/y)	%IE
Blank (H_2SO_4)	1.00	0.020	-2095.30	-280.17	0.39	-
CH_3-CH_2-CH_2-NH_2	0.1236	0.007		-288.90	0.01	96.01
	0.2472	0.009		-286.81	0.09	66.74
	0.3708	0.009		-286.81	0.10	61.43
	0.4944	0.012		-284.42	0.13	54.05
	0.6180	0.014		-283.14	0.15	49.05
HO-CH_2-CH_2-NH_2	0.1136	0.009		-286.81	0.07	25.99
	0.2272	0.012		-284.42	0.10	18.50
	0.3409	0.012		-284.42	0.17	16.20
	0.4545	0.014		-283.14	0.23	15.22
	0.5681	0.018		-281.14	0.29	14.22

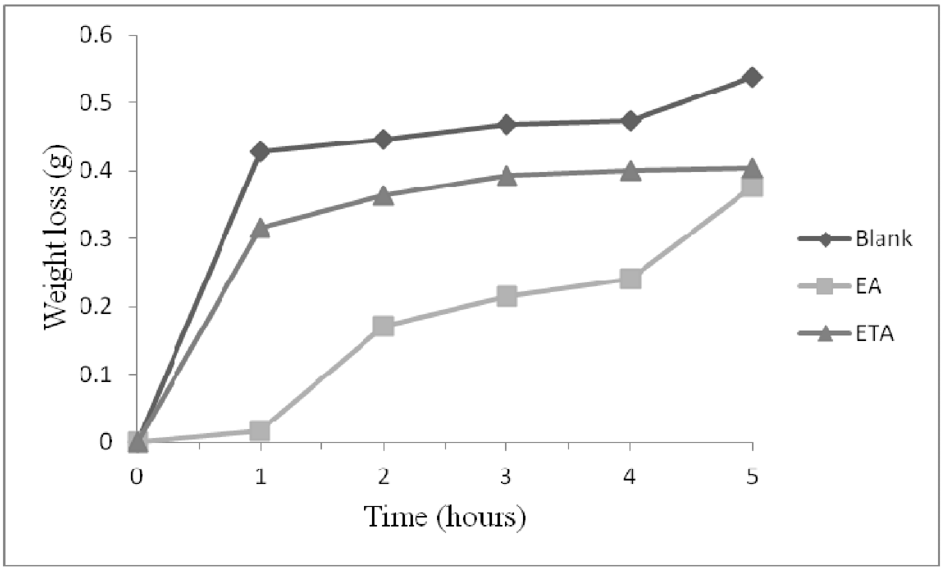

Figure 1: Variation of weight loss of mild steel in the absence and presence of 1.5ml of the inhibitors (EA and ETA) in 1M H_2SO_4

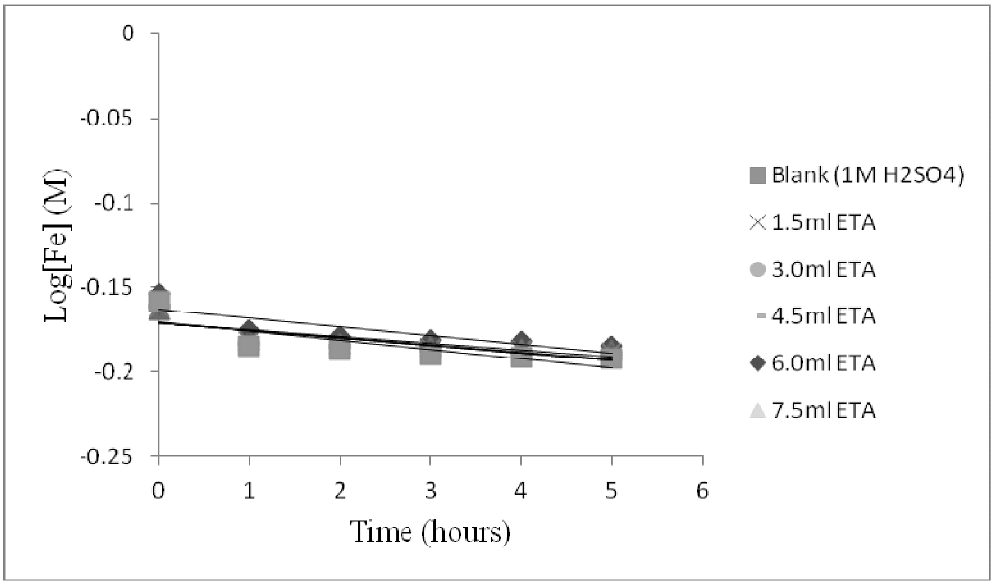

Figure 2: Plot of log [Fe] (M) versus time (hours) for mild steel corrosion in 1M H_2SO_4 (Blank) with different concentration of ethanolamine (ETA)

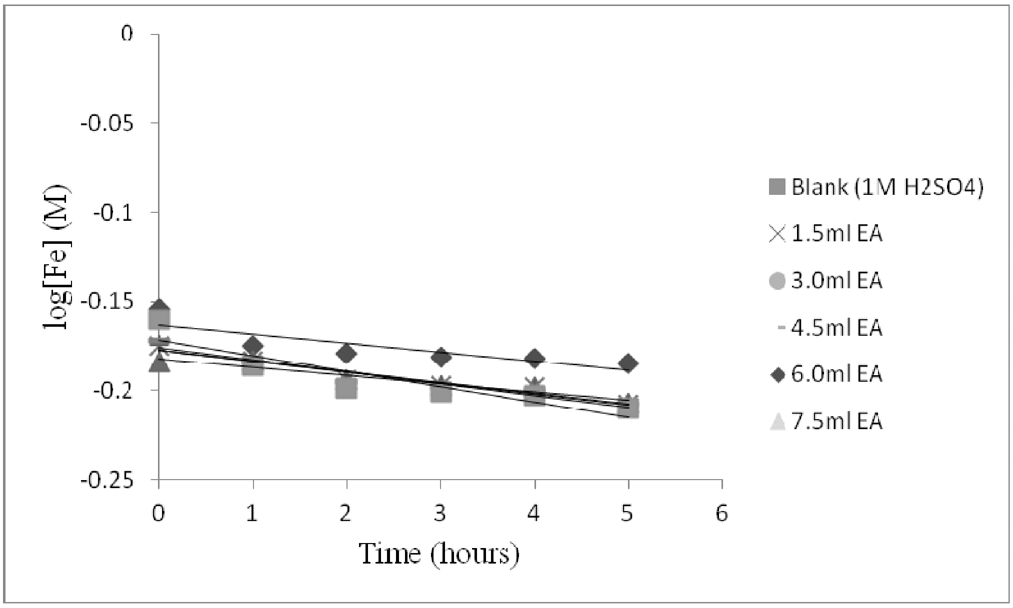

Figure 3: Plot of log [Fe] (M) versus time (hours) for mild steel corrosion in 1M H_2SO_4 (Blank) with different concentration of ethylamine (EA)

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