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

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ABSTRACT

The corrosion inhibition of aluminium in 1mol/l HCl in the presence of ethanolamine and ethylamine at room temperature was studied using the weight loss technique at room temperature (25°C). The results obtained show that ethylamine inhibits corrosion more efficiently having had maximum inhibition efficiency of 95.80% against ethanolamine's 89.08%. The inhibition efficiency was found to increase with decrease in concentration of the inhibitors and decrease in time. The thermodynamic parameters such as equilibrium constant (k), enthalpy (H) and entropy (S) were obtained through the theory of absolute reaction rates and its transition equations. The entropy of the aggressive ions was found to have significantly reduced on the introduction of the inhibitors into the corrodent medium.

KEYWORDS

Corrosion inhibition;
Aluminium;
Ethanolamine;
Ethylamine;
HCl solution;
Entropy content.

INTRODUCTION

In as much as ions are very useful in everyday chemistry, there is need to contain them in several other conditions –including their inhibition during corrosion control.

The enormous cost of the loss of materials by corrosion warrants appreciable expenditure in opposing corrosion[1]. It has been found that, of the available techniques used in combating corrosion problems, the use of chemical inhibitors remains the most cost effective and practical method[2-10].

Aluminium has a wide range of industrial applications which exposes it to acidic environment and requires protection against the impending effect –corrosion. A survey of available literature has shown that nitrogen containing organic compounds have been used as corrosion inhibitors in acidic corrodents[4,11].

Aggressive ions in solution tend to facilitate the corrosion of materials. Studies of the adsorption entropy content of such systems have revealed that inhibitors help to contain the aggressive ions by hindering them from the active sites[12], making the medium more ordered, and ultimately reducing the rate at which the materials involved deteriorate. This, apparently is achieved by adsorption of the inhibitors on the surfaces of the materials by means of their chemical structure.

In our recent work[13], we have reported on the effects of ethanolamine and ethylamine on the entropy content of the corrosion of galvanised steel in sodium chloride solution. The efficient inhibitory effect of these inhibitors at low concentrations prompted their consideration within an acidic medium in this present work.

EXPERIMENTAL

Materials

Commercially available grade of aluminium sheets of 0.07cm in thickness used in this study were identified and obtained locally. The sheets were mechanically pressed cut into 4cm by 5cm 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 distilled water and air-dried before use[7,8,13-15]. The concentrations of the hydrochloric acid, ethanolamine and ethylamine solutions were prepared by dilution method[16,17]. The chemicals used were analytical grade without further purification[18-20].

Weight loss measurements

The specimens were immersed in eleven 250ml beakers out of which one was labelled "BLANK" containing 1mol/l of hydrochloric (HCl) acid (corrodent). The next set of five beakers were labelled A-E containing 1mol/l HCl 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 1mol/l HCl and a corresponding 1.5ml, 3.0ml, 4.5ml, 6.0ml and 7.0ml of ethylamine (EA) as inhibitor. The calculation as regards the molar concentration was discussed in our previous publication[13]. 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 distilled water, degreased with acetone, air-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[19-24]:

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

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

The corrosion rate of aluminium was calculated (in mp/y–millimetre penetration per year) using the equation[3,10,13,24-26]:

$$CR = \frac{87.6W}{DAT} \qquad (2)$$

where W = weight loss (g); D = density of aluminium ($2.7 g/cm^3$); T = exposure time (h); A = area of metal in cm^2.

RESULTS AND DISCUSSION

Weight loss measurements

The effect of introduction of ethanolamine and ethylamine at different concentrations on the corrosion of aluminium in 1mol/l HCl was studied at room temperature (25°C). The results obtained show that the corrosion rate increases with time as shown in TABLE 1, 2 and 3. The inhibitors achieved maximum inhibition efficiency at low concentrations as indicated on the trends of percentage inhibition efficiency (%IE) values in TABLE 2 and 3. It is also observed that ethylamine inhibited corrosion more efficiently than ethanolamine at low and high concentrations as shown in Figure 1a and 1b. The actions of these inhibitors at low concentration are consistent with the findings of Mabrouk et al.[2]

It is worthy to note that the inhibitors exhibit better inhibitory effect in acidic medium than in a neutral medium when compared with our studies previously reported[13]. In addition, studies have shown that N-containing compounds tend to demonstrate good protection to aluminium in acidic media[11,27].

TABLE 1 : Calculated values of corrosion rate, CR, for the corrosion of aluminium in 1mol/l HCl

Time (h)	CR (mp/y)x10^{-2}
0	-
1	6.115
2	6.971
3	9.389
4	9.863
5	10.28

Application of absolute reaction rate theory

The theory of absolute reaction rates,[28], frequently also called the transition-state theory, 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

$$\underset{\text{reactants}}{A + B} \rightleftharpoons \underset{\text{activated complex}}{[A.B]^*} \xrightarrow{K} \text{Products}$$

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

$$2Al_{(s)} + 6HCl_{(aq)} \underset{}{\overset{K^*}{\rightleftharpoons}} 2[Al(H_2O)_6]Cl_3^* \xrightarrow{K} AlC_3{}^{\cdot}xH_2O + AlCl_3 \quad (3)$$

Following the above ideas, Eyring[28] showed that the rate constant k of any reaction irrespective of the order

TABLE 2 : Calculated values of corrosion rate, CR and inhibition efficiency (%IE) for the corrosion of aluminium in 1mol/l HCl with ethanolamine (ETA) as inhibitor

Concentration of ethanolamine (ETA), (mol/l)	Time (h)	CR (mp/y) $x10^{-2}$	%IE
0.0989	0	-	-
	1	1.578	77.73
	2	2.025	74.19
	3	2.051	70.88
	4	3.018	70.58
	5	3.140	68.06
0.1978	0	-	-
	1	1.026	89.08
	2	1.696	72.16
	3	1.999	71.02
	4	3.472	66.16
	5	3.835	61.16
0.2967	0	-	-
	1	1.380	81.57
	2	1.815	77.44
	3	2.209	68.07
	4	3.708	63.88
	5	5.791	41.29
0.3955	0	-	-
	1	1.657	77.31
	2	2.130	72.74
	3	2.209	68.07
	4	4.653	54.72
	5	4.860	50.72
0.4944	0	-	-
	1	2.012	71.81
	2	2.683	66.98
	3	3.892	43.73
	4	7.417	27.73
	5	7.195	27.09

TABLE 3 : Calculated values of corrosion rate, CR and inhibition efficiency (%IE) for the corrosion of aluminium in 1mol/l HCl with ethylamine (EA) as inhibitor

Conc. of Ethylamine (EA), (mol/l)	Time (h)	CR (mp/y) $x10^{-2}$	%IE
0.0909	0	-	-
	1	0.395	95.80
	2	2.249	63.23
	3	2.709	60.84
	4	4.750	53.60
	5	4.774	50.79
0.1818	0	-	-
	1	1.114	87.39
	2	1.118	81.29
	3	1.815	73.64
	4	3.057	70.25
	5	3.519	64.32
0.2727	0	-	-
	1	0.513	93.28
	2	0.631	91.63
	3	2.183	68.37
	4	3.511	65.76
	5	3.566	63.91
0.3636	0	-	-
	1	0.434	93.16
	2	0.579	92.90
	3	0.631	91.59
	4	3.235	68.52
	5	3.409	65.44
0.4545	0	-	-
	1	1.973	73.13
	2	2.499	67.84
	3	2.525	63.88
	4	5.886	41.29
	5	6.036	40.34

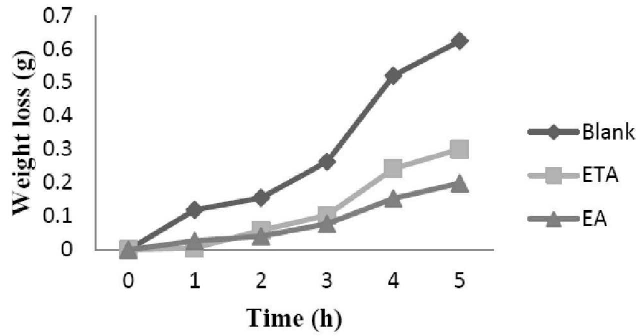

Figure 1a : Variation of weight loss of aluminium without and with 3ml of inhibitors (EA and ETA) in 1mol/l HCl solution

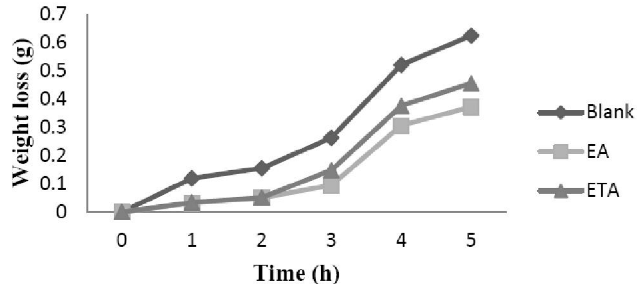

Figure 1b : Variation of weight loss of aluminium without and with 7.5ml of inhibitors (EA and ETA) in 1mol/l HCl solution

or molecularity is given by the expression

$$k = \frac{RT}{Nh}K^* \tag{4}$$

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*

$$\ln K^* = \frac{-\Delta G^*}{RT} \tag{5}$$

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

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

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

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

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

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

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

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 aluminium (calculated from molar mass-weight of substance relation) and time as shown in Figure 2 and 3 and TABLE 4.

From equation 3, the enthalpy of the reaction was evaluated from standard tables to be -2411.6J/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^*.

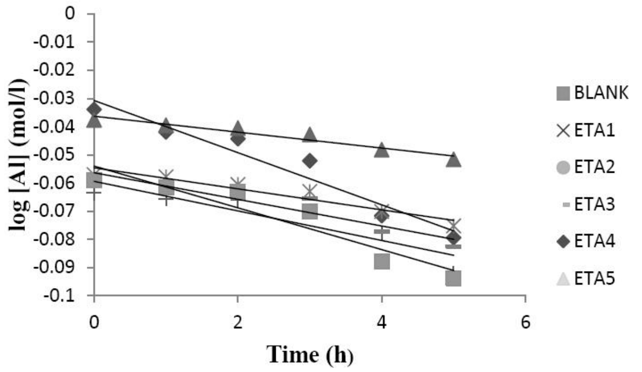

Figure 2 : Plot of log [Al] (mol/l) versus time (days) for aluminium corrosion in 1mol/l NaCl (Blank) with 1.5ml (ETA1), 3.0ml (ETA2), 4.5ml (ETA3), 6.0ml (ETA4) and 7.5ml (ETA5) of ethanolamine as inhibitor at room temperature (298K)

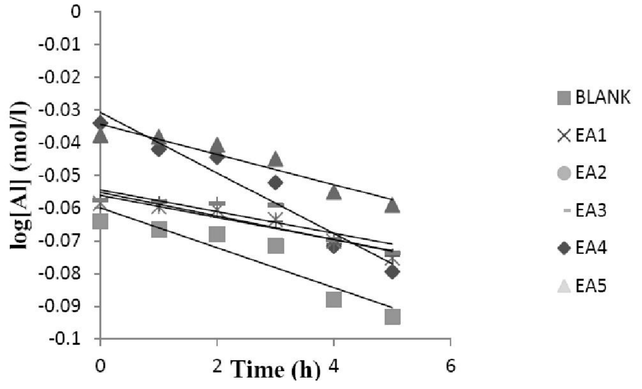

Figure 3 : Plot of log [Al] (mol/l) versus time (days) for aluminium corrosion in 1mol/l NaCl (Blank) with 1.5ml (EA1), 3.0ml (EA2), 4.5ml (EA3), 6.0ml (EA4) and 7.5ml (EA5) of ethylamine as inhibitor at room temperature (298K)

It can be seen from TABLE 4 that the values of

TABLE 4 : Thermodynamic parameters for the corrosion of galvanized steel in 1mol/l HCl with and without the presence of different concentrations of inhibitors at room temperature (298K)

System	Concentration (mol/l)	K	ΔH* (J/K/mol)	ΔS* (J/K/mol)
Blank	1.00	0.010	-2411.60	-291.29
Ethanolamine HO-CH_2-CH_2-NH_2	0.0989	0.005		-297.05
	0.1978	0.007		-294.25
	0.2967	0.009		-292.16
	0.3955	0.019		-285.94
	0.4944	0.024		-284.01
Ethylamine CH_3-CH_2-NH_2	0.0909	0.004		-298.90
	0.1818	0.005		-294.25
	0.2727	0.006		-293.53
	0.3636	0.008		-293.14
	0.4545	0.011		-290.50

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 higher order state than at the initial state[9,29,31]. 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[13,30].

The solution which had the aggressive ions in the most ordered state was obtained with about 0.0909mol/l of ethylamine as inhibitor with ΔS* value of -298.90K/J/mol with a corresponding highest corrosion efficiency of 95.80%. This excellent inhibitory effect can be attributed to chemisorption of the lone pair of electrons of the nitrogen on the metal surface. Attempt to correlate the chemical structure of the inhibitors to the mechanism of inhibition had previously been reported[13].

CONCLUSION

It has been shown in this study that the addition of ethanolamine and ethylamine to HCl reduces the corrosion rate of aluminium in the acid. The inhibitors achieved maximum efficiency at lower concentrations (≤0.29mol/l). The entropy content of the corrodent was observed to have significantly reduced on the introduction of the inhibitors.

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