

## A STUDY ON THE RETARDATION OF THE CORROSION OF Al-Mn ALLOY IN HYDROCHLORIC ACID SOLUTION

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The effect of KSCN, NaCN,  $\text{NaN}_3$ ,  $(\text{CH}_3)_2\text{SO}$  and  $\text{CH}_3\text{NH}_2$  on the corrosion of Al-Mn alloy in 3.0 N hydrochloric has been investigated using Mylius thermometric technique. It has been found that KSCN, NaCN,  $(\text{CH}_3)_2\text{SO}$  and  $\text{CH}_3\text{NH}_2$  act as inhibitors while  $\text{NaN}_3$  acts as accelerator at all concentrations used. KSCN has higher inhibition effect, while  $\text{CH}_3\text{NH}_2$  is the lowest one. The extent of inhibition of the studied compounds was found in agreement with the difference in charge, electronic structure and the basicity of the sulphur, oxygen and nitrogen sites involved.

**Key words:** Corrosion, Inhibitors, Thermometric method, Al-Mn alloy.

### INTRODUCTION

The study of inhibition of acid corrosion of aluminium and its alloys mainly Al-Mg and Al-Mn alloys is a subject with great industrial significance. Several studies [1-6] have been made on the effect of certain organic and inorganic compounds on the corrosion of Al and its alloys in different media. It is found that the addition of these compounds to the reaction medium effect on the reaction numbers and this effect depend upon the type and concentration of the surfactant.

In this paper, the effect of KSCN, NaCN,  $\text{NaN}_3$ ,  $(\text{CH}_3)_2\text{SO}$  and  $\text{CH}_3\text{NH}_2$  on the corrosion of Al-Mn alloy in hydrochloric acid solution was investigated.

### EXPERIMENTAL

All the chemicals used were of analytical reagent grade. The solutions were prepared in double distilled water. Experiments were carried out at  $22 \pm 1.0^\circ$ . Duplicate runs were performed for each concentration and the mean values were recorded. Each experiment was carried out with 25 ml of the test solution and with a new test piece.

The reaction vessel used in testing the corrosion rate was basically as described by Mylius [7]. The vessel was placed in a dewar flask to minimize heat losses by radiation. The test pieces of 1x10 cm surface area was bent in U form. The variation of the temperature of the system was measured to  $\pm 0.5^\circ$  by the thermometer. Before use, the test pieces were cleaned by recommended procedures [8, 9]. The chemical composition of the alloy is 98% Al and 2% Mn.

The reaction number (R.N.) of the studied compounds in presence of 3.0M hydrochloric acid can be evaluated using Mylius formula as given in equation (1)

$$\text{R.N.} = \Delta T/t \quad ^\circ\text{C}/\text{min.} \quad \dots\dots\dots(1)$$

where  $\Delta T = T_m - T_o$ ,  $T_m$  and  $T_o$  are the maximum and initial

temperature of the system for each experiment respectively, and  $t$  is the time in minutes taken to reach  $T_m$ .

On the other hand, the degree of retardation of corrosion, i.e. inhibition is defined as given in equation (2).

$$A = (\Delta\text{R.N.})/(\text{R.N.})_{\text{free}} \times 100 \quad \dots\dots\dots(2)$$

where  $A$  is the percentage inhibition.  $\Delta\text{R.N.} = [(\text{R.N.})_{\text{free}} - (\text{R.N.})_{\text{inh}}]/(\text{R.N.})_{\text{free}}$  and  $(\text{R.N.})_{\text{inh}}$  are the reaction numbers in absence and presence of any inhibitor respectively.

### RESULTS AND DISCUSSION

The effect of hydrochloric acid concentrations on the corrosion of Al-Mn alloy was investigated covering the range 2 – 4.5 M. It has been found that as the acid concentration increase, the corrosion rate increases and the maximum temperature  $T_m$  increase with decreasing the time ( $t$ ) needed to reach  $T_m$ . The same conclusions were reported by Talati *et al.* [10]. The observed high corrosive action of HCl may be due to the formation of aluminium chloride complex which catalyses the dissolution process of the alloy. The results obtained are given in Table 1.

Table 1. Effect of HCl concentrations on the corrosion rate of Al-Mn alloy

Conc. M	$T_m$ $^\circ\text{C}$	$t$ , min.	R.N. $^\circ\text{C}/\text{min}$
2.5	75	74	0.71
3.0	92	30	2.28
3.5	97	27	2.74
4.0	98	21.24	3.81
4.5	99.5	14.24	5.65

Temperature change of the system involving Al-Mn alloy in 3.0 M HCl was followed in absence and presence of different additive concentrations. Figure 1 represents tem-

perature-time curves for KSCN, NaCN and  $(\text{CH}_3)_2\text{SO}$  at concentration around  $1 \times 10^{-4}$  M and  $\text{CH}_3\text{NH}_2$  at  $1 \times 10^{-2}$  M in 3.0 M HCl. From the figure the maximum temperature measured in absence of any additives in  $92^\circ$  which is attained after 30 minutes. This corresponds to reaction number (R.N.) of  $2.28^\circ \text{min}^{-1}$ . On increasing the concentration of the additives, the time required to reach  $T_m$  increases. This indicates that the above mentioned additives retard the dissolution of the alloy presumably by their absorption on the surface of the alloy. The extent of retardation depends on the degree of coverage of the alloy surface with the adsorbate and the temperature-time curves provide a means of differentiating between weak and strong adsorption [2, 4]. Typical temperature-time curves were obtained in presence of different concentrations of the same additive. Strong adsorption is observed for KSCN ( $A = 87.1\%$  at  $8 \times 10^{-4}$  M),  $(\text{CH}_3)_2\text{SO}$  ( $A = 57.8\%$  at  $1 \times 10^{-4}$  M) and NaCN ( $A = 49.9\%$  at  $1 \times 10^{-4}$  M) where a simultaneous increase in time ( $t$ ) and a diminution in  $T_m$  takes place and both factors cause a large decrease in the reaction number (R.N.) of the system. Weak adsorption is observed within  $\text{CH}_3\text{NH}_2$  ( $A = 22.7\%$  at  $1 \times 10^{-2}$  M).

The results recorded in Table 2 reveal that the efficiency of corrosion inhibition  $A$  as determined from per-

Table 2. The relative decrease or increase in the reaction number (R.N.) and inhibition efficiency  $A_{\%}$  (in parentheses) for the effect of KSCN, NaCN,  $(\text{CH}_3)_2\text{SO}$ ,  $\text{CH}_3\text{NH}_2$  and  $\text{NaN}_3$  on corrosion of Al-Mn alloy in 3N HCl.

KSCN						
Conc., M	0.00	$8 \times 10^{-8}$	$8 \times 10^{-7}$	$8 \times 10^{-6}$	$4 \times 10^{-5}$	$8 \times 10^{-4}$
R.N.	2.28	1.12	0.99	0.90	0.89	0.29
$A_{\%}$	(0.00)	(51.1)	(56.7)	(60.7)	(60.9)	(87.1)
NaCN						
Conc., M	0.00	$1 \times 10^{-6}$	$1 \times 10^{-5}$	$1 \times 10^{-4}$	$1 \times 10^{-3}$	$1 \times 10^{-2}$
R.N.	2.28	1.58	1.34	1.15	0.78	0.73
$A_{\%}$	(0.00)	(30.9)	(41.1)	(49.9)	(66.0)	(68.0)
$(\text{CH}_3)_2\text{SO}$						
Conc., M	0.00	$1 \times 10^{-4}$	$1 \times 10^{-3}$	$1 \times 10^{-2}$	$5 \times 10^{-2}$	$1 \times 10^{-1}$
R.N.	2.28	0.96	0.67	0.63	0.60	0.48
$A_{\%}$	(0.00)	(57.8)	(70.7)	(72.4)	(73.9)	(78.8)
$\text{CH}_3\text{NH}_2$						
Conc., M	0.00	0.01	0.02	0.04	0.06	0.10
R.N.	2.28	1.77	1.77	1.33	1.11	0.66
$A_{\%}$	(0.00)	(22.7)	(22.5)	(41.6)	(51.4)	(71.0)
$\text{NaN}_3$						
Conc., M	0.00	0.06	0.08	0.1	0.2	0.3
R.N.	2.28	2.75	5.76	4.68	7.15	9.59
$A_{\%}$	-	-	-	-	-	-

centage reduction in reaction number (R.N.) varies with the type of the compound used. The order can be arranged as following with decreasing the inhibition efficiency  $A$ :

$\text{KSCN} \gg (\text{CH}_3)_2\text{SO} > \text{NaCN} > \text{CH}_3\text{NH}_2$ . The compound  $\text{NaN}_3$  is not included in the previous order where an acceleration in the corrosion rate was observed.

Figure 2 represents the relation between the inhibitor concentrations and their inhibition efficiencies  $A$ . The observed efficiency of these compounds in acidic medium may be due to the less negative potential of alloy in the acid solution favouring adsorption of the added compounds [11, 12].

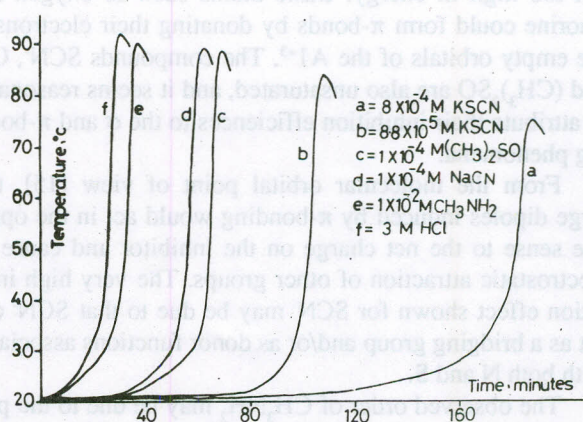


Fig. 1. Temperature - time curves for KSCN,  $(\text{CH}_3)_2\text{SO}$ , NaCN and  $\text{CH}_3\text{NH}_2$  in presence of 3M HCl.

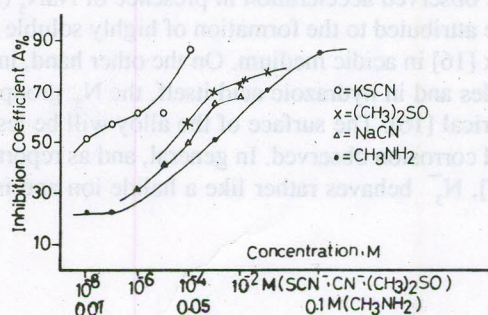


Fig. 2. Inhibition % - concentration curves of KSCN,  $(\text{CH}_3)_2\text{SO}$ , NaCN and  $\text{CH}_3\text{NH}_2$  in presence of 3M HCl.

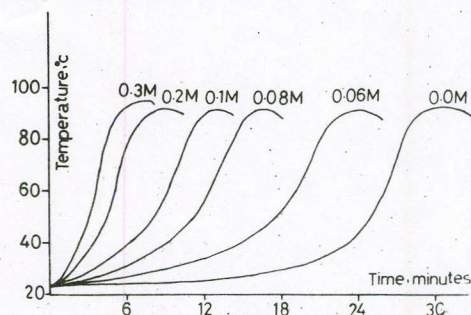


Fig. 3. Temperature time curves for  $\text{NaN}_3$  at different concentrations in presence of 3M HCl.

On the basis of electrostatic attraction principal [13], the anions  $\text{SCN}^-$  and  $\text{CN}^-$  should show higher inhibition than uncharged molecules  $(\text{CH}_3)_2\text{SO}$  and  $\text{CH}_3\text{NH}_2$ . The principal is quite valid for  $\text{SCN}^-$  but not for  $\text{CN}^-$  where  $(\text{CH}_3)_2\text{SO}$  gave relatively high inhibition than  $\text{CN}^-$ . However, due to the fact that sulphur is a stronger Lewis base than oxygen and nitrogen, the order of  $(\text{CH}_3)_2\text{SO}$  can be accepted.

In addition to  $\sigma$  bonding interactions between  $\text{Al}^{+3}$  and the added compounds, Chatt [14] has reported that class (a) acids e.g.  $\text{Al}^{+3}$  would have tightly held outer electrons, but also there would be empty orbitals available, not too high in energy. Basic atoms such as oxygen and fluorine could form  $\pi$ -bonds by donating their electrons to the empty orbitals of the  $\text{Al}^{+3}$ . The compounds  $\text{SCN}^-$ ,  $\text{CN}^-$  and  $(\text{CH}_3)_2\text{SO}$  are also unsaturated, and it seems reasonable to attribute their inhibition efficiencies to the  $\sigma$  and  $\pi$ -bonding phenomena.

From the molecular orbital point of view [15], the large dipoles induced by  $\pi$ -bonding would act in the opposite sense to the net charge on the inhibitor and cause an electrostatic attraction of other groups. The very high inhibition effect shown for  $\text{SCN}^-$  may be due to that  $\text{SCN}^-$  can act as a bridging group and/or as donor functions associated with both N and S.

The observed order of  $\text{CH}_3\text{NH}_2$  may be due to the protonation of  $\text{NH}_2$  group in hydrochloric acid medium leading to the blocking the free electrons and could be attributed to the absence of unsaturated bonds.

The observed acceleration in presence of  $\text{NaN}_3$  (Fig. 3) could be attributed to the formation of highly soluble azido-complex [16] in acidic medium. On the other hand, in covalent azides and in hydrazoic acid itself, the  $\text{N}_3^-$  group is unsymmetrical [16]. The surface of the alloy will be less covered and corrosion observed. In general, and as reported before [17],  $\text{N}_3^-$  behaves rather like a halide ion and is com-

monly considered as a pseudohalide.

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