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The Inhibitive Effect of Some Glycine Derivatives Towards the Corrosion of Aluminium in Hydrochloric Acid Solution

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Polarization and thermometric methods have been used to study the inhibition of aluminium corrosion in HCl solution, by some glycine derivatives. The inhibition efficiencies obtained from the two methods are in good agreement and are dependent upon the concentration of the inhibitor, its molecular size and its chemical composition. The results of polarization method indicate that the compounds act as mixed inhibitors. The inhibitors appear to function through general adsorption following the Langmuir adsorption isotherm. The change in the free energy for adsorption of inhibitors has been calculated and discussed.

INTRODUCTION

The corrosion of metals represents a terrible waste of both natural resources and money. Aluminium is an industrially important metal and is corroded by several corrosive agents of which the aqueous acids are the more dangerous. The corrosion of aluminium and its alloys in hydrochloric acid solutions has been extensively studied[1–8]. The effect of nitrogen-containing compounds like amines[9], aldehydes[10], heterocyclic compound[7,8] and β-diketo compounds[11], on the dissolution of aluminium in HCl solution, has been investigated. The present work is developed to study the effect of some glycine derivatives on the dissolution of aluminium in HCl solution.

EXPERIMENTAL

The chemical composition of aluminium used is: Al 99%, Fe 0.2%, Cu 0.2%, Si 0.2%, Ti 0.03% and Zn 0.08% and the chemicals used were of AR quality. The solution of 2M HCl was prepared with double-distilled water. All test pieces measuring 0.1 × 10 × 100 mm were used for thermometric, while for the galvanostatic measurements, electrodes were constructed from analytical reagent grade aluminium wire having a diameter of 0.55 mm. A 20 mm length wire was inserted into the small opening of a tube so that about 10 mm extended beyond the end of the tube. Degreasing mixture and additive solutions were prepared as previously described[12]. All experiments were carried out at 25 ± 1°C.

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The galvanostatic method used for steady state polarization studies consisted of a constant current device and digital multimeter (Kethly type, USA) for measuring corrosion potentials. All potentials were measured with respect to SCE. The inhibitive efficiency was calculated from the formula:

$$\%\ \text{Inhibition efficiency} = \left(1 - \frac{I'}{I}\right) \times 100 \qquad (1)$$

where I and I′ are the corrosion currents without and with inhibitor, respectively.

Inhibitive efficiencies were also calculated from the thermometric method[13] using the following equation:

$$\%\ \text{Inhibition} = \left(1 - \frac{RN_{inh.}}{RN_{free}}\right) \times 100 \qquad (2)$$

where $RN_{inh.}$ and RN_{free} are the reaction numbers in presence and absence of inhibitors. RN is defined as:

$$RN = \frac{T_m - T_i}{t}\ {}^{\circ}\text{C min.}^{-1} \qquad (3)$$

where T_m and T_i are the maximum and initial temperature, respectively and t is the time (in minutes) required to reach the maximum temperature.

The potential at any given current under similar experimental conditions was reproducible within ±7%.

RESULTS AND DISCUSSION

In this paper, the corrosion of aluminium immersed in 2 M HCl and in the presence of varying molar concentration of glycine dervatives was investigated using thermometric and polarization techniques.

Thermometric method

Temperature changes of the system involving aluminium in 2M HCl were followed in the absence and presence of different concentration of glycine derivatives. The results obtained are represented graphically in Fig. 1. At first there is a period during which the temperature varies only slightly. These parts of the curves can be ascribed to both an incubation period, during which the oxide film protects the metal from dissolution, and to an induction period representing the breakdown of the film and the start of attack[13]. Along the rising parts of the curves of Fig. 1, metal dissolution takes place according to the overall reaction:

$$Al + 3H^+ = Al^{3+} + 3/2H_2,\ \Delta H = 125.4\ \text{kcal/g. atom} \qquad (4)$$

Also, the curves of Fig. 1 show that, by increasing the concentration of the N-acetyl glycine, the maximum temperature slightly decreases, whilst the time necessary to reach T_m increases. This indicates that all the additives investigated retard the dissolution of aluminium in 2 M HCl. The inhibitive character of the additive should depend upon its concentration as well as on its chemical constitution.

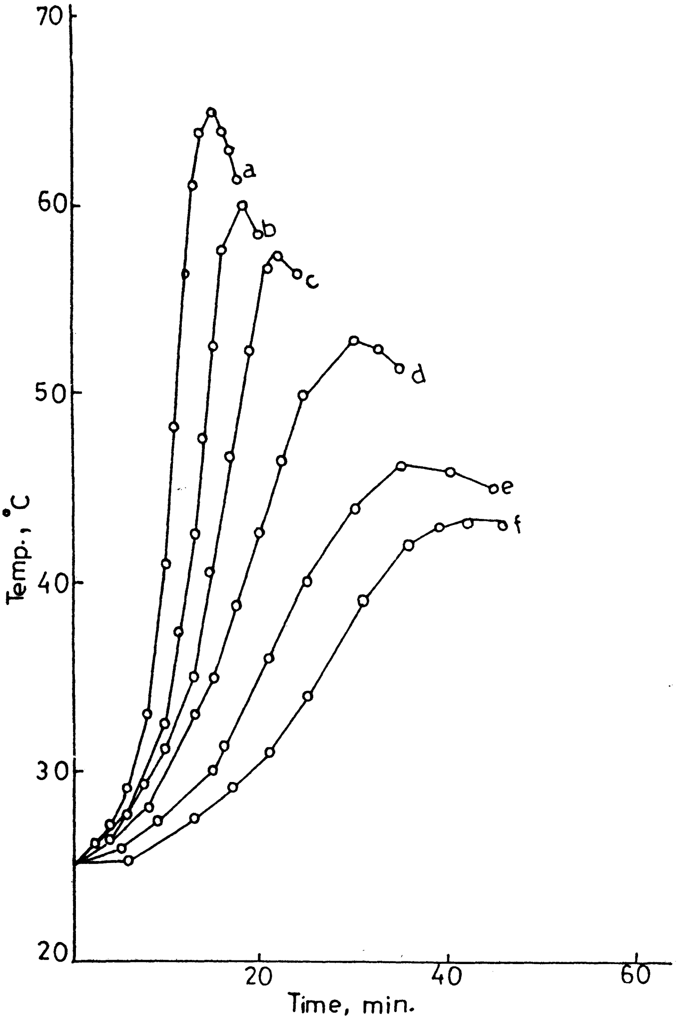

Fig. 1 Temperature-time curves for N-acetyl glycine: (a) free acid, (b) 1×10^{-6} M, (c) 1×10^{-5} M, (d) 1×10^{-4} M, (e) 5×10^{-4} M and (f) 1×10^{-3} M.

RN values are known as a relative measure of retardation (or acceleration) of a dissolution process; therefore, the RN values are plotted against log concentration of the glycine derivatives used. (Fig. 2). These curves are characterized by the sigmoid nature, substantiating the idea that the glycine derivatives reduce the corrosion rate by way of adsorption.

The degree of surface coverage θ of aluminium by different concentrations of glycine derivatives used was calculated using the following equation:[14]

$$\theta = \left(1 - \frac{RN_{inh.}}{RN_{free}}\right) \qquad (5)$$

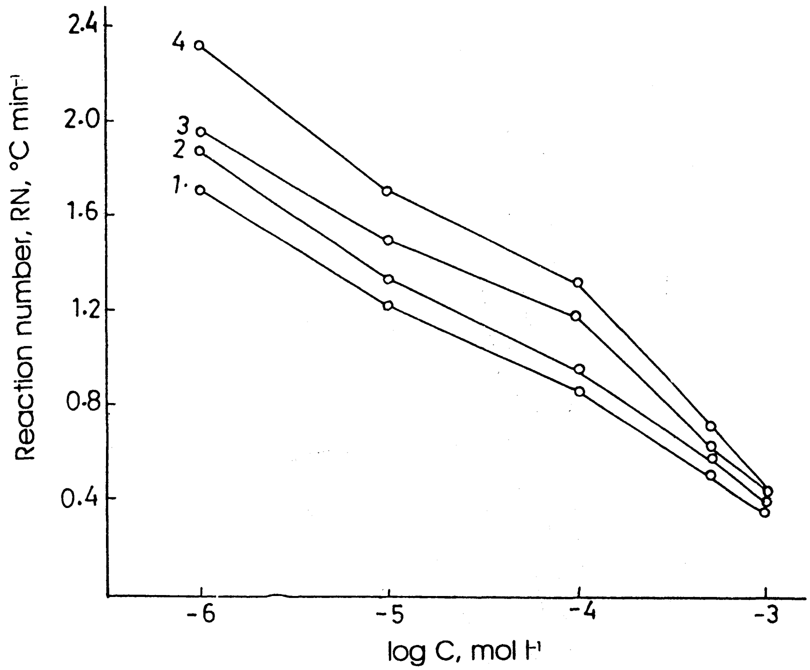

Fig. 2 Variation of the reaction number with logarithm of concentration of the additive for aluminium in 2M HCl: (1) [N-(*p*-aminobenzoyl)] glycine, (2) N-benzoyl glycine, (3) N-acetyl glycine and (4) glycine.

Fig. 3 shows the plot of log $\frac{\theta}{1-\theta}$ vs. log of molar concentration; straight lines were obtained and are in good agreement with the Langmuir adsorption isotherm (Eq. 6).

$$\log C = \log \frac{\theta}{1-\theta} - \log A \tag{6}$$

$$\log A = -1.74 - \frac{\Delta G^{\circ}_{ads.}}{2.303RT} \tag{7}$$

Interaction of adsorbed species by mutual repulsion or attraction would make the slope of the plot deviate a little from unity.

The order of inhibition efficiency of the additives as determined by the percentage reduction in reaction number is: [N-(*p*-aminobenzoyl)] glycine > N-benzoyl glycine > N-acetyl glycine > glycine.

As with the studied compounds, the inhibition efficiency of the additives is roughly proportional to their molecular weight, as can seen in Fig. 4. It is to be observed that the efficiency depends on concentration, as well as increasing with increasing molecular weight. These results support the given arrangement of the additives used in inhibiting corrosion of aluminium metal in 2M HCl solution.

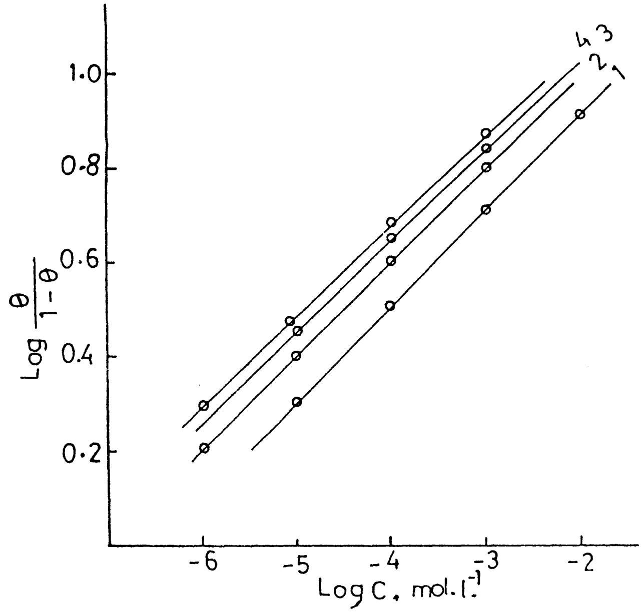

Fig. 3 Log $\frac{\theta}{1-\theta}$ vs. log C of all compounds:

(1) [N-(*p*-aminobenzoyl)] glycine, (2) N-benzoyl glycine, (3) N-acetyl glycine and (d) glycine.

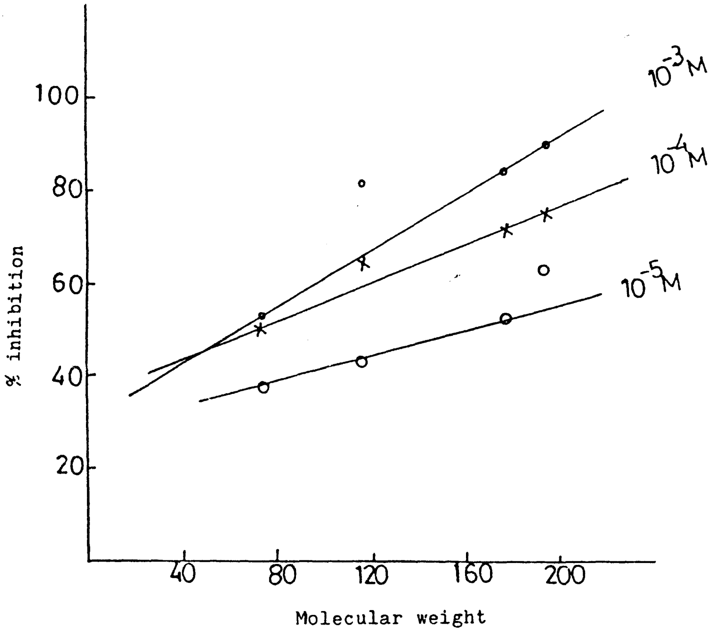

Fig. 4 Dependence of % inhibition of glycine derivatives on their molecular weights.

Polarization method

The results of anodic and cathodic polarization measurements on aluminium in 2M HCl containing different concentrations of N-acetyl glycine are plotted in Fig. 5. The results obtained for the other inhibitors were quite similar. As the inhibitor concentration increases, the Tafel lines of the hydrogen evolution rate are shifted to more negative values relative to the blank curve in case of cathodic polarization and to more positive values relative to thc blank in case of anodic polarization. The results suggest that all the tested materials are cathodic and anodic inhibitors. But cathodic polarization is more pronounced in all cases.

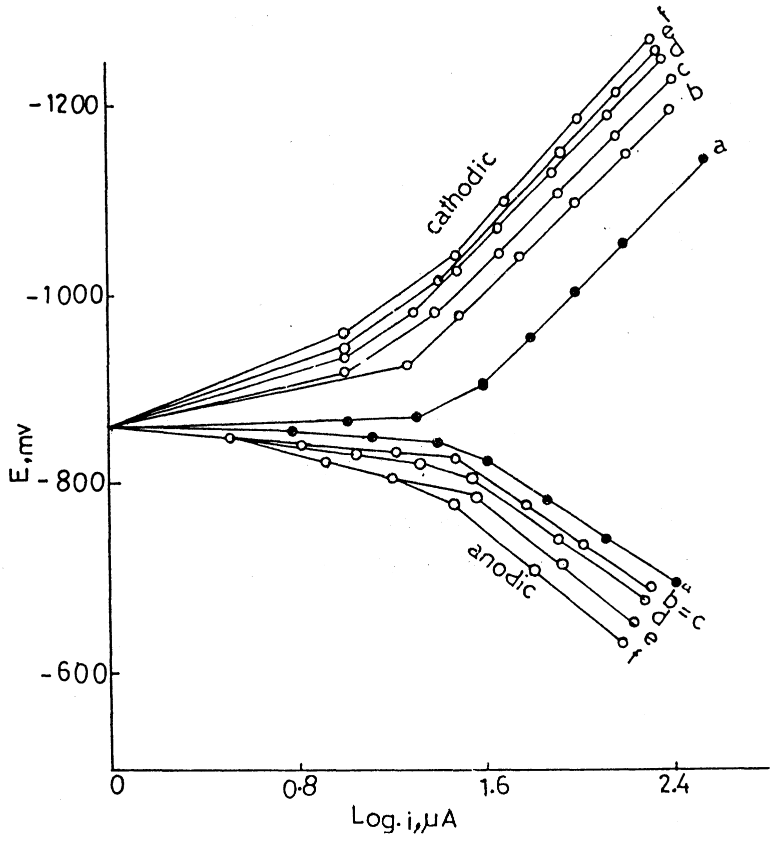

Fig. 5 Galvanostatic polarization curves of aluminium in 2M HCl alone and containing different concentrations of N-acetyl glycine: (a) 2M HCl, (b) 1×10^{-6} M, (c) 1×10^{-5} M, (d) 1×10^{-4} M, (e) 4×10^{-4} M and (f) 1×10^{-3} M.

Table 1 shows the effect of N-acetyl glycine concentration on Tafel slopes (β_a, β_b), corrosion currents ($I_{corr.}$) and percentage inhibition. The decrease of $I_{corr.}$ with increase in additive concentration demonstrates the efficiency of the tested compound as a corrosion inhibitor.

The corrosion current densites were determined by extrapolating anodic and cathodic Tafel lines to free corrosion potential values.

TABLE 1
CATHODIC AND ANODIC TAFEL PARAMETERS OF CORROSION OF ALUMINIUM IN 2M HCl AND IN PRESENCE OF DIFFERENT CONCENTRATIONS OF N-ACETYL GLYCINE AT 25°C

Concentration M	$-E_{corr.}$ (mV)	$I_{corr.}$ μA	β_a mV/dec.	β_c mV/dec.	% Inhibition
Free acid	860	26.3	160	250	—
1×10^{-6}	865	13.18	170	230	49.9
1×10^{-5}	900	11.22	170	215	57.3
1×10^{-4}	900	9.66	170	200	63.3
5×10^{-4}	905	9.12	200	250	65.3
1×10^{-3}	890	7.59	210	250	71.1

The inhibition efficiencies and the free energy of adsorption ($\Delta G^{\circ}_{ads.}$) are given in Table 2. In this table the compounds examined are arranged in the order of decreasing inhibition efficiency. The inhibition efficiency increases in the order:

TABLE 2
COMPARISON BETWEEN EFFICIENCY OF SOME GLYCINE DERIVATIVES AS DETERMINED BY THERMOMETRIC AND POLARIZATION TECHNIQUES IN 2M HCl AT 1×10^{-3} M INHIBITOR CONCENTRATION, AT 25 ± 1°C.

Inhibitor	% Inhibition		$\Delta G^{\circ}_{ads.}$
	Thermometric	Polarization	kcal/mol.
[N-(*p*-aminobenzoyl)] glycine	91.8	92.3	7.467
N-benzoyl glycine	87.1	85.2	7.604
N-acetyl glycine	83.6	71.1	7.645
glycine	64.0	60.6	7.687

[N-(*p*-aminobenzoyl)] glycine > N-benzoyl glycine > N-acetyl glycine > glycine as in the thermometric method.

The negative values of $\Delta G^{\circ}_{ads.}$ indicate that the adsorption of inhibitors on the aluminium surface is a spontaneous process and it lies nearly within the limit which have been observed for the majority of organic inhibitors of various types in aqueous media[7,8].

The inhibition efficiency of the compounds would depend on the number of adsorption sites and their basicity and on the molecular size. The basicity of the compounds will depend on the type of the substituent attached to the $-NHCH_2COOH$ and which increases the charge density on the adsorption sites. It is clear that the N-atom of the NH group and the O-atom of the carbonyl group (C=O) are the probable centres for cathodic and anodic adsorption[15] of substituted N-glycine over the aluminium surface. All the additives have the same number of adsorption sites. The results (Table 2) indicate that N-(*p*-aminobenzoyl) glycine exhibits the highest percentage inhibition. This may due to: (a) larger molecular size, (b) the presence of $-NH_2$ group in the *p*-position of the aromatic nucleus, which increases the basicity of the molecule, and (c) the aromatic nucleus might be expected to lie flat on the aluminium surface, providing larger surface coverage area. Compounds, N-benzoyl glycine, N-acetyl glycine and glycine come after the above compound. This is due to their lower molecular sizes. Glycine in the acid medium may be in the form of cationic species resulting from the reaction:

$$NH_2CH_2COOH \xrightarrow{HCl} Cl^-N^+H_3CH_2COOH \qquad (8)$$

The presence of Cl^- has been proposed to facilitate the adsorption of the organic cation, due to the fact that they form intermediate bridges in which the negative ends of the Cl^- metal dipoles may be oriented towards the solution.

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