RETARDING EFFECT OF SOME BENZALDEHYDE DERIVATIVES ON THE DISSOLUTION OF BRASS ALLOY IN NITRIC ACID SOLUTION

Fawzi Hassan ASSAF and Moustafa Hassan M. ABOU-EL-WAFA
Chemistry Department, Faculty of Science at Qena, Egypt

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The effect of benzaldehyde and its *ortho* and *para* -OH and -OCH_3 derivatives on the rate of dissolution of Brass alloy in nitric acid was investigated using thermometric technique. The results were treated by two different methods. It has been found that all compounds act as inhibitors and their effect increases with increasing concentration. The *o*-OH and *o*-OCH_3 derivatives have the highest inhibition effect.

Copper alloys are of industrial importance. Many investigations in different media and in presence of different organic compounds have been carried out[1-7] on such alloys in order to improve their corrosion resistance. The inhibition mechanism of organic substances used as corrosion inhibitors was studied by many authors[6-10]. The observed weak inhibiting action of some organic chelating compounds was attributed[11] to the instability of the chelate complex formed between such compounds and metal surface. The thermometric behaviour of copper in nitric acid solution has been reported[9]. The mechanism for the autocatalytic attack and production of HNO_2 has been discussed in details by Evans[12].

This work is devoted to the study of inhibiting effects of some benzaldehyde derivatives (R = H, *o*-OH, *p*-OH, *o*-OCH_3 and *p*-OCH_3) on the corrosion of brass alloy (70 Cu–30 Zn) in 35% HNO_3 solution using thermometric technique[13] and the treatment suggested earlier by several authors[14-16].

EXPERIMENTAL

The reaction vessel used was basically the same as that described previously[13]. The percentage chemical composition of the alloy (1×5 cm^2) sheet is 70 Cu–30 Zn. The alloy test pieces were abroded successively with 0·00 and 000 emery paper and then thoroughly cleaned with distilled water and acetone and dried between filter papers. This treatment was carried out immediately before making the tests. Each experiment was carried out with a new clean specimen in 25 ml of corroding solution. The temperature was measured by thermometer which have been calibrated using NPL standard thermometer, and was found to fluctuate by less than 0·02°C. The initial temperature in all experiments was 25 ± 0·1°C. All the chemicals used were of AR quality and were used without further purification.

THEORETICAL

Reaction Number Method

The reaction number (N_R) [$K\,min^{-1}$] of the studied compounds is defined[13] as:

$$N_R = (T_m - T_i)/t\,, \tag{1}$$

where T_m and T_i are the maximum and initial temperatures respectively and t is the time in minutes necessary to reach T_m.

The inhibition efficiency I of a given compound was evaluated as the degree of reduction in N_R, i.e.

$$I = [(N_R)_{free} - (N_R)_{inh}]/(N_R)_{free}\,. \tag{2}$$

Where $(N_R)_{free}$ and $(N_R)_{inh}$ are reaction numbers of brass alloy dissolution in pure acid and in the presence of the additive respectively.

Quantitative Treatment Method

Over a wide range of temperature, the rise in temperature (ΔT) as a function of the corrosion rate can be represented by the empirical equation[14–16]:

$$t = a + b \log \Delta T\,. \tag{3}$$

Plotting of $\log \Delta T$ vs t gives a straight line with a slope b and intercept a, where a is the time needed for the temperature to reach $\Delta T = 1{\cdot}0$ and b is the slope of the Eq. (*3*), $b = \mathrm{d}t_{(\Delta T)}/\mathrm{d}(\log \Delta T)$, (i.e. is the time needed for the temperature increase from 26 to the high degree). At ($\Delta T + X$) where X is a small fraction of degree,

$$t_{(\Delta T + X)} = a + b \log(\Delta T + X) \tag{4}$$

and

$$t_{(\Delta T - X)} = a + b \log(\Delta T - X) \tag{5}$$

in which $\mathrm{d}T = (\Delta T + X) - (\Delta T - X) = 2X$ and $\mathrm{d}t = t_{(\Delta T + X)} - t_{(\Delta T - X)}$, and hence the following differential equation is derived:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_T = \frac{2X}{t_{(\Delta T + X)} - t((_{\Delta T - X})}\,. \tag{6}$$

Substituting $t_{(\Delta T + X)}$, $t_{(\Delta T - X)}$ using Eqs (*4*) and (*5*) in Eq. (*6*) one obtains:

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_T = \frac{2X}{b \log\left[(\Delta T + X)/(\Delta T - X)\right]}\,. \qquad (7)$$

At a given value of ΔT and X, the part $2X/\{\log\left[(\Delta T + X)/(\Delta T - X)\right]\}$ in Eq. (*7*) becomes constant,

$$\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_T = \frac{1}{b}K'\,, \qquad (8)$$

where $1/b$ represents a function of the dissolution rate of the internal layers of the alloy. Further, the temperature rise of the system (ΔT) is proportional to the quantity of the metal dissolved i.e.,

$$V_T = K\left(\frac{\mathrm{d}T}{\mathrm{d}t}\right)_T\,, \qquad (9)$$

where V_T is the corrosion rate at the temperature T, $(\mathrm{d}T/\mathrm{d}t)_T$ is the rate of the temperature increase at the same temperature and $K = WC_\mathrm{p}/Q$, where W is the mass of the system, C_p is the apparent specific heat of the system and Q is the heat of metal dissolution. Inhibition coefficient I can be obtained from the relation,

$$I = \left[(V_T - V_T')/V_T\right]\,, \qquad (10)$$

where V_T and V_T' are the corrosion rates in absence and presence of the additives respectively. Substituting $V_T = K(\mathrm{d}T/\mathrm{d}t)_T = 1/b\ K'$ and $V_T' = K(\mathrm{d}T'/\mathrm{d}t)_T = 1/b'K'$ in Eq. (*10*), the equation (*11*) is obtained.

$$I_{\Delta T > 1^\circ\mathrm{C}} = \left(1 - \frac{b}{b'}\right) \qquad (11)$$

At $\Delta T = 0{\cdot}5^\circ\mathrm{C}$, the values of $1/a$ (Eq. *3*) in pure acid and $1/a'$ in the presence of the additive can be considered as a function of corrosion rates V_T and V_T' respectively of the most outer layers of the alloy. Substituting $V_T = 1/a$ and $V_T' = 1/a'$ in Eq. *10*, results in the Eq. (*12*)

$$I_{\Delta T = 0.5^\circ\mathrm{C}} = \left(1 - \frac{a}{a'}\right). \qquad (12)$$

RESULTS AND DISCUSSION

The curves in Fig. 1 represent the variation of the temperature against time for the reaction between brass alloy and 35% HNO_3 in presence of different concentrations

(0·1 – 8·0 mmol) of *ortho*-hydroxy benzaldehyde. At first there was a period, depending upon the concentration of the additive, during which the temperature remained constant or varied slightly followed by a rapid rise to attain a maximum value. On increasing the concentration, the time required to reach T_m increases and a decrease in the reaction number (N_R) is observed. Other compounds exhibited qualitatively the same behaviour (Table I), which may indicate that they retard the dissolution of the alloy presumably by their adsorption on the surface of the alloy. The surface alloy in the acidic solution is positively charged which favours the

TABLE I

Effect of concentration of some benzaldehyde derivatives (R-C_6H_4CHO) on the dissolution rate of Brass alloy in 35% HNO_3. Inhibition percentage I (in brackets) is determined by reduction in reaction number (N_R)

c mmol l^{-1}	R = H	R = *o*-OH	R = *o*-OCH_3	R = *p*-OH	R = *p*-OCH_3
0·00	0·353	0·353	0·353	0·353	0·353
0·10	0·262 (25·77)	0·260 (26·34)	0·300 (15·01)	0·322 (8·78)	0·348 (1·42)
0·30	0·247 (30·02)	0·25 (29·17)	0·235 (33·43)	0·301 (14·73)	0·307 (13·03)
1·00	0·234 (33·71)	0·240 (32·01)	0·200 (43·34)	0·239 (32·30)	0·229 (35·13)
3·00	0·157 (55·53)	0·110 (68·84)	0·131 (62·89)	0·213 (39·66)	0·204 (36·54)
8·00	0·102 (71·10)	0·083 (76·49)	0·087 (75·35)	0·188 (46·74)	0·203 (42·86)

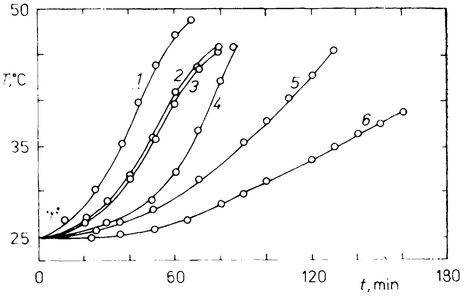

FIG. 1

Temperature–time curves for *o*-OH-benzaldehyde at different concentrations (mmol . l^{-1}) in 35% HNO_3: *1* free acid, *2* 0·1, *3* 0·3; *4* 1·0, *5* 3·0, *6* 8·0 adsorption of anions on the surface[17]. The absorbed anions change the structure of the double layer which in turn may hinder the inflow of aggresive anions. Hence a depression in the corrosion rate is quite possible.

The inhibition–concentration dependencies (Table I) for the all studied aldehydes consisted of an initial rising section section levelling off to a constant region (~2·0 mmol l^{-1}) which indicated the completion of the adsorption. Similar curves for some hydrazone compounds were obtained[18].

The data were also treated in the light of the second method mentioned above (see Experimental). In Table II, numeric values of the inhibition efficiency I_1 at $\Delta T = 0{\cdot}5°$, I_2 at $\Delta T \leqq 2°$ and I_3 at $\Delta T \leqq 6°$ are given. The values of I_1 and I_2 were found to be higher than I_3. As the corrosion process progresses, the alloy surface is activated and the temperature starts to rise which results in a decrease in the adsorbability relative to I_1 ($\Delta T = 0{\cdot}5°$). Another factor which may contribute significantly to the

TABLE II

Effect of some benzaldehyde derivatives (R-C_6H_4CHO) on the different stages of corrosion of Brass alloy in 35% HNO_3

c mmol l^{-1}	I_1, %	I_2, %	I_3, %	c mmol l^{-1}	I_1, %	I_2, %	I_3, %
R = H				R = *p*-OH			
0·10	75·00	9·09	2·44	0·10	52·94	14·28	11·10
0·30	78·95	14·29	11·11	0·30	57·90	22·68	11·10
1·00	82·61	25·00	20·00	1·00	71·43	44·44	31·97
3·00	85·19	52·00	50·00	3·00	71·43	50·81	36·50
8·00	90·70	57·20	56·40	8·00	82·61	48·20	42·85
R = *o*-OH				R = *p*-OCH_3			
0·10	60·00	14·28	11·11	0·10	33·33	0·00	0·00
0·30	73·33	25·00	13·04	0·30	68·00	9·75	3·09
1·00	81·80	31·81	15·43	1·00	71·43	44·44	31·97
3·00	84·00	48·27	46·66	3·00	77·78	50·00	38·46
8·00	89·04	63·85	60·00	8·00	85·19	42·79	33·33
R = *o*-OCH_3							
0·10	73·34	4·00	0·00				
0·30	80·00	18·40	12·08				
1·00	81·80	20·00	16·60				
3·00	83·33	48·27	46·66				
8·00	91·48	63·00	60·00				

decrease in inhibition with temperature increase is the altered rate of the corroding surface. As the corrosion rate increases, the net rate of adsorption must decrease to a certain extent. Thus this method of treatment gave a more quantitative illustration of the corrosion process and inhibition than the N_R method.

The inhibition efficiency, as determined from the two methods of calculation, was found to decrease in the order: o-OCH$_3$ $\sim$ o-OH $\geqq$ H $>$ p-OH $>$ p-OCH$_3$ which is mainly due to the nature of the substituent and its position. It is well known that[19] different substituents on the organic molecule polarize the functional group in a different manner, thus the adsorbability is affected by the different substituents. All the studied compounds have the C=O group as a key atom for the process of adsorption. In addition, delocalized π-electrons on the aromatic ring make the molecule more planar and a new center of adsorption is involved. The position of the substituent plays also a significant role.

The presence of OCH$_3$ and OH groups in the *ortho* position may increase the polarity of the carbonyl group leading to the observed high adsorption. On the other hand, and on the basis of the chelating character of the o-OH group, one should expect that the compound o-hydroxy benzaldehyde exhibits higher inhibition effect than o-OCH$_3$ and other compounds, but the expected hydrogen bonding between the hydrogen of the aldehyde O=C—H at the oxygen of the o-OH may lead to a decrease of the functional group polarity and subsequently to the adsorption and chelation processes. The order of p-OH and p-OCH$_3$ can be accepted on the basis that these groups are out of any chelate formation and, in addition to it, their effect on polarity of C=O group is less than that of o-OH and o-CH$_3$ groups.

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