CORROSION BEHAVIOUR OF COPPER IN ACID SOLUTIONS OF DIFFERENT ANIONS

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The effect of anion concentration on corrosion of copper does not follow Brasher's theory. The corrosion rate almost independent of anion concentration.

In 0.999 M Cu^{2+}, corrosion rate of copper in sulphate and nitrate solutions amounted to 8 $mg/dm^2/hr$; this is about three times that in the Cu^{2+} free solutions. In chloride solution, the rate amounted to 210 $mg/dm^2/hr$. This shows that a solution containing Cu^{2+} and chloride ions is very destructive to metallic copper.

It is a well-established fact that certain anions promote corrosion while others act as inhibitors. The behaviour in a particular case is said to depend on the solubility of the reaction product [1], adsorption [2], ion size and charge [3], ion deformability [4], and/or the electrostatic field set up by the negative charge of the anion on the adsorption sites [5]. Among the well-known corrosive anions are Cl^-, Br^-, I^-, NO_3^- and SO_4^{2-}. On the other hand the phosphate, chromate and nitrite ions are generally accepted as corrosion inhibitors.

Brasher disagrees with the rigid classification of anions into corrosion promoters and inhibitors. According to the Brasher theory [5,6] all anions are corrosive when present in large dilutions but become, or tend to be inhibiting in relatively concentrated solutions. It is noteworthy that Brasher's work was carried out on an active metal. It was of interest to examine whether the general characteristics of Brasher's theory are also valid for noble metals.

The available data on corrosion of copper [7-11] are however not sufficient to decide whether Brasher's theory is applicable. In the present investigation, the corrosion behaviour of pure copper is studied in wide concentration ranges of different anions in aqueous solutions. It is observed [12] that the presence of cupric salts modifies the mechanism of anodic dissolution of the metal. Hence, the present investigation is extended to solutions containing the metal salts also.

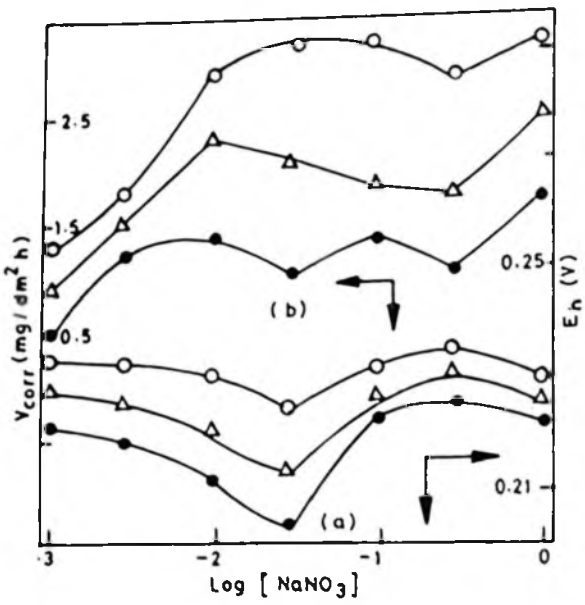
EXPERIMENTAL

The potential of the copper electrode vs SCE was measured as a function of time within a period of 4 hours in 0.001-1 M aqueous solution of $NaNO_3$, Na_2SO_4 NaCl and NaH_2PO_4, in presence of 0.01 - 0.1 M of the corresponding acids. The test electrodes were prepared from pure copper (5 mm in dia from, Johnson & Matthey). Before use, the electrode was abraded successively to 00 finish, degreased with acetone and then washed thoroughly with water. Each experiment was carried out with a newly polished electrode and with a fresh portion of solution.

Weight loss experiments were performed on copper pieces measuring 5 x 10 cm and 1 mm thick, cut from copper sheets (Johnson & Matthey). The test pieces were first degreased with acetone and then etched in an acid solution for 5 min. They were then washed with conductivity water rinsed in alcohol, ether dried and then weighed. The specimen was suspended in 200 ml of aerated, unstirred, test solution for 24 hours. The specimen was then removed, rinsed with conductivity water, finally dried and weighed. Results were duplicated and the mean computed.

RESULTS AND DISCUSSION

The copper electrodes were immersed in 0.001-1M aqueous solutions of $NaNO_3$, Na_2SO_4, NaCl and NaH_2PO_4, in presence of 0.01-0.1 M of the corresponding acids and potentials were measured at 30°C within a period of 4 hours. The steady state potentials, which are mixed or corrosion potentials, were plotted as a function of the logarithm of the molar concentration of the different salts. Typical results in nitrate and sulphate solutions, are presented in Fig 1&2. The potential fluctuated about a value which depends on the nature of



○ 0.1 M HNO_3 + $NaNO_3$ △ 0.05 M HNO_3 + $NaNO_3$
● 0.01 M HNO_3 + $NaNO_3$

Fig. 1 Effect of concentration of ($NaNO_3$) on corrosion of copper

a - Corrosion potential vs log [$NaNO_3$]
b - Corrosion rate vs log [$NaNO_3$]

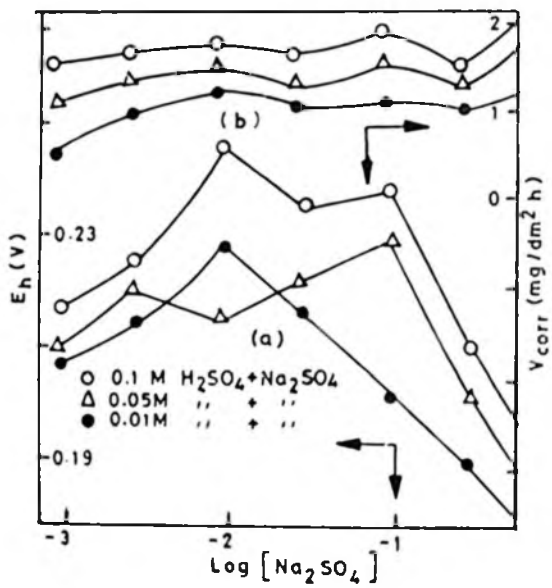


Fig. 2 Effect of concentration of Na_2SO_4 on corrosion of copper

a- Corrosion potential vs log [Na_2SO_4]
b- Corrosion rate vs log [Na_2SO_4]

the anion; but the linear logarithmic relations with negative slopes, as proposed by Brasher [5] were not observed.

The corrosion rates, V_{corr} expressed in mg/dm^2/h were measured from weight loss experiments. Typical results are given in Fig 1a and 2a. It is seen that V_{corr} is almost independent of the anion concentration and ranges from 1 to 3 mg/dm^2/h in different solutions. It is again evident that influence of anions in corrosion of copper is not in the manner proposed by Brasher.

It is worth noting that Cu is more electropositive than hydrogen; and hence, the metal does not dissolve through the discharge of H^+ ions. The complementary cathodic reaction is thus the reduction of the dissolved oxygen. This accounts for the very small rates of corrosion of copper. It is possible that the rate of corrosion is determined by the cathodic reaction rate. In order to prove this point, we measured the corrosion rate in 0.01-0.5 M $K_2Cr_2O_7$, acidified with 0.01-0.1 chromic acid. As evident from Fig. 3, the rate of corrosion increased steeply with the reducible anion concentration, amounting to 55 mg/dm^2/h in the 0.5 M dichromate solution acidified with 0.1 chromic acid.

Inspection of Figs 1 and 2 reveals a slight increase of corrosion potential and corrosion rate with increase of the acid concentration. This is in agreement with the results of Ammar et al [10], who observed that below 1 M HCl,

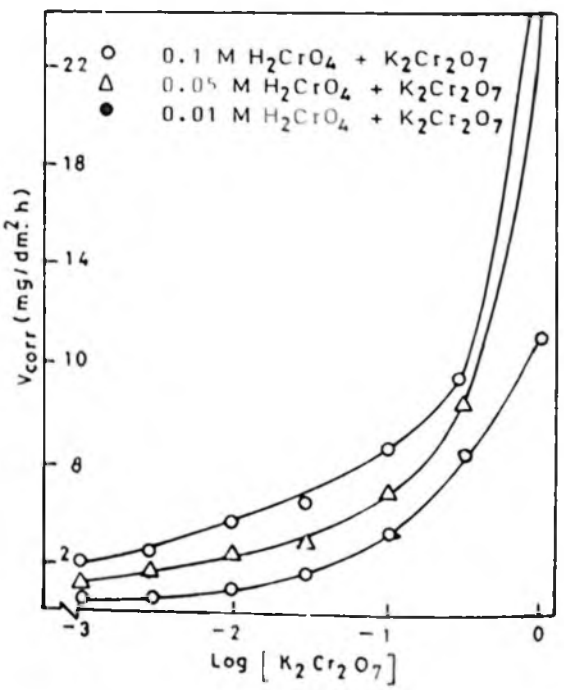


Fig. 3 Rate of corrosion of copper in $K_2Cr_2O_7$ solutions containing 0.01 - 0.1 M H_2CrO_4.

the increase of the acid concentration brings about a slight increase in the corrosion rate of Cu in dichromate solutions. We have carried out measurements in different series of solutions with acid concentration varying from 0.001 to 1M, while the anion concentration was kept constant at 1 M through the addition of the corresponding sodium salt. Thus any acceleration of the anodic reaction with the anion is excluded. The results in phosphoric acid-primary phosphate mixtures (Fig-4) indicate that both E_{corr} and V_{corr} increase with the acid content of the mixture, particularly above 0.1 M acid. We concluded, therefore, that the corrosion of Cu is not fully controlled by diffusion of oxygen. This conclusion is consistent with the proposal of Weeks and Hill [13], that dissolution of Cu in presence of O_2 as a depolariser proceeds first by adsorption of O_2 from solution to form a surface film. This is followed by reaction with H^+ ions to form cuprous and peroxide ions,

$$2\,Cu + H^+ + O_2 \longrightarrow 2\,Cu^+ + HO_2^- \qquad ...(1)$$

Previous work [14] on the effect of temperature on the corrosion of Cu in aerated solutions of Cl^- showed that Arrhenius equations is valid for solutions containing a constant oxygen concentration particularly in the acid range. The value of activation energy calculated for pH = 2 and 960 ppm Cl^- + 2.5 ppm O_2 amounts to 9 Kcal/mole.

It has been recently shown that the mechanism of dissolution of copper anodes is greatly influenced by the addition of copper salts [12]. So, the effect of Cu^{2+} ions on the corrosion behaviour of the metal was investigated. The corrosion potentials and corrosion rates were measured in solutions of different copper salts, acidified with the corresponding acids; the total molarity of the acid and salt was kept constant (1 M), in order to minimise the effect of the anion.

Fig 5 and 6 show the values of corrosion rates in copper nitrate, sulphate and chloride solutions. Corrosion rates of 7,8 and 210 mg/dm^2/h were observed in the 0.999 M Cu^{2+} in the nitrate, sulphate and chloride solutions respectively. These values are much higher than those obtained in Cu^{2+} free solutions (amounting to 3 mg/dm^2/h).

The marked increase in the corrosion rate on adding cupric salts indicates that a cathodic reaction other than the reduction of dissolved oxygen is involved in the corrosion process. The only possible cathodic reaction is the reduction of cupric to cuprous ion; the standard potential of the system Cu^{2+}/Cu^+ is 0.15 V [15]. The $Cu^{2+} \longrightarrow Cu^+$ transformation becomes suitable as a complementary cathodic reaction in the corrosion process only when its potential becomes higher than that of the anodic

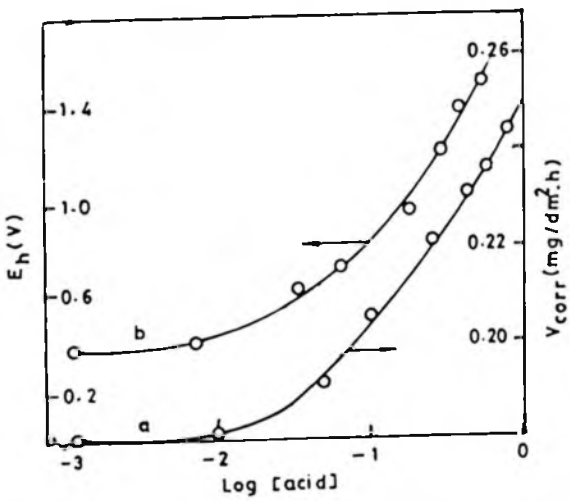


Fig.4 Effect of acid concentration in (H_3PO_4) + NaH_2PO_4) mixtures on the potential and corrosion rate of copper

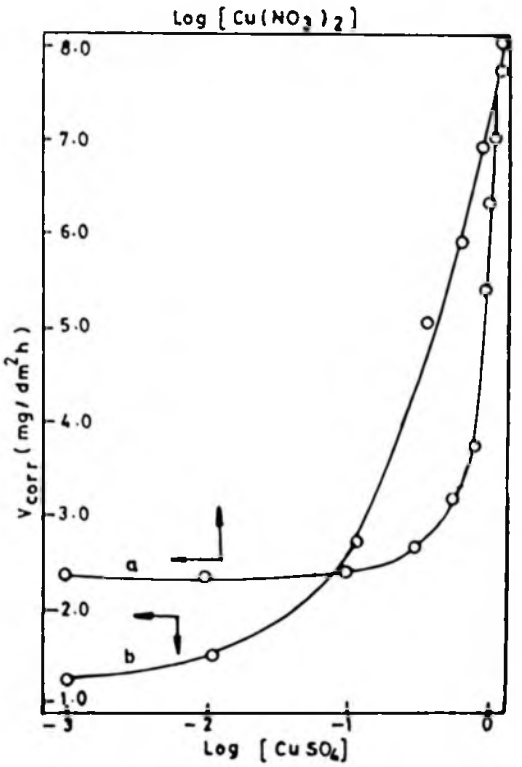


Fig. 5 Rate of corrosion of copper in acidified Cu $(NO_3)_2$ and $CuSO_4$ solutions.

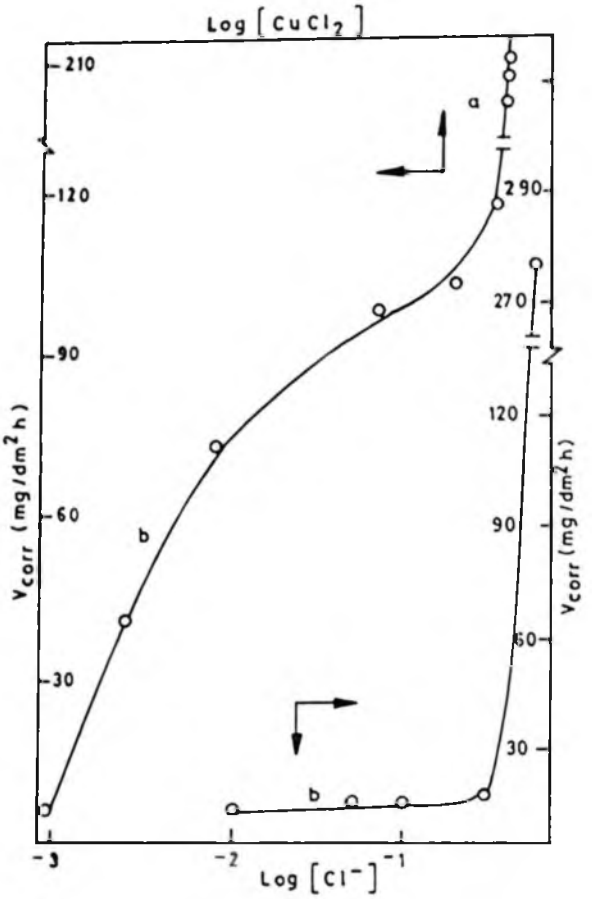


Fig. 6a Rate of corrosion of copper in acidified $CuCl_2$ solutions
6b Effect of Cl^- ion on the rate of corrosion of copper in 0.1 M $CuCl_2$.

half reaction, namely, $Cu \longrightarrow Cu^{2+} + 2e$. The potential of the Cu^{2+}/Cu^+ couple rises with increase of curpic ion concentration; this accounts for the effect of copper ion concentration on the corrosion. More important, however, is the diminution of cuprous ion concentration, through for instance, the formation of stable complexes. Hence, the cupric ion exhibited its corrosive action at 0.2 and 0.5M Cu^{2+} ion in sulphate and nitrate solutions respectively (Fig 5). In chloride solution tho destructive effect appeared at 0.002 M $CuCl_2$, owing to the ability of the chloride ion to form stable complexes like Cu Cl and $CuCl_2$ [15](Fig. 6). The role of chloride ion is confirmed by measuring the rate of corrosion in a series of 0.1M $CuCl_2$ solutions, containing 0.01-1M HCl. The results in Fig.(6a) reveal that V_{corr} increases markedly with Cl^- concentration, reaching a value of 280 mg/dm^2 /h in presence of the 1 M acid.

The two complementary half reactions during the corrosion of copper in presence of copper salts might be represented by:

anodic reaction: $Cu \longrightarrow Cu^{2+} + 2e$
cathodic reaction: $2\ Cu^{2+} + 2e \longrightarrow 2\ Cu^+$

The toal reaction is thus,

$$Cu + Cu^{2+} \longrightarrow 2\ Cu^+$$

The main purpose of this paper is to point out the destructive action of the medium containing Cu^{2+} and Cl^- on metallic copper.

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