

Electrochemical Behaviour of Copper in Acid Chloride Solution

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It has been verified that the anodic dissolution of copper in chloride solutions goes to the monovalent state. This reaction and its reverse cathodic deposition reaction have been studied in various acid chloride solutions by means of a slow galvanostatic technique. The reactions are under all conditions found to obey the relationship

$$V = E_R + (RT/nF)\ln(1 \pm i/i_{lim})$$

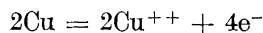
for pure concentration polarization and, by stirring experiments, shown to be under diffusion control.

From the effect of the chloride molality on the reversible potential and on the dissolution rate at given potentials, a value of 0.6 is found for the ratio β_2/β_3 between the stability constants of the 1:2 and the 1:3 cuprous chloride complex. On a somewhat uncertain activity estimate, the same data indicate $\beta_2 = 2.9 \cdot 10^5$ and $\beta_3 = 4.8 \cdot 10^5$.

1.0 INTRODUCTION

It has long been known^{1,2} that the dissolution of copper in some solutions (*e.g.* perchlorate, sulphate, phosphate, acetate) mainly leads to the cupric state and in other solutions (*e.g.* chloride, bromide, cyanide) mainly to the cuprous state. It is now further well known that the anions involved in the latter case are typical cuprous ion stabilizing complexing agents^{3,4}.

In a recent series of papers⁵, the electrochemical behaviour of copper in solutions of the former type (especially sulphate solutions) has been described. It is there concluded that the transfer between the metallic and the cupric state most probably is a direct one, and that the reaction of the $\text{Cu}/\text{Cu}_{\text{aq}}^{++}$ electrode under stationary conditions are represented by the "kinetic unit equation":



indicating a double metal ion mechanism which also has been found to govern the $\text{Fe}/\text{Fe}_{\text{aq}}^{++}$ electrode reactions (with the addition of a catalytic hydroxyl ion interaction)⁶.

In the present work, analogous studies have been made on the behaviour of copper in chloride solutions, being representative for the latter of the above mentioned solution types. The main purpose of this work is to elucidate the mechanism of the copper/cuprous reactions at *active* copper electrodes, to compare this with what has been found for the copper/cupric reactions, and to determine the effect of the complexing chloride ions on the rate of the former reactions.

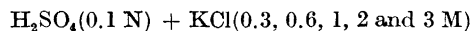
2.0 EXPERIMENTAL

The experimental work consists in determinations of current efficiency and potential-time curves for anodic dissolution and cathodic deposition of copper at constant current densities (10^{-5} – 10^{-2} A/cm²) in various pure and mixed solutions of hydrochloric acid, sulphuric acid, potassium chloride, and cuprous chloride.

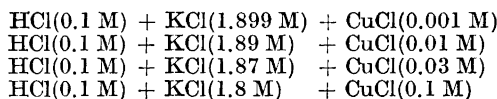
Some introductory measurements were first made at 25°C with the solutions:



Some more comprehensive series of experiments were then made at 20°C with the solutions:



in which the chloride content varies, and with the solutions:



in which the total chloride content is kept constant at 2 M.

The experimental technique and equipment have been exactly the same as previously described ^{5,6}. This also applies to the type and the pretreatment of the high purity copper electrodes used ⁵. The electrolytes were prepared from Analar quality acids and salts in water distilled from a "pure" fresh water. They were further presaturated with hydrogen ⁶. The experiments at 20°C were performed in a thermostated room ($\pm 0.5^\circ\text{C}$) and those at 25°C in a water thermostat ($\pm 0.1^\circ\text{C}$). In most experiments, no stirring was applied in the cell. When stirring was applied (this is notified in the text), this was performed with a magnetic stirrer which was placed close to the electrode studied.

The potentials were measured against saturated calomel electrodes, which have been ascribed the potentials ⁷ 0.245 and 0.242 V on the normal hydrogen scale (NHS) at 20 and 25°C, respectively. No attempts have been made to correct for liquid junction potentials between the test solutions and the saturated potassium chloride solution. According to values tabulated by Milazzo ⁸, however, these potentials are assumed very low and probably negligible in the present cases.

3.0 RESULTS

The weight measurements clearly show that the anodic dissolution of copper under the present conditions goes to the *cuprous* state. The current efficiency found for this process was in most cases close to 100 %. In some cases, however, the weight loss gave an apparent efficiency slightly higher than 100 %. This mainly occurred at low current densities (long experimental time) in the solutions richest in cuprous chloride, and was found to be due to corrosion. The corrosion correspondingly gave an apparent deposition efficiency slightly lower than 100 %, the anodic and cathodic deviations from this figure mostly being mutually symmetric.

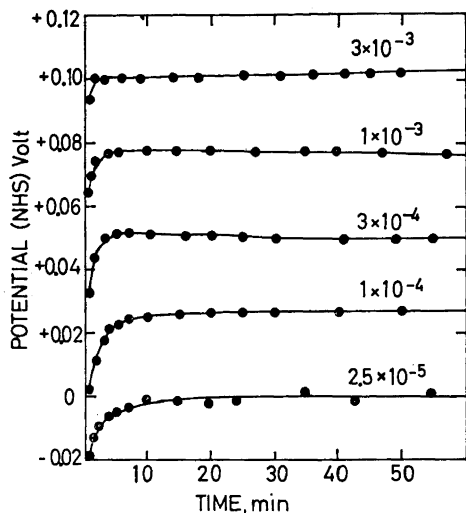


Fig. 1. Anodic potential/time curves for copper at various current densities (A/cm^2) in unstirred 0.1 N sulphuric acid + 1 N potassium chloride at 20°C .

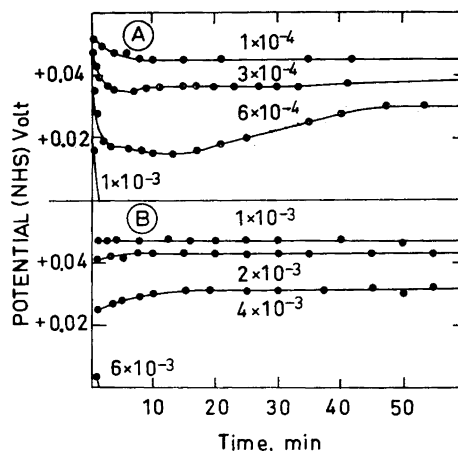


Fig. 2. Cathodic potential/time curves for copper at various current densities (A/cm^2) in unstirred (A) and stirred (B) 0.03 M cuprous chloride + 0.1 M hydrochloric acid + 1.87 M potassium chloride at 20°C .

At cathodic current densities exceeding the limiting diffusion current for deposition (see below), loosely adherent powdery deposits (of the type also obtained in sulphate solutions⁵) were formed. This resulted in erratic efficiency values. In these cases, however, there also was hydrogen evolution at the cathodes, whereby the actual deposition efficiency certainly must have been lower than 100 %.

At the highest anodic current densities in the solution of lowest chloride content (0.3 M), the anodic efficiency values obtained were lower than 100 %. This was found to be due to a precipitation of cuprous chloride on the anode surface, making the experimental weight loss too small.

The potential-time curves obtained in the present work are exemplified in Figs. 1 and 2. The initial rise in the anodic potential to a stationary value, as shown by the curves in Fig. 1, is typical for the anodic behaviour observed in the present work with unstirred solutions of no or low copper content. In solutions of higher copper content, this initial rise was usually not observed, the stationary potential mostly prevailing from the very first reading (1/2 or 1 min). This also applies in the case of initially copper free solutions when stirring was applied at the anode, the stirring lowering the stationary potential (see below). This is indicative of a diffusion controlled polarization. The observed potential rise, therefore, is most likely due to an increased concentration of reaction products being built up in the anolyte.

The cathodic potential-time curves shown in Fig. 2, are typical for those obtained under conditions giving nearly 100 % deposition efficiency. These

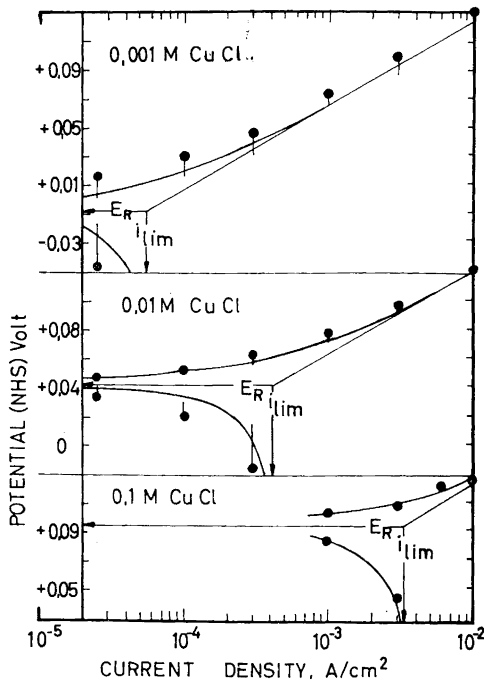


Fig. 3. Tafel diagrams for anodic dissolution and cathodic deposition of copper in unstirred x M cuprous chloride + 0.1 M hydrochloric acid + $(1.9-x)$ M potassium chloride at 20°C.

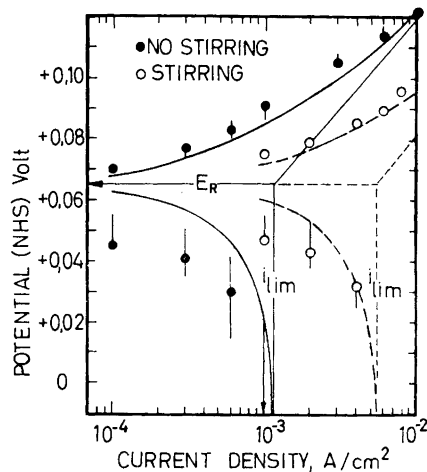


Fig. 4. Tafel diagram for anodic dissolution and cathodic deposition of copper in 0.03 M cuprous chloride + 0.1 M hydrochloric acid + 1.87 M potassium chloride at 20°C (effect of stirring).

curves clearly show the generally observed increasing instability of the deposition potential with increasing current density and the effect of stirring in transferring the onset of this instability to higher current densities. At sufficiently high current densities (dependent on the stirring conditions and the cuprous chloride content of the solution), the cathode potential falls down to values comparable to those for hydrogen evolution on copper at the same current densities in cuprous free solutions of the same pH. This is just what is to be expected when the applied current exceeds the limiting current for deposition.

The polarization data obtained for the anodic dissolution and cathodic deposition of copper under some of the conditions studied, are presented in the form of Tafel diagrams in Figs. 3–6. The various points in these diagrams represent the most stationary potentials observed, and the vertical lines extending from most of these points, indicate the range over which the potential has varied.

The anodic Tafel lines suggested in these diagrams have all been drawn with slopes of:

$$b_a = 2.303 \frac{RT}{F} \quad (1)$$

and those in Figs. 3 and 4 have moreover been placed so as to intersect with the corresponding limiting current lines for deposition (i_{lim}) at the observed reversible potential (E_{R}). Both this intersection and the suggested Tafel slope value are what to be expected for a monovalent metal/metalion electrode when its reactions are under diffusion control. In that case, the polarization behaviour should namely with good approximation be given by ⁹:

$$V = E_{\text{R}} + (RT/nF)\ln(1 \pm i/i_{\text{lim}}) \quad (2)$$

where, in the double sign, + and - apply to anodic and cathodic reactions, respectively. This equation shows not only the approach to a Tafel line of the above type at high anodic reaction rates ($i \gg i_{\text{lim}}$), but also how the anodic and cathodic polarization theoretically should be at lower reaction rates. The curves drawn in Figs. 3 and 4 have been constructed from (2) by applying the E_{R} and i_{lim} values given in the respective diagrams, and they show reasonable agreement with the experimentally obtained polarization data.

The limiting current (i_{lim}) given in Figs. 3 and 4 for the deposition reaction in unstirred solutions of x M cuprous chloride + $(1.9 - x)$ M potassium chloride + 0.1 M hydrochloric acid (x being in the range 0.001–0.1), seems best represented by the formula:

$$i_{\text{lim}} = 0.027(\text{Cu})^{0.9} \text{ A/cm}^2 \quad (3)$$

where (Cu) is the total cuprous molality in the solution. This is of the right magnitude for limiting diffusion currents in unstirred solutions, but one should perhaps have expected a somewhat larger concentration exponent ⁹.

The results in Fig. 4 further show that the limiting current is greatly increased by stirring. It is increased by a factor of about 5 by the stirring applied in the present work. On the basis of (2), one should thus also expect an equal

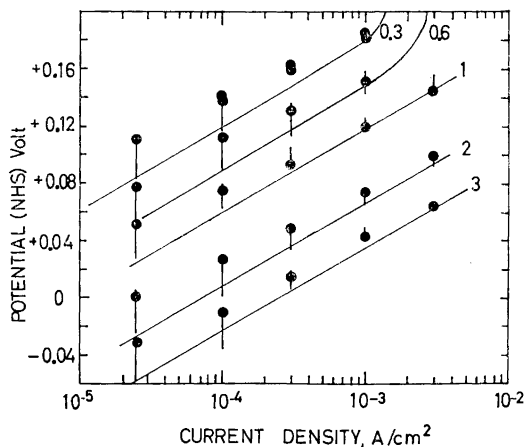


Fig. 5. Tafel diagram for anodic dissolution of copper in unstirred 0.1 N sulphuric acid solutions of potassium chloride at various chloride molalities at 20°C.

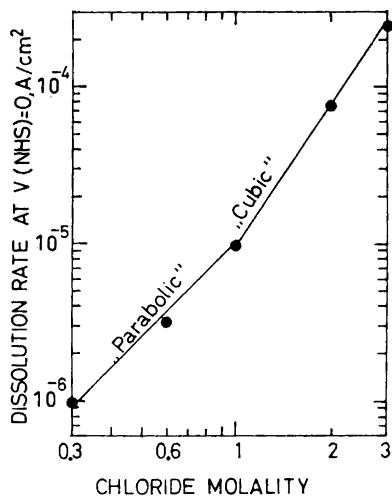


Fig. 6. Effect of the chloride molality on the anodic dissolution of copper in unstirred 0.1 N sulphuric acid solutions of potassium chloride at 20°C.

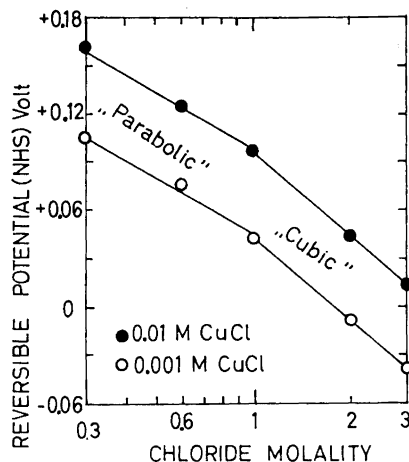


Fig. 7. Effect of the total chloride and cuprous molality on the reversible potential of copper in 0.1 N sulphuric acid solutions of cuprous chloride and potassium chloride at 20°C.

stirring at anodes to shift the anodic polarization curve towards higher current densities by the same factor. That it really is so, is satisfactorily verified by the results in Fig. 4, and also by results obtained in initially cuprous free solutions. This effect of stirring verifies that the reactions are under diffusion control.

The acidity of the electrolyte was found to have no effect on the anodic polarization of copper in 1 M chloride solutions of pH from about 1 to about 7.

The chloride content greatly affects the anodic dissolution reaction. This is demonstrated for unstirred solutions by the results in Fig. 5 and more explicitly shown in Fig. 6, where the rate of anodic dissolution at the standard hydrogen potential (as found by interpolation and extrapolation of the Tafel lines in Fig. 5) is plotted versus the chloride molality. The straight lines in Fig. 6 correspond to a parabolic and a cubic relationship at low and high chloride concentrations, respectively. When also (1) is considered, these relationships may be written (20°C, no stirring):

$$i = 9.9 \cdot 10^{-6}(\text{Cl})^2 \exp(FV/RT) \text{ A/cm}^2 \text{ at } (\text{Cl}) < 1 \text{ M} \quad (4a)$$

$$i = 9.9 \cdot 10^{-6}(\text{Cl})^3 \exp(FV/RT) \text{ A/cm}^2 \text{ at } (\text{Cl}) > 1 \text{ M} \quad (4b)$$

where V is the electrode potential referred to the normal hydrogen scale, and (Cl) is the total chloride molality. That the numerical factors in these two equations are mutually equal, is a simple consequence of the transition between the two relationships occurring very near to a chloride molality of 1 (Fig. 6).

The reversible potential (E_R) of copper in a series of hydrogen saturated 0.1 N sulphuric acid solutions of cuprous and potassium chloride at 20°C (in addi-

tion to those described above) has been measured as described in the third paper of Ref.⁵. The results are presented in Fig. 7, where the straight lines correspond to the relationships:

$$E_R = 0.200 + (RT/F)\ln \frac{(\text{Cu})^{0.9}}{(\text{Cl})^2} \text{ Volt at } (\text{Cl}) < 1 \text{ M} \quad (5a)$$

$$E_R = 0.200 + (RT/F)\ln \frac{(\text{Cu})^{0.9}}{(\text{Cl})^3} \text{ Volt at } (\text{Cl}) > 1 \text{ M} \quad (5b)$$

where (Cu) and (Cl) mean the total cuprous and chloride molality, respectively. The cuprous molality exponent of 0.9 is first of all found from the reversible potential data in Figs. 3 and 4.

The results in (5) show a quite analogous chloride dependence to those in (4). They further indicate the transition in this dependence at the chloride molality of 1 to be due to a reversal in the mutual activity relationship of the complexes CuCl_2^- and CuCl_3^- at this chloride concentration. As the activity of potassium chloride in a 1 M solution is about 0.6 (Ref.¹⁰), this means that we for the stability constants of these complexes should have:

$$\beta_2/\beta_3 = 0.6 \quad (6)$$

where β_n is defined by the activity relationship $(\text{CuCl}_n^{(n-1)-})/(\text{Cu}^+)(\text{Cl}^-)^n$. By further assuming the activity coefficients of the complexes also to be 0.6 in the 1 M chloride solution, and adopting the value 0.521 V for the standard $\text{Cu}/\text{Cu}_{\text{aq}}^+$ -potential, we have from (5a) and (6), when neglecting the exponent of 0.9: $\beta_2 = 2.9 \cdot 10^5$ and $\beta_3 = 4.8 \cdot 10^5$. This is not far from many values previously given for these stability constants^{3,4}, but the rough activity estimate makes the values somewhat uncertain.

The results in (3), (4), and (5) may be used for a further check of the validity of the theoretical equation (2) for pure concentration polarization in the present cases. By combining these results, we easily have:

$$V = (E_R - 0.001) + (RT/F)\ln(i/i_{\text{lim}}) \text{ Volt} \quad (7)$$

Remembering that the polarization data in (4) apply to cases where $i/i_{\text{lim}} \gg 1$, this result must be regarded an excellent confirmation of the anodic dissolution of copper in all the applied chloride solutions obeying (2) and, thereby of it exhibiting pure concentration polarization.

4.0 DISCUSSION

The weight changes, the anodic Tafel slopes, the reversible potentials, and the chloride ion effect observed in the present work, are mutually in agreement in showing that copper in acid (and neutral) chloride solutions behaves as a copper/cuprous electrode, the cuprous ions being complexed by chloride ions. The anodic and cathodic polarization data, the cathodic limiting current data, and the reversible potential data obtained, combine excellently with

each other to show that the reactions of this electrode in unstirred solutions give rise to a pure concentration polarization. This is further supported by the observed effect of stirring on the polarization. The stirring experiments indicate this type of polarization to be due to slow diffusion and to be predominant even at stirring rates giving a five-fold increase of the limiting current.

These results obviously mean that the electrode reactions themselves and their possibly accompanying chemical reactions are fast compared to the transport of cuprous species in the electrolyte to (cathodic) and from (anodic) the electrode surface. In such a case, the polarization is independent of the mechanism of the electrode reactions (as demonstrated by the absence of kinetic parameters as i_o , α , and ν in eqn. (2) above) and does, therefore, not reveal anything exact of their kinetics. The only conclusion one in this respect can draw from the above results, is:

$$i_o > 5i_{\text{lim},o} \quad (8)$$

where i_o is the exchange current, and $i_{\text{lim},o}$ is the cathodic limiting current in unstirred solution. This is contrary to what is found for the copper/cupric electrode⁵, and it is easily seen by comparison that this is mainly due to the immensely stimulating effect of the chloride ions on the anodic dissolution of copper, and of this stimulation being more pronounced than the possible retardation in deposition ability when going from cupric ions to complex cuprous chloride species.

To the author's knowledge, this is the first example in which the reactions of a solid metal/metalion electrode has been proved to be under diffusion control and thereby to exhibit pure concentration polarization. Several examples of such a behaviour exist for amalgam electrodes⁹, however, and a quite analogous behaviour has recently been found in our laboratory for copper in bromide solutions¹¹.

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