Dissolution of Cuprous Chloride in Acid Chloride Solution

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The dissolution rate (v) of cuprous chloride in various 0.1 N sulphuric acid solutions of potassium chloride and cuprous chloride at 20°C has been studied and in unstirred solutions found to be:

$$v = 6.1 \, [(Cu)_s - (Cu)]^{1.25} \, 10^{-7} \, mole(CuCl)/cm^2sec$$

where (Cu) is the actual cuprous molality in the solution and $(Cu)_s$ its saturation value. The latter value is further found to be given by

$$(Cu)_s = 9.7 \, (Cl) \, 10^{-2} \, M$$
$$(Cu)_s = 1.4 \, (Cl)^2 10^{-1} \, M$$

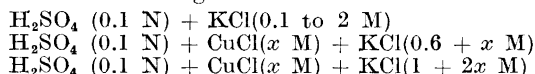at chloride concentrations (Cl) below and above about 0.7 M, respectively.

The dissolution rate is greatly increased by stirring, and all results indicate the dissolution to be controlled by the diffusion of cuprous species from the crystal surface to the bulk of the solution.

1.0 INTRODUCTION

During the last decade, electrochemical theories of the type applying to metal/metal ion electrodes have been introduced also to the field of dissolution and growth of ionic crystals in solutions (as reviewed and described by Vetter [1]). Following previous work on the copper/cuprous electrode in complexing chloride solutions [2,3] and on the deposition of cuprous chloride on copper by its reaction with cupric ions in such solutions [4], it was therefore assumed desirable to study also the dissolution of cuprous chloride in solutions of the same type.

2.0 EXPERIMENTAL

The experiments have been performed with high purity copper sheets (14 cm² geometrical surface area) having been immersed for one hour in H_2SO_4 (0.1 N) + $CuSO_4$ (0.1 M) + KCl (0.05 M). This immersion gives a cuprous chloride layer of about 2 mg/cm² on the copper surface [4]. The following three series of solutions have been used:

$$H_2SO_4 \ (0.1 \ N) + KCl(0.1 \ to \ 2 \ M)$$
$$H_2SO_4 \ (0.1 \ N) + CuCl(x \ M) + KCl(0.6 + x \ M)$$
$$H_2SO_4 \ (0.1 \ N) + CuCl(x \ M) + KCl(1 + 2x \ M)$$

All solutions have been made from A.R. quality acid and salts in water distilled from a rather pure tap water. The cuprous containing solutions were made up in deaerated water and were stored and used under an atmosphere of purified hydrogen (streaming). The cuprous free solutions were exposed to air.

The dissolution rate measurements have been performed both by the semi-continuous quartz helix technique previously described [5] and by intermittent weighing. In all experi-

ments, the cuprous chloride covered copper sheets were vertically immersed in separate portions of 0.5 to 1 l test solution.

The experiments have been carried out in a thermostated room at about 20°C. In most experiments, no stirring has been applied in the solution. In a few cases only, a magnetic stirrer has been used at the bottom of the test beaker. These cases are notified in the text.

3.0 RESULTS

In all solutions applied, the rate curves were nearly linear until most of the cuprous chloride layer was dissolved, whereafter they relatively fast become horizontal as the dissolution rate dropped to zero at complete dissolution of the layer (as already shown by Fig. 3 of Ref.[4]). The slope of the linear part of such a curve is a measure of the dissolution rate.

In Fig. 1, the values obtained for the dissolution rate (v_0) of cuprous chloride in initially cuprous free solutions are plotted *versus* the chloride molality (Cl). The straight lines drawn there correspond to the relationships:

$$v_0 = 3.3(Cl)^{1.25}10^{-8} \text{ mole(CuCl)/cm}^2\text{sec} \tag{1a}$$
$$v_0 = 5.4(Cl)^{2.5} \ 10^{-8} \text{ mole(CuCl)/cm}^2\text{sec} \tag{1b}$$

at low and high chloride concentrations, respectively. Except for the exponential factor of 1.25, these results indicate a transition from a linear to a parabolic chloride dependence at a chloride concentration slightly below 1 M (see Fig. 1). This is analogous to the parabolic/cubic transition previously found for the anodic dissolution of copper in solutions of the same type [2,3].

In Fig. 2, the 1.25-root of the values obtained for the dissolution rate (v) of cuprous chloride in unstirred cuprous containing solutions of essentially
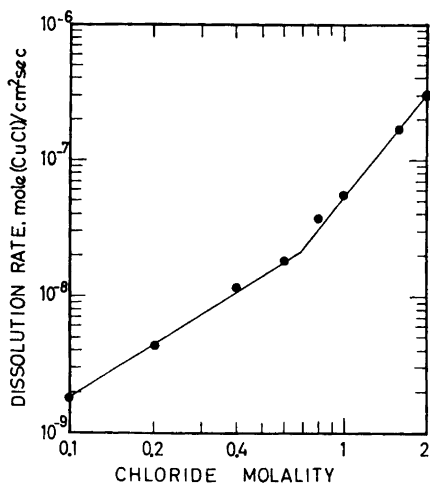

Fig. 1. Rate of dissolution of cuprous chloride in unstirred 0.1 N sulphuric acid solutions of potassium chloride at 20°C.
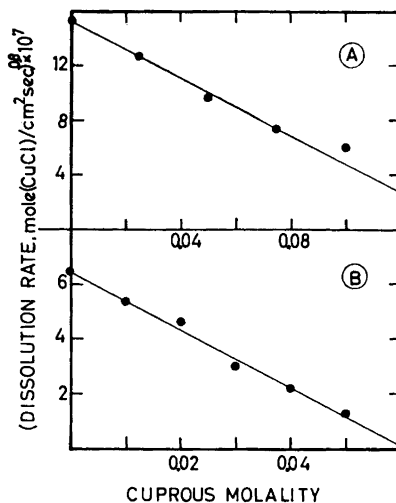
Fig. 2. Rate of dissolution of cuprous chloride in unstirred solutions of (A) 0.1 N sulphuric acid + (1 + 2x) M potassium chloride + x M cuprous chloride and (B) 0.1 N sulphuric acid + (0.6 + x) M potassium chloride + x M cuprous chloride at 20°C.

constant chloride ion molality (0.6 and 1) is plotted *versus* the cuprous molality (Cu). The straight lines drawn there, both correspond to the relationship:

$$v = v_0 \left(1 - \frac{(Cu)}{(Cu)_s}\right)^{1.25} \tag{2}$$

where $(Cu)_s$ is the cuprous molality given by the intersection of the lines with the molality axis, at 0.060 and 0.145 M for the 0.6 and the 1 M chloride solutions, respectively. The two lines in Fig. 2 are further very nearly parallel to each other, both of them giving by their slope:

$$v_0 = 6.1 \ (Cu)_s^{1.25} \ 10^{-7} \ \text{mole(CuCl)/cm}^{-2}\text{sec} \tag{3}$$

when $(Cu)_s$ is given in molality units. It is good reason to believe that (2) and (3) apply not only to solutions of the two chloride ion concentrations for which they here have been established.

$(Cu)_s$ most probably represents the saturation concentration of cuprous chloride in the solutions applied. This is somewhat substantiated by the fact that in the 0.6 M chloride series we did not succeed in dissolving all the cuprous chloride weighed in for a 0.07 M cuprous chloride solution, and that some immersion experiments with cuprous chloride covered sheets in this saturated solution did not show any distinct weight changes. From eqns. (1) and (3), it is easily seen that the saturation molality with good approximation is given by

$$(Cu)_s = 9.7 \ (Cl) \ 10^{-2} \ M \tag{4a}$$
$$(Cu)_s = 1.4 \ (Cl)^2 \ 10^{-1} \ M \tag{4b}$$

at low and high chloride concentrations, respectively.

All the above results concern unstirred solutions. It is possible, however, that (2) to some extent also applies to stirred solutions, but v_0 is strongly increased by stirring. The latter was shown by experiments with a magnetic stirrer in 0.1 N sulphuric acid + 0.3 M potassium chloride. The stirring applied raised the dissolution rate by a factor of about 12. Even though no exact measure is available for the stirring rate, the stirring effect clearly shows the dissolution to be under diffusion control. As is discussed below, this is in agreement also with the results in unstirred solutions.

The reproducibility of the above rate measurements has been well within 5 % in unstirred and 10 % in stirred solutions. The poorer reproducibility in stirred solutions may be due to uncontrolled variations in the stirring rate.

4.0 DISCUSSION

All the above results in unstirred solutions may be represented by the single rate equation:

$$v = 6.1[(Cu)_s - (Cu)]^{1.25} \ 10^{-7} \ \text{mole(CuCl)/cm}^2\text{sec} \tag{5}$$

where $(Cu)_s$ is as given by (4). This is of the right type and magnitude for limiting diffusion currents in the case of natural convection (Ref.[1], pp. 170—174) and indicates the rate determining process to be the diffusion of cuprous species from the crystal surface, where the cuprous concentration is $(Cu)_s$, to the bulk of the solution, where the cuprous concentration is (Cu). The diffusion layer

thickness is thus assumed to be inversely proportional to the 0.25 power of the concentration difference. Stirring should further be expected to reduce this thickness and, thereby, to increase the dissolution rate. This is in accordance with what has been observed in the present case.

The results obtained thus indicate that the exchange of cuprous chloride species between a crystal and a chloride solution of this salt is fast enough to maintain essentially equilibrium conditions at the crystal surface (i.e., to make the solution there saturated) even during relatively rapid dissolution in initially cuprous free solutions. Except for this, the results can tell nothing as to the rate and mechanism of these exchange reactions. The chloride dependence shown by eqns. (4), however, indicates that the dissolution mainly goes to $CuCl_2^-$ at low and to $CuCl_3^{2-}$ at high chloride concentrations (see also Fig. 1). This is in accordance with what has previously been found for the anodic dissolution of copper in solutions of the same type [2,3], and is also what to be expected from stability data for the mentioned complexes [6] and from solubility data for cuprous chloride in chloride solutions [7].

In a more rigorous treatment of the cuprous chloride dissolution, regards have to be made of the possibly different diffusion coefficients of the varies species involved, of the possible reactions between these species in the diffusion layer, and of the possibility of transport influencing electric fields being set up in this layer. Such a treatment necessitates the solution of an intricate system of differential equations and will therefore not be given here. This is even more due to the above simple considerations showing clearly enough what is controlling the dissolution rate. One difficulty in these considerations, however, is that they give a rather satisfactory picture without taking into account that the chloride concentration may possibly be lower at the crystal surface than in the bulk of the solution, especially at high dissolution rates. In the absence of any electric field effects in the diffusion layer and unless the diffusion coefficient should be much lower for the cuprous species than for the chloride ions, one should namely expect such a chloride concentration lowering to have caused an increasing downwards departure in the dissolution rate from the "parabolic" chloride dependence observed. The absence of this departure could probably have some explanation through a more rigorous treatment of the type suggested above.

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