JOURNAL OF APPLIED ELECTROCHEMISTRY 13 (1983) 173–176

Determination of equilibrium silver sulphate concentration in the system Cu–H_2SO_4–$CuSO_4$–H_2O–Ag_2SO_4–Ag as a function of composition

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Received 20 May 1982

The value of the ratio $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ ($\gamma_{Cu^{2+}}$, γ_{Ag^+} – are the mean activity coefficients of copper and silver ions, respectively) was calculated from the measured emf of the cell

$$Cu(Hg)|H_2SO_4\ (c_x) - CuSO_4\ (c_y)|Hg_2SO_4, Hg$$

and the solubility of Ag_2SO_4 in H_2SO_4 (c_x) and $CuSO_4$ (c_y) solutions. The concentration of H_2SO_4 in the solution was varied from 0.5 to 2.1 mol dm^{-3} that of $CuSO_4$ from 0.4 mol dm^{-3} to saturation. The results were presented as a function:

$$\frac{\gamma_{Cu^{2+}}}{\gamma^2_{Ag^+}} = a_0 + a_1 c_x + a_2 c_y + a_3 c_x^2 + a_4 c_x c_y + a_5 c_y^2 .$$

This function allows the estimation of the equilibrium silver ion concentration $c^{eq}_{Ag^+}$ in solutions containing both H_2SO_4 and $CuSO_4$ in the presence of metallic copper. The function is also very useful for the estimation of the $c^{eq}_{Ag^+}$ near a working copper electrode.

1. Introduction

The main purpose of the electrorefining of copper is the separation of impurities and Ag. It is well known that some Ag contained in anodes is transferred to the copper cathode during electrorefining. This may be caused by mechanical or cataphoretic sedimentation of the slime suspension (Ag or its compounds) circulating with the electrolyte, or by an electrochemical mechanism (codeposition). There are many different opinions as to the contributions of each of these processes to total Ag transfer [1–8]. Formerly the suspension mechanism was favoured [1–3] but now the ionic mechanism is preferred [4–8]. Whatever mechanism of silver transfer predominates it must be recognized that the electrolyte bath always contains small amounts of silver ions (~ 0.5 ppm).

Hence, the calculation of the equilibrium silver ion concentration in typical electrorefining solutions in the vicinity of metallic copper, as well as polarized copper electrodes is a very important matter. These values cannot be calculated theoretically without precise values of the Cu^{2+} and Ag^+ ion activity coefficients, although in practice, it is enough to know the ratio $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ (γ – single ion activity coefficient) only.

The purpose of this paper is to estimate the value of the ratio $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ in solutions containing H_2SO_4 and $CuSO_4$ in the industrial concentration range. A knowledge of this ratio as a function of the electrolyte composition allows an estimate of the equilibrium silver ion concentration in the presence of metallic copper or at a copper electrode.

2. Analysis of system

A system containing Cu–H_2SO_4–$CuSO_4$–H_2O–$AgSO_4$–Ag was studied. The equilibrium state is described by Nernst's equation,

$$E_{\mathrm{Cu/Cu^{2+}}} = E^0_{\mathrm{Cu/Cu^{2+}}} + \frac{RT}{2F} \ln a_{\mathrm{Cu^{2+}}}$$

$$= E^0_{\mathrm{Ag/Ag^+}} + \frac{RT}{F} \ln a_{\mathrm{Ag^+}} = E_{\mathrm{Ag/Ag^+}} \tag{1}$$

and since

$$a_{\mathrm{Cu^{2+}}} = \gamma_{\mathrm{Cu^{2+}}} c_{\mathrm{Cu^{2+}}}$$

and

$$a_{\mathrm{Ag^+}} = \gamma_{\mathrm{Ag^+}} c_{\mathrm{Ag^+}},$$

$$c^{\mathrm{eq}}_{\mathrm{Ag^+}} = \left(\frac{\gamma_{\mathrm{Cu^{2+}}}}{\gamma^2_{\mathrm{Ag^+}}} c_{\mathrm{Cu^{2+}}} \right)^{1/2} \times \exp \frac{F}{RT} \left(E^0_{\mathrm{Cu/Cu^{2+}}} - E^0_{\mathrm{Ag/Ag^+}} \right). \tag{2}$$

The ionic activity coefficients $\gamma_{\mathrm{Cu^{2+}}}$ and $\gamma_{\mathrm{Ag^+}}$ in Equation 2 are generally dependent on the solution composition. The shape of this function is difficult to predict theoretically because of the highly concentrated solutions used in electrorefining. The other problem is the incomplete dissociation of sulphuric acid. Furthermore, it is known that under some circumstances dissociation of sulphuric acid depends on both the concentration of H_2SO_4 and $CuSO_4$ [9]. The function $\gamma_{\mathrm{Cu^{2+}}}/\gamma^2_{\mathrm{Ag^+}} = f(c_{\mathrm{H_2SO_4}}, c_{\mathrm{CuSO_4}})$ can be determined experimentally by measuring the emf of the cell

$$\mathrm{Cu(Hg)|H_2SO_4, CuSO_4|Hg_2SO_4, Hg}$$

and the solubility of Ag_2SO_4 under similar solution conditions.

It is convenient to assume, that $\gamma_{\mathrm{Ag^+}}$ is independent of the Ag^+ concentration. This assumption seems justified since the solubility of Ag_2SO_4 in these solutions is very small, and then, the contribution of the products of Ag_2SO_4 dissociation to the total ionic strength is negligible. Thus we have:

$$E_{\mathrm{cell}} = E^0_{\mathrm{Hg, Hg_2SO_4/SO_4^{2-}}} - E^0_{\mathrm{Cu(Hg)/Cu^{2+}}} - \frac{RT}{2F} \ln a_{\mathrm{Cu^{2+}}} a_{\mathrm{SO_4^{2-}}} \tag{3}$$

$$I = a_{\mathrm{SO_4^{2-}}} (a_{\mathrm{Ag^+}})^2 \tag{4}$$

and therefore

$$\frac{\gamma_{\mathrm{Cu^{2+}}}}{\gamma^2_{\mathrm{Ag^+}}} = \frac{c^2_{\mathrm{Ag^+}}}{c_{\mathrm{Cu^{2+}}}} \frac{1}{I} \exp \left[\frac{2F}{RT} (E^0 - E_{\mathrm{cell}}) \right] \tag{5}$$

where $E^0 = E^0_{\mathrm{Hg, Hg_2SO_4/SO_4^{2-}}} - E^0_{\mathrm{Cu(Hg)/Cu^{2+}}}$.

3. Experimental procedure

3.1. *Reagents*

Solutions were prepared from recrystallized $CuSO_4 \cdot 5H_2O$ p.a. (POCH Poland), H_2SO_4 p.a. (Merck) and distilled water, by weight. Hg_2SO_4 was prepared by anodic dissolution of distilled mercury in the solution of H_2SO_4. After washing and drying it was ground into a paste with mercury.

Two-phase copper amalgams were obtained by electrolytic deposition of copper onto the mercury surface from a $CuSO_4$ solution using vigorous agitation. The amalgam was prepared a few days before use and was kept under a solution to exclude atmospheric oxygen. The other reagents used were of p.a. purity.

3.2. *Solubility of Ag_2SO_4*

The solution (about 50 cm^3) containing ~ 1 g Ag_2SO_4 was shaken in a flask in a water bath for one hour and filtered at 26° C. The saturated solution was then placed in a thermostat at the temperature 25 ± 0.1° C for one hour. This time was sufficient for the excess Ag_2SO_4 to crystallize. Two 10 cm^3 samples free from precipitate were collected and diluted with distilled water followed by addition of 2 mol dm^{-3} NaOH to pH = 2. EDTA solution (10% excess) was then added in order to obtain the copper complex.

Theoretical calculations show that at pH = 2 in solutions containing both copprer and silver ions, EDTA reacts with copper ions only. This was confirmed by blank experiments. The silver ion concentrations in such solutions were measured by potentiometric titration with 0.1 mol dm^{-3} (or 0.05 mol dm^{-3}) KSCN solution using an OP-S-7111-C Radelkis (Hungary) ion selective electrode and silver–silver chloride reference electrode type OP 831 with a 1 mol dm^{-3} KNO_3 junction. This method was tested by us previously. Two samples of the solution examined were titrated with the accuracy of ± 0.02 cm^3. The values differed less than 0.3%. The mean $c_{\mathrm{Ag^+}}$ value was used for further calculations.

3.3. *The emf measurements*

The emf of the cell

$$\mathrm{Cu(Hg)|H_2SO_4}\,(c_x),\ \mathrm{CuSO_4}\,(c_y)\mathrm{|Hg_2SO_4, Hg}$$

was measured at 25 ± 0.05° C with a high-resistance digital voltmeter.

The cell had double walls and was thermostated with water. Additionally, the vessel was placed in an air thermostat. The temperature was measured by a precision mercury-in-glass thermometer immersed in the solution. The measurements began after filling the vessel with the solution and allowing it to equilibrate in the thermostat several hours. Afterwards, the cells were shaken, short-circuited for about 30 s and left in order to achieve the equilibrium emf value. The values obtained before and after the above

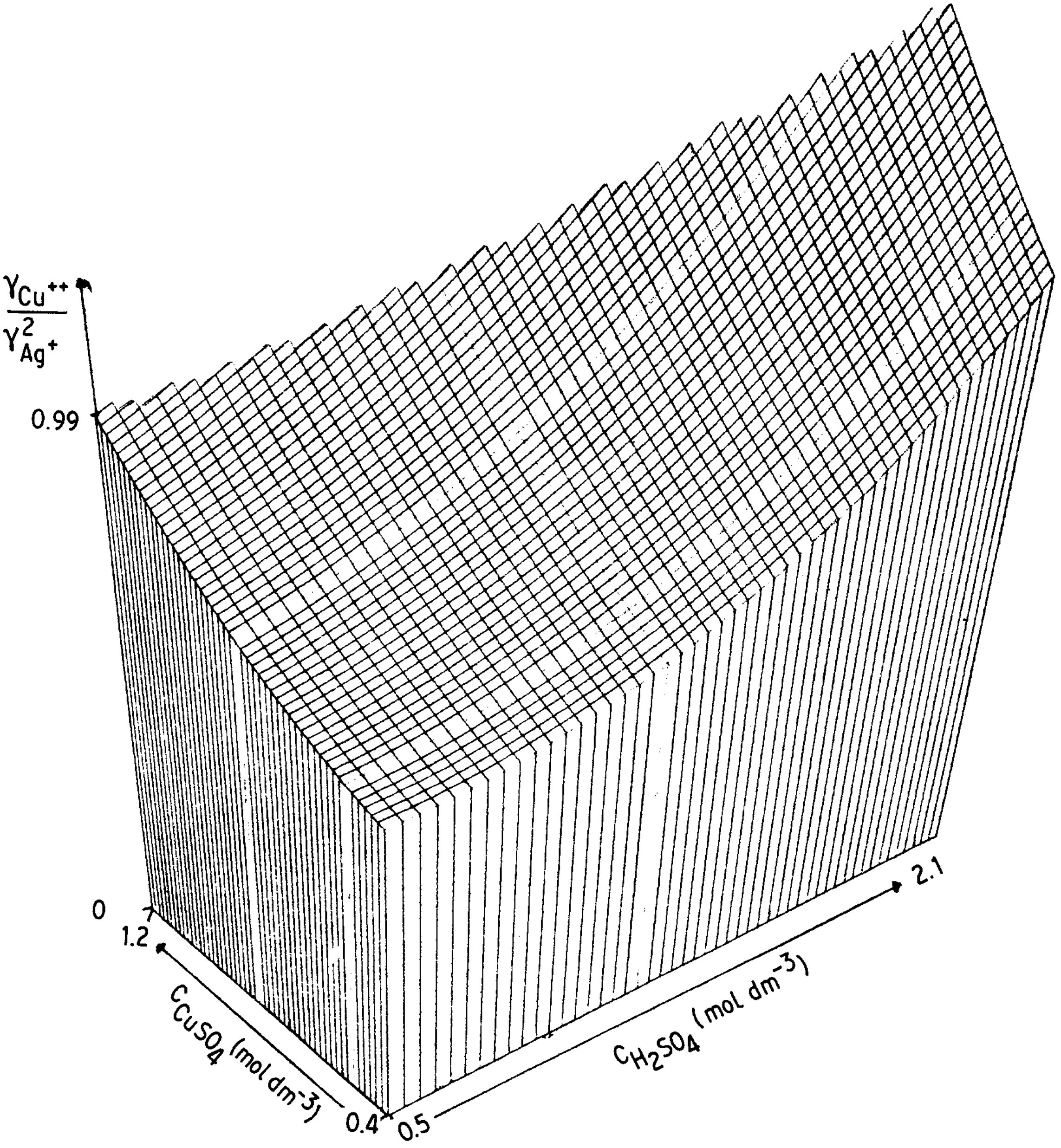

Fig. 1. The dependence of $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ on H_2SO_4 and $CuSO_4$ concentrations.

treatment differed by less than 0.1 mV. This error was comparable with the error caused by a temperature deviation of 0.1° C [10]. For each solution examined, two cells were prepared and the difference between the measured values was always less than 0.1 mV. As a test of the procedure and the reagent purity (especially of copper amalgam) the emf of the cell filled with saturated $CuSO_4$ solution was measured. Our result of 346.7 mV is in good agreement with the literature data [11]. The test was repeated periodically.

4. Results and conclusions

The values of emf and c_{Ag^+} for 30 different solutions were obtained. The values of $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ were calculated by substituting the values of emf and c_{Ag^+} into Equation 5 and putting $E^0 = E^0_{Hg,Hg_2SO_4/SO_4^{2-}} - E^0_{Cu(Hg)/Cu^{2+}} = 270.96$ mV (calculated from literature data [11]) and $\log I = -4.835$ [12].

The value of the above ratio is a function of the H_2SO_4 and $CuSO_4$ concentrations and it was approximated with a 2nd degree polynomial. The least squares method gave

$$\frac{\gamma_{Cu^{2+}}}{\gamma^2_{Ag^+}} = 0.5978 - 0.3853x - 0.2329y + 0.2228x^2 + 0.6045xy + 0.2930y^2 \qquad (6)$$

where

$$x = c_{H_2SO_4}$$

$$y = c_{CuSO_4}.$$

The experimental values and those calculated from the polynomial (Equation 6) differed (in the extreme case) by less than 3%. The above formula described properly $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ in the concentration range

$$0.5\,\text{mol dm}^{-3} \leqslant c_{H_2SO_4} \leqslant 2.1\,\text{mol dm}^{-3}$$

$$0.4\,\text{mol dm}^{-3} \leqslant c_{CuSO_4} \leqslant \text{saturated solution.}$$

Figure 1 shows the dependence of $\gamma_{Cu^{2+}}/\gamma^2_{Ag^+}$ on H_2SO_4 and $CuSO_4$ concentrations in this region. The function was convergent in this range. According to Equations 2 and 6, the equilibrium silver ions concentrations $c^{eq}_{Ag^+}$ in the solution containing $CuSO_4$ and H_2SO_4 at the presence of metallic copper is given by:

$$c^{eq}_{Ag^+} = \exp \frac{F}{RT}(E^0_{Cu/Cu^{2+}} - E^0_{Ag/Ag^+}) (0.5978y - 0.3853xy - 0.2329y^2 + 0.2228x^2y + 0.6045xy^2 + 0.2930y^3)^{1/2}. \qquad (7)$$

Using formula 7, the value of $c^{eq}_{Ag^+} = 1.37 \times 10^{-8}$ mol dm^{-3} (0.0015 μg Ag cm^{-3}) was obtained for the electrolyte often applied in industrial practice (50 g Cu dm^{-3} and 100 g H_2SO_4 dm^{-3}). This result is in good agreement with the experimental value of $c_{Ag^+} < 0.05$ ppm, which is obtained from Atomic Adsorption Spectrometry measurements at its sensitivity limit. The above equations are very useful in the consideration of silver transfer during the copper electrorefining process.

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