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The diffusion coefficient of Cu(II) ions in sulfuric acid–aqueous and methanesulfonic acid–methanol solutions

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Abstract

When using a copper working electrode to study the diffusion of Cu(II) ions it is necessary to polish the electrode between experiments to maintain a smooth surface. To eliminate the required polishing, a platinum working electrode can be used. The copper layer established on the electrode surface during experimentation can be removed between experiments by anodic stripping. When using a platinum disk working electrode, the most reliable method of analysis involves double potential step chrono-amperometry method as opposed to voltammetry. By applying this method diffusion coefficients for Cu(II) ions in sulphuric acid – aqueous and methanesulfonic acid (HMSA) – methanol solutions were determined.

List of symbols

I	current (A)
I_d	diffusion-limiting current (A)
I_k	kinetically limited current (A)
I_l	limiting current (A)
i	current density (A cm^{-2})
i_d	diffusion-limiting current density (A cm^{-2})
n	number of electrons involved in electrode reaction
F	Faraday number, $F = 96487$ C mol^{-1}
A_e	electrode surface area (cm^2)
D	diffusion coefficient (cm^2 s^{-1})
v	kinematic viscosity of solution (cm^2 s^{-1})
c	concentration of ions in bulk solution (mol cm^{-3})
ω	angular frequency of rotation (s^{-1}); $\omega = 2\pi f$
f	frequency of rotation (s^{-1})
q	charge (C)
t	time (s)

Subscripts

e	electrode
c	cathodic
c,Cu	cathodic copper
a,30	anodic, 30 s
a,5	anodic, 5 s
the	theoretical
exp	experimental

1. Introduction

The diffusion coefficient of Cu(II) ions in sulphuric acid solutions have been widely investigated mostly using a copper disk electrode made from a copper rod [1, 2, 3, 4, 5]. Reported results from 1984 to 1996 vary over a wide range [1]. The corrected diffusion coefficient of Cu(II) at infinite Cu(II) dilution and 298 K in aqueous sulphuric acid solutions varies from 5.4×10^{-6} to 9.7×10^{-6} cm^2 s^{-1}. Moreover, the mean value of the diffusion coefficients of Cu(II) obtained when using the rotating disk electrode method was 15% smaller than the mean values obtained from other methods. To improve the reproducibility, it is desirable to work with a platinum electrode. By using a platinum electrode the polishing required between experiments, when using a copper electrode, is eliminated. In addition, it avoids the anodic dissolution of the copper substrate in the presence of dissolved oxygen.

Several methods can be applied to determine the diffusion coefficient for Cu(II) ions. The purpose of this investigation was to identify a consistently reliable electrochemical method that can be applied when using a platinum disk instead of a copper disk and to determine the diffusion coefficient of Cu(II) ions in $CuSO_4$ – methanesulfonic acid (HMSA) and $CuCO_3 \cdot CuO_2H_2$ – HMSA – methanol solutions. In the future, HMSA–methanol solutions will be applied in industry; the present application cannot be mentioned in this paper, for property reasons.

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Diffusion coefficients for Cu(II) ions in 1 and 0.1 M H_2SO_4 aqueous supporting electrolyte solutions were also determined to control the various methods. The results were compared with diffusion coefficients from the literature. The most reliable method was then used for Cu(II) – methanol solutions with HMSA as supporting electrolyte.

2. Experimental

2.1. *Electrolysis cell*

The electrolysis cell used was an open cylindrical glass vessel of inner diameter of 5 cm. The cell was filled with approximately 160 cm^3 of solution and a thermostat (Lauda, Germany) was used to maintain a constant temperature. Rotating platinum and copper disks were used as the working electrodes. The metal disk electrodes were embedded centrally in a plastic rod of 1 cm diameter. The electrode surface areas were 0.503 cm^2 ($d = 0.8$ cm) and 0.283 cm^2 ($d = 0.6$ cm) for the platinum and copper disks, respectively. The working electrode was located in the middle of the cylindrical vessel, placing the electrode surface approximately 1 cm below the solution surface. A variable speed motor (MotoMatic® Motor Generator, Electro-Craft Corporation, USA) was used to rotate the working electrode. The rotation speed was regulated by a digital tachometer (MotoMatic® Speed Control, Electro-Craft Corporation, USA). The experiments were carried out at 4, 9, 16, 25, 36, 49 and 64 rps.

The counter electrode was composed of a platinum sheet with a total surface area of 5 cm^2. The counter electrode was situated below the working electrode. The distance separating the two electrodes was approximately 2 cm. A Ag–AgCl electrode, used as a reference, was placed in a side-branch of the cell and connected to the cell by a Luggin capillary. The distance between the opening at the capillary tip and the working electrode was approximately 0.5 cm.

2.2. *Solutions*

Deionised water was used to prepare the aqueous solutions. The methanol solutions were prepared using pure methanol (Merck). Sulphuric acid (Merck), methanesulfonic acid (Merck), copper(II) sulfate anhydrous (Riedel-De Haën) and/or copper(II) carbonate basic (Acros Organics) were used in the aqueous and methanol solutions. All solution components were of pro-analysis grade. The solutions were not deoxygenated prior to experimentation since open cells were exclusively used.

To determine the diffusion coefficient of Cu(II), a copper concentration of 0.010 M was used. Many researchers have selected this relatively high concentration, probably to suppress the effect of dissolved oxygen and to minimize the formation of Cu(I) ions during the two-step process for the reduction of Cu(II) to Cu.

For a 0.01 M $CuSO_4$–0.1 M H_2SO_4 solution it was found that the limiting current density for copper reduction is larger than the calculated diffusion limiting current density for the reduction of oxygen to water by a factor of 10. Moreover, it was found that the difference between i_c and $i_{c,Cu}$ at a potential of -0.65 V is 4×10^{-3} A cm^{-2} and does not depend on the rotation speed. This means that these difference is almost equal to the current density for hydrogen evolution and that the effect of oxygen reduction is negligible.

2.3. *Electrochemical measurements*

Two electrochemical methods were used. The first method involved the use of voltammograms. These were recorded using a digital potentiostat (Autolab, PG STAT20, EcoChemie, the Netherlands) operating at a scan rate of 10 mV s^{-1} for most experiments and operating exceptionally at a scan rate of 100 mV s^{-1}. The second method used double potential step chronoamperometry [6]. The resulting cathodic and anodic current vs. time curves, both at fixed potentials, were recorded for analysis. Moreover, the total anodic charge to dissolve deposited copper was recorded.

3. Results and discussion

3.1. *$CuSO_4$–H_2SO_4 aqueous solutions*

3.1.1. *Voltammetric method*

Experimentation was conducted using 0.010 M $CuSO_4$ in 1 and 0.1 M H_2SO_4 aqueous solutions with a platinum disk as the working electrode. The voltammograms were recorded for potential sweeps between 0.1 and -0.7 V. After the completion of the first negative sweep from 0.1 to -0.7 V the platinum electrode surface was completely covered with a copper layer.

The current–potential curve for the first negative sweep was observed to deviate slightly from the subsequent curves for the negative sweeps. This deviation occurred because the platinum surface was not covered with copper at the start of the experiment. After the first cycle, the platinum surface was covered with copper and very little hysteresis was observed.

The current–potential curve for the second negative sweep was consistently used for the determination of the diffusion coefficient. In general, the current–potential curves for the negative sweeps displayed better defined limiting diffusion control for the deposition of copper relative to the positive sweeps. Typical current density–potential curves for the 0.010 M $CuSO_4$–1 M H_2SO_4 solution are shown in Figure 1 for various rotation speeds. Similar curves were obtained for the 0.010 M $CuSO_4$–0.1 M H_2SO_4 solution.

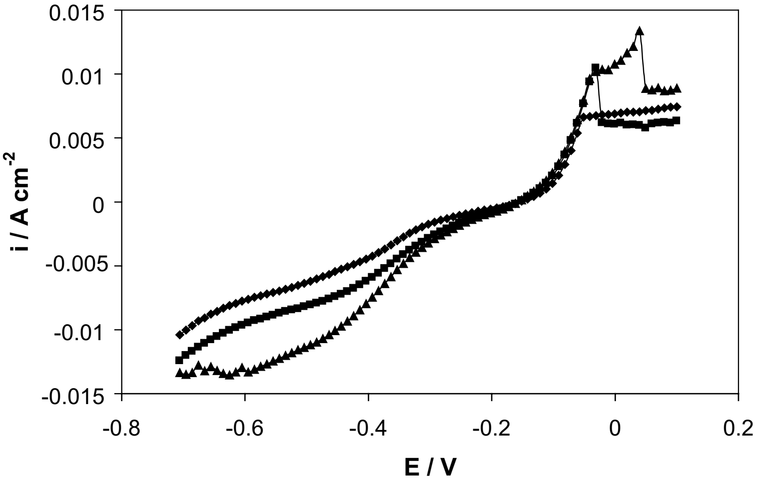

Fig. 1. Current density as a function of potential obtained from a platinum rotating disk working electrode covered with a copper layer in a 0.010 M $CuSO_4$–1 M H_2SO_4 aqueous solution at 298 K with rotation speeds at 9 (◆), 25 (■) and 64 (▲) rps. The scan rate was 10 mV s^{-1}. Only the curves for the negative sweep, after the copper layer had been established, are presented.

The current density plateau is not well defined in the plotted curves. As a result, the simple Levich equation (1) cannot be applied successfully [6].

$$I_d = 0.62nFA_eD^{\frac{2}{3}}\nu^{-\frac{1}{6}}c\omega^{\frac{1}{2}} \tag{1}$$

The mixed control Levich equation (2) for a first-order reaction at an electrode was used [7].

$$1/I = 1/I_k + 1/(0.62nFA_eD^{\frac{2}{3}}\nu^{-\frac{1}{6}}c\omega^{\frac{1}{2}}) \tag{2}$$

Plots of the inverse of the current at a fixed potential vs the inverse root of the rotation speed (I^{-1} vs $f^{-1/2}$) did not give straight lines. Specifically, the results for the 0.010 M $CuSO_4$–0.1 M H_2SO_4 aqueous solution exhibited systematic deviations from the expected linear relationship. These deviations depended strongly on the electrode potential in the range of −0.3 to −0.7 V. It was concluded that the voltammetric method, with a generally accepted potential scan rate, is not a useful method to determine diffusion coefficients for Cu(II) ions in an aqueous sulphuric acid solution when using a platinum disk covered with a thin layer of copper as the working electrode.

The experimental conditions applied by various authors are very surprising and questionable. In [1, 2] linear $I^{-1}/\omega^{-1/2}$ curves are presented, but the applied rotation speed range is very small. Namely, the difference between the lowest and highest rotation speed is only a factor of 2.5 in [2] and 6.0 in [1]. This difference is too small to obtain reliable results. We applied a much wider range of rotation speeds (4–64 rps). It was found that the $I^{-1}/f^{-1/2}$ curves are not straight and not parallel to each other. In [3] a scan rate of 100 mV s^{-1} was used. According to many electrochemists this scan rate is too high to determine diffusion coefficients. Surprisingly, the presented voltammograms for the rotating copper disc look very good. Using the Gregory–Riddiford equation the diffusion coefficient for Cu(II) in a 0.011 N $CuSO_4$–1.0 N H_2SO_4 solution at 298 K is 5.41×10^{-6} cm^2 s^{-1} [3]. The simple Levich equation gives a value of 5.14×10^{-6} cm^2 s^{-1}, which is about 5% smaller. The experiments of [3] were repeated in this investigation. Similar results were obtained.

Milora et al. [7] conducted voltammetric experiments with a rotating platinum disk electrode at a high potential scan rate, namely 41.6 mV s^{-1}. Only the first cathodic sweep was considered for a 0.10 M $CuSO_4$–1.0 M H_2SO_4 aqueous solution at 298 K. The diffusion coefficient for Cu(II) ions was reported to be 5.23×10^{-6} cm^2 s^{-1}. Milora et al. used an unusually high copper concentration and unfortunately the voltammograms were not presented.

3.1.2. *Double potential step chrono-amperometric method*

The double potential step chrono-amperometric method was used for 0.010 M $CuSO_4$–0.1 M H_2SO_4 aqueous solutions. The potential was maintained at a constant level, while the current was measured as a function of time. To determine the cathodic potential, where the limiting current for copper deposition is attained, the rotation speed of the platinum disk working electrode was maintained at the highest rotation speed, namely 64 rps, while the potential was varied. The current as a function of time was recorded, as were the cathodic (q_c) and anodic (q_a) charges. The cell was maintained at a cathodic potential for 30 s depositing copper, while the anodic potential was maintained until the current through the cell returned to zero (130 s were sufficient) indicating that all copper had been stripped from the electrode surface.

It was desired that this method be conducted at a cathodic potential within the range of potentials that will produce a constant q_a at a fixed anodic potential for the dissolution of copper. The value of q_a represents only the copper deposited on the working electrode whereas the value of q_c may be influenced by other reactions such as hydrogen formation, Cu(I) formation and oxygen reduction.

The strong current decline caused by a change in the nature of the electrode surface (from Pt to Cu) during the first few seconds was eliminated by considering only the final 25 s of the 30 s time interval in the calculation of the diffusion coefficient. This was done by subtracting the anodic charge found during stripping after 5 s of cathodic copper deposition ($q_{a,5}$) from the anodic charge found during stripping after 30 s of cathodic copper deposition ($q_{a,30}$). The current density for copper deposition, $i_{c,Cu}$, was determined using Equation 3 where n_{the} is the theoretical number of electrons used in the oxidation of Cu to Cu(II) having a value of 2, n_{exp} is the experimental number of electrons used in the oxidation of Cu, Δt is 25 s and A_e is the electrode surface area.

$$i_{c,Cu} = \frac{(q_{a,30} - q_{a,5})}{\Delta t A_e} \frac{n_{the}}{n_{exp}} \tag{3}$$

The stripping potential selected to obtain the anodic charge was 0.15 V based on [4, 5]. Anodic stripping was conducted without rotation to minimize the diffusion of Cu(I), formed during the anodic dissolution of copper, to the bulk solution. To determine n_{exp} a copper sheet with an exposed surface area of 7.7 cm^2 was polarized at 0.15 V for 70 min. The weight loss and the charge passed were determined and it was found that n_{exp}=1.9 due to some Cu(I) formation. This agrees with those found in [4, 5]. The total cathodic current density (i_c) and copper current density ($i_{c,Cu}$), both during the final 25 s of the 30 s interval, are plotted vs the cathodic potential in Figure 2. From this figure, it follows that $i_{c,Cu}$ is constant for potentials between −0.5 and −0.7 V. The difference between i_c and $i_{c,Cu}$ increases strongly as the cathodic potential becomes more negative.

The second step of this method was to maintain a constant cathodic potential of −0.65 V, while varying the rotation speed of the working electrode. In Figure 3, i_c and $i_{c,Cu}$ at a potential of −0.65 V and considering only the final 25 s of the 30 s interval are plotted vs the root of the rotation speed. The difference between the current density curves is indicative of hydrogen formation during cathodic polarization. Using the simple Levich equation the diffusion coefficient of Cu(II) ions in 0.010 M $CuSO_4$–0.1 M H_2SO_4 aqueous solution was calculated using the slope of $i_{c,Cu}$ vs $f^{1/2}$ and found to be 5.10×10^{-6} cm^2 s^{-1} (Figure 3). This value is in reasonable agreement with published results [3, 8].

Experiments by Quickenden and Jiang [2] were repeated at 298 K and a potential of −0.45 V vs a copper reference electrode for a rotating copper disk electrode at 6 rps. The Cu/Cu(II) equilibrium potential was found to be −0.06 V vs a Ag–AgCl reference electrode. Using the obtained cathodic current, the diffusion coefficient was determined to be 6.65×10^{-6} cm^2 s^{-1}. This result agrees with the value 7.22×10^{-6} cm^2 s^{-1} found by Quickenden and Jiang [2]. From Figure 2, however, at potentials where the limiting current was found by Quickenden and Jiang [2], i_c is clearly larger than $i_{c,Cu}$. It follows that hydrogen formation cannot be ignored at potentials where the limiting current for copper deposition occurs. Quickenden and Jiang [2] ignored the effects of hydrogen formation and, consequently, the value reported for the diffusion coefficient for Cu(II) ions is inflated.

It was concluded that the double potential step chrono-amperometric method is the superior method of determining diffusion coefficients of metal ions in solution when using a platinum disk working electrode.

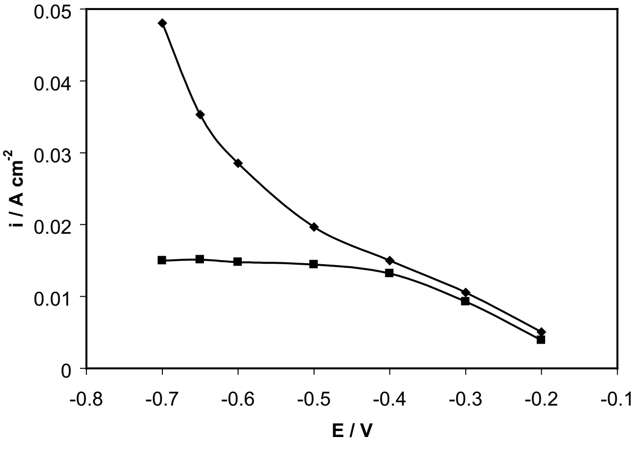

Fig. 2. Cathodic current density, i_c, (◆) and copper current density, $i_{c,Cu}$, (■) as a function of potential in a 0.010 M $CuSO_4$–0.1 M H_2SO_4 aqueous solution. The working electrode had a rotation speed of 64 rps during cathodic deposition.

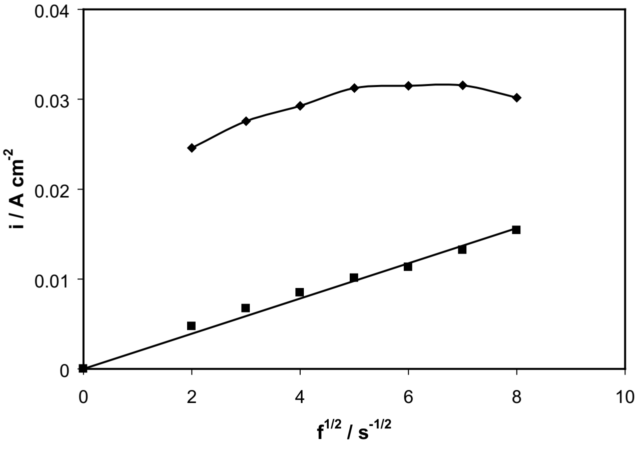

Fig. 3. Total cathodic current density, i_c, (◆) and copper current density, $i_{c,Cu}$, (■) as a function of the root of rotation speed for a 0.010 M $CuSO_4$–0.1 M H_2SO_4 aqueous solution at 298 K. The copper current density is linear (solid line) through the origin.

3.2. *$CuSO_4$–HMSA–methanol solutions*

3.2.1. *Voltammetric method*

The voltammetric procedure discussed in section 3.1.1 was applied to 0.010 M $CuSO_4$–1 and 10 wt.% HMSA–99 and 90 wt.% methanol solutions, respectively. Voltammograms, similar to those obtained for the $CuSO_4$–H_2SO_4 aqueous solutions shown in Figure 1, were found for the $CuSO_4$–HMSA–methanol solutions. Again, it was concluded that when using a platinum disk as the working electrode at a potential scan rate of 10 mV s^{-1} no acceptable results for the diffusion coefficient of Cu(II) ions are found.

3.2.2. *Double potential step chrono-amperometric method*

The double potential step chrono-amperometric method was applied to the $CuSO_4$–HMSA–methanol solutions. Potentials of −0.55 and −0.65 V were used for copper deposition in 0.010 M $CuSO_4$–1 and 10 wt.% HMSA–99 and 90 wt.% methanol solutions, respectively, while a potential of 0.2 V was used for copper dissolution in both solutions. The values of q_a and q_c were recorded and the current density for copper deposition ($i_{c,Cu}$) was determined using Equation 3. For the final 25 s of the 30 s interval, plots of i_c and $i_{c,Cu}$ vs the cathodic potential are shown in Figures 4 and 5 for 0.010 M $CuSO_4$–1 and 10 wt.% HMSA–99 and 90 wt.% methanol solutions, respectively. From Figures 4 and 5 it follows that $i_{c,Cu}$ is constant for cathodic potentials between −0.5 and −0.7 V for both solutions.

To determine the extent of Cu(I) formation during copper dissolution, a copper sheet was polarized at potentials ranging from 0.2 to 0.6 V in the 1 and 10 wt.% HMSA–99 and 90 wt.% methanol solutions. The weight loss and the charge passed were determined. To calculate the number of electrons per atom of copper, it was assumed that the charge was used only for the oxidation of copper. The values of n_{exp} as a function of potential are shown in Figure 6. This figure shows that the solution composition affects the n_{exp}/E relationship.

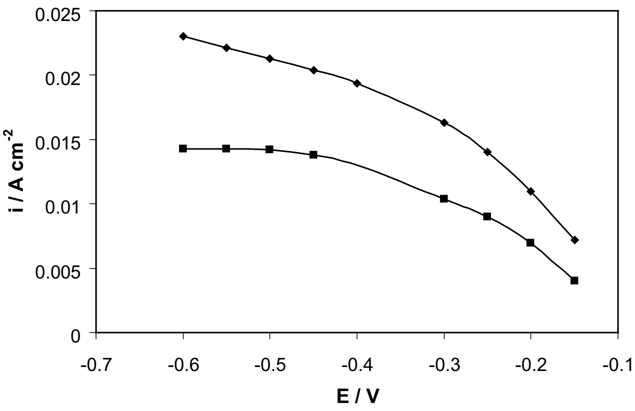

Fig. 4. Cathodic current density, i_c, (♦) and copper current density, $i_{c,Cu}$, (■) as a function of potential in a 0.010 M $CuSO_4$–1 wt.% HMSA–99 wt.% methanol solution. The working electrode had a rotation speed of 64 rps during cathodic deposition.

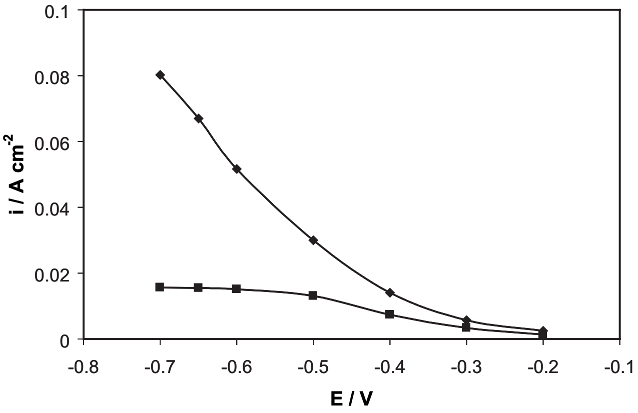

Fig. 5. Cathodic current density, i_c, (♦) and copper current density, $i_{c,Cu}$, (■) as a function of potential in a 0.010 M $CuSO_4$–10 wt.% HMSA–90 wt.% methanol solution. The working electrode had a rotation speed of 64 rps during cathodic deposition.

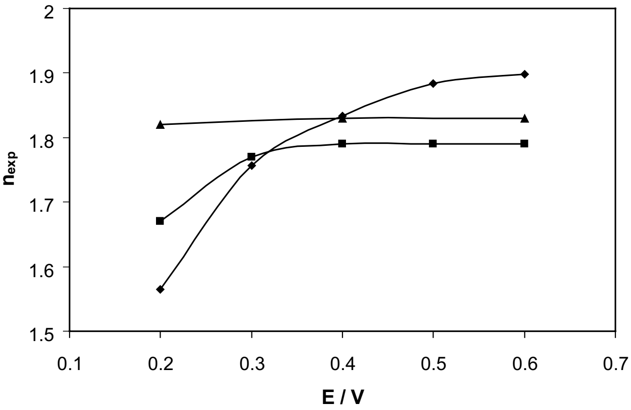

Fig. 6. n_{exp} for 1 (♦) or 10 (■) wt.% HMSA–99 or 90 wt.% methanol solutions and for 10 wt.% HMSA–10 wt.% H_2O–80 wt.% methanol solution (▲) obtained from anodic stripping of a copper sheet.

Using the slope from $i_{c,Cu}$ vs $f^{1/2}$ lines (Figure 7) and applying the simple Levich equation, the diffusion coefficient for Cu(II) ions in 0.010 M $CuSO_4$–1 and 10 wt.% HMSA–99 and 90 wt.% methanol solutions at 293 K were found to be 4.93×10^{-6} and 5.33×10^{-6} cm^2 s^{-1}, respectively. It is assumed that the kinematic viscosity used for both solutions was 7.49×10^{-3} cm^2 s^{-1} based on the kinematic viscosity of pure methanol at 293 K.

The diffusion coefficient for Cu(II) ions in a 0.010 M $CuSO_4$–10 wt.% H_2O–10 wt.% HMSA–80 wt.% methanol solution was also determined. For this solution n_{exp} is also given in Figure 6, i_c and $i_{c,Cu}$ vs E at a rotation speed of 64 rps in Figure 8 and $i_{c,Cu}$ vs $f^{1/2}$ at $E =$ −0.65 V in Figure 9. It was found that the Cu(II) diffusion coefficient for 0.010 M $CuSO_4$–10 wt.% H_2O–10 wt.% HMSA–80 wt.% methanol solution is 2.80×10^{-6} cm^2 s^{-1} at 293 K. Comparing this result with those for the water-free solutions, it follows that the water content strongly affects the diffusion coefficient of Cu(II).

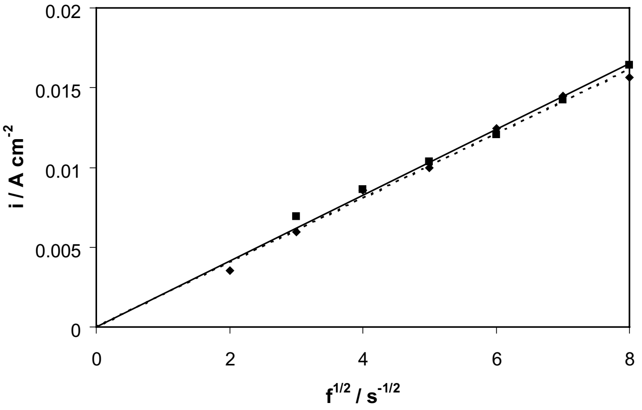

Fig. 7. Copper current density ($i_{c,Cu}$) as a function of the root of rotation speed for 0.010 M $CuSO_4$–1 (◆ and dotted line) or 10 (■ and solid line) wt.% HMSA–99 or 90 wt.% methanol solutions at 293 K.

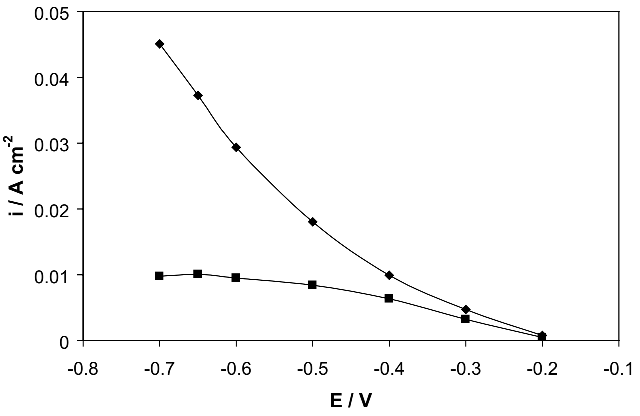

Fig. 8. Cathodic current density, i_c, (◆) and the copper current density, $i_{c,Cu}$, (■), as a function of potential in a 0.010 M $CuSO_4$–10 wt.% HMSA–10 wt.% H_2O–80 wt.% methanol solution. The working electrode had a rotation speed of 64 rps during cathodic deposition.

From Figure 6 it follows that for the solution with a water content of 10%, n_{exp} is practically independent of the potential.

3.3. *$CuCO_3 \cdot CuO_2H_2$–HMSA–methanol solutions*

The double potential step chrono-amperometric method was applied to a 0.010 M copper carbonate-hydroxide ($CuCO_3 \cdot CuO_2H_2$)–10 wt.% HMSA–90 wt.% methanol solution. The carbonate ions disappear from the solution through a reaction with H^+ ions forming a small quantity of water. The water produced represents about 0.05 wt.% of the final solution. The diffusion coefficient for Cu(II) ions in a 0.020 M Cu(II) solution at rotation speeds from 9 to 64 rps was first found to be 3.32×10^{-6} cm^2 s^{-1} and reproduced as 3.26×10^{-6} cm^2 s^{-1} giving an average of 3.29×10^{-6} cm^2 s^{-1} at 293 K. Comparing these results with the results from Section 3.2.2 it follows that the diffusion coefficient of Cu(II) is sensible for the water content and small concentration of the sulfate ions has a little effect on the diffusion coefficient of Cu(II). From diffusion coefficients determined for a temperature range of 293–313 K, the activation energy was found to be 11.2 kJ mol^{-1}.

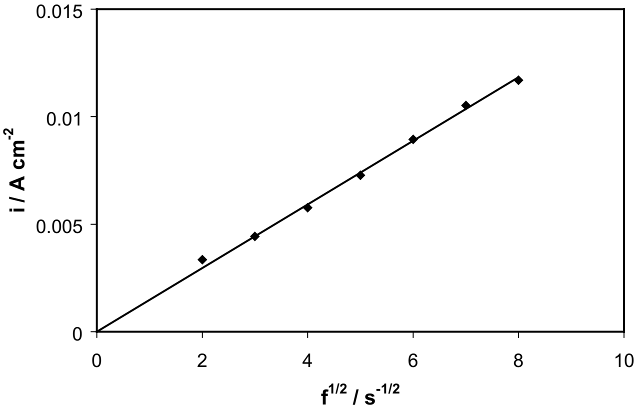

Fig. 9. Copper current density ($i_{c,Cu}$) as a function of the root of rotation speed for 0.010 M $CuSO_4$–10 wt.% H_2O–10 wt.% HMSA–80 wt.% methanol solution at 293 K.

4. Conclusions

To determine the diffusion coefficients for Cu(II) ions in $CuSO_4$–H_2SO_4 aqueous solutions, it was found that the double potential step chrono-amperometric method is most reliable when using a platinum working electrode. In this method the quantity of copper deposited during cathodic polarization was determined by anodic dissolution. This method was applied to $CuSO_4$–HMSA–methanol and $CuSO_4$–HMSA–H_2O–methanol solutions.

The double potential step chrono-amperometric method is a very useful tool to determine diffusion coefficients for many metal ions, especially if hydrogen formation occurs simultaneously with the metal deposition.

References

1. T.I. Quickenden and Q. Xu, *J. Electrochem. Soc.* **143** (1996) 1248.
2. T.I. Quickenden and X. Jiang, *Electrochim. Acta* **29** (1984) 693.
3. L. Grambow and W. Vielstich, *J. Electrochem. Soc.* **12** (1974) 779.
4. L.J.J. Janssen, *J. Appl. Electrochem.* **18** (1988) 339.
5. M-C. Petit, *Electrochim. Acta* **10** (1964) 291.
6. A.J. Bard and L.R. Faulkner, 'Electrochemical Methods' (John Wiley and Sons, New York, 1980).
7. R.N. Adams, 'Electrochemistry at Solid Electrodes' (Marcel Dekker, New York, 1969), p. 92.
8. C.J. Milora, J.F. Henrickson and W.C. Hahn, *J. Electrochem. Soc.* **120** (1973) 488.