Solvation of Ions. Some Applications. II†
Electrolysis of Copper(I) Sulphate
in Water–Nitrile Mixtures

Ian D. MacLeod,[A] *David M. Muir,*[A,B] *Alan J. Parker*[A]
and Pritam Singh[A]

[A] Mineral Chemistry Research Unit, Murdoch University,
Murdoch, W.A. 6153.
[B] To whom correspondence should be addressed.

Abstract

Organic nitriles stabilize acidic aqueous copper(I) sulphate solutions. Electrolysis of such solutions provides an alternative for the electrowinning and electrorefining of copper. The Cu^+/Cu^0 and Cu^{2+}/Cu^+ standard reduction potentials in aqueous solutions containing acetonitrile or 3-hydroxy-propanenitrile (hydracrylonitrile) differ from those in water, due to the specific solvation and stabilization of the copper(I) ion by either nitrile. In the mixed solvent, the solvation sphere around the copper(I) ion contains organic nitrile, rather than water, and this reduces the mobility of Cu^+ and slows its diffusion to the electrode surface in a working cell. The copper(II) ion contains water in its solvation shell in the mixed solvent. Thus for dilute solutions, the diffusion coefficient of the copper(I) ion in 10 mole % aqueous acetonitrile is about two-thirds and in 10% 3-hydroxypropane-nitrile–water is about one-fifth that of the copper(II) ion in water. In concentrated solutions containing sulphuric acid, the copper(II) ion diffuses as ion pairs and this reduces its mobility. This effect is not observed for copper(I) ions. Cell voltages measured during the electrolysis of copper(I) sulphate solutions by using soluble copper, insoluble platinum or insoluble carbon anodes are analysed in terms of the ohmic resistance, the equilibrium potential, the charge-transfer overpotential and the diffusion polarization of the working cell. There is a significant charge-transfer overpotential for the oxidation of Cu^+ to Cu^{2+} at an insoluble graphite anode in 6 mol dm^{-3} acetonitrile–water solutions; the rate constant is 4×10^{-4} cm s^{-1}. At platinum the rate constant is $1 \cdot 6 \times 10^{-2}$ cm s^{-1}.

Introduction

In water the copper(I) ion is unstable and readily disproportionates (reaction (1))

$$Cu^0 + Cu^{2+} \underset{}{\overset{K_1}{\rightleftharpoons}} 2Cu^+ \tag{1}$$

but, like the silver cation,[1] the copper(I) ion is better solvated by organic nitriles than by water. The Cu^+ ion has a filled d^{10} outer electron shell, which back-bonds in a specific $d\pi$–$p\pi$ interaction with the π^* orbital of the nitrile group. Typically, with the addition of at least four moles of acetonitrile per mole of Cu^+ to water, K_1 changes from 10^{-6} mol dm^{-3} in water to about 10^{10} mol dm^{-3} in acetonitrile–water. Stable, colourless solutions of copper(I) salts persist even at high (e.g. 3 mol dm^{-3}) concentrations of copper(I), provided that at least 2–4 moles of acetonitrile (depending on pH and counter anion) are present per mole of copper(I)

† Part I, *Aust. J. Chem.*, 1974, **27**, 721.

[1] Avraamides, J., Diggle, J. W., and Parker, A. J., *Aust. J. Chem.*, 1974, **27**, 721.

Results and Discussion

(a) *Electrode Potentials and Solvation of Copper*(I) *Ion*

The stabilization of the copper(I) ion in water by acetonitrile is reflected in the changes of the potential of the Cu^+/Cu^0 electrode on transfer from water to acetonitrile–water mixtures. Values are in Table 1. Measurements were made against the saturated calomel reference electrode then converted to the n.h.e. as reference. The free energy of transfer of the copper(I) ion from water to dilute acetonitrile–water mixtures is exoenergetic by about 40 kJ g-ion^{-1} (TATB assumption),[5] provided that at least four moles of acetonitrile per mole of Cu^+ are present. The standard potential of the Cu^+/Cu^0 electrode (from measurements on 0·01 mol dm^{-3} $CuClO_4$ solutions) in 6 mol dm^{-3} acetonitrile is 0·18 V at 25°.[7]

Table 1. Reduction potentials of the Cu/Cu_2SO_4 electrode and the $Pt/CuSO_4/Cu_2SO_4$ electrode in water containing acetonitrile

pH 3–3·5, unless otherwise stated. $E°$ (± 5 mV) calculated for 1 mol dm^{-3} solutions of Cu^+ and Cu^{2+} from observed e.m.f., for solutions at the concentrations shown, by assuming Nernstian behaviour

Solvent [MeCN] (mol dm^{-3})	Cu/Cu_2SO_4 electrode		$Pt/CuSO_4/Cu_2SO_4$ electrode		
	[Cu$^+$] (mol dm^{-3})	$E°$ (mV $v.$ n.h.e.)	[Cu$^+$] (mol dm^{-3})	[Cu^{2+}] (mol dm^{-3})	$E°$ (mV $v.$ n.h.e.)
0·0	1·0	520 (lit.)	1·0	1·0	160 (lit.)
2·0	0·01	270	0·01	0·01	480
6·0	0·01	180	0·01	0·01	560
10·0	0·01	140	0·01	0·01	630
2·0[A]	0·50	290[A]			
3·8[B]			0·25	0·25	485[B]
6·0[A]	0·50	120[A]			
6·0[A,C]	0·50	160[A,C]			

[A] Solution contains 2 mol dm^{-3} H_2SO_4.   [B] Solution contains 0·32 mol dm^{-3} H_2SO_4.   [C] Solvent is 3-hydroxypropanenitrile, not acetonitrile.

In electrolyte compositions of practical interest,[2,3] e.g. those containing 2 mol dm^{-3} sulphuric acid, 6 mol dm^{-3} acetonitrile and about 0·50 mol dm^{-3} Cu^+ ions as sulphates, the potential for reduction of Cu^+ to copper is about 0·1 V $v.$ n.h.e. (cf. Table 1). This is significantly less cathodic than the standard reduction potential for Cu^{2+}/Cu^0 in water (0·34 V) and explains the different behaviour of impurity elements during copper electrorefining and electrowinning of $CuSO_4/H_2O$ against $Cu_2SO_4/RCN/H_2O$. For example, antimony and bismuth are often present in blister copper anodes. They oxidize from copper anodes containing these elements at similar potentials to copper during conventional electrorefining in $CuSO_4/H_2SO_4/H_2O$ solutions. However, during electrolysis of $Cu_2SO_4/RCN/H_2O$ solutions with a soluble impure copper anode, elements like antimony and bismuth will not oxidize and will report to the anode slimes.[2,3] Ions like Ni^{2+}, H^+, Zn^{2+} and Fe^{2+} are not reduced at a cathode in solutions containing $CuSO_4$ or Cu_2SO_4, except that in solutions containing $>0·8$ mole fraction acetonitrile, H^+ is reduced in preference to Cu^+, i.e. H_2SO_4 dissolves copper in the presence of a large proportion of acetonitrile.

[7] Parker, A. J., Clarke, D. A., Couche, R. A., Miller, G., Tilley, R. I., and Waghorne, W. E., *Aust. J. Chem.*, 1977, in press.

The standard reduction potential of the Cu^{2+}/Cu^+ electrode at insoluble platinum or graphite is 0.5 ± 0.1 V (n.h.e.) in 2–10 mol dm^{-3} acetonitrile as shown in Table 1. Thus the potential for oxidation of Cu^+ (-0.5 V) at platinum or graphite in $Cu_2SO_4/RCN/H_2O$ solutions is considerably less anodic than that (-1.24 V) required to produce oxygen and H_2SO_4 at a lead anode, during electrolysis of $CuSO_4/H_2O/H_2SO_4$ solutions. The overall cell potential is less also.

(b) Solvation Shells of Copper Ions in Nitrile–Water Mixtures

In water, the copper(II) ion is strongly solvated. Water and not acetonitrile molecules occupy the solvation shell of copper(II) ions in aqueous acetonitrile containing more than 60 mole % water. This is confirmed by n.m.r. studies.[6,7] The copper(I) ion, however, is strongly solvated by even small amounts of acetonitrile or 3-hydroxypropanenitrile and the solvation (coordination) shell of Cu^+ contains much nitrile in aqueous mixtures. The predominant copper(I) complex is $Cu(MeCN)_2^+$, but $Cu(MeCN)_3^+$ and $Cu(MeCN)_4^+$ are present if there is excess of acetonitrile. The silver ion also complexes with acetonitrile, but does so considerably less strongly than does the copper(I) ion.[5]

Proton magnetic resonance studies have shown that the inner solvation shells of Na^+ and Cu^{2+} are almost entirely composed of water, but those of Ag^+ are half occupied by acetonitrile and half by water in 15 mole % acetonitrile–water, containing 10^{-2} mol dm^{-3} of these ions.[5] Since acetonitrile solvates Cu^+ more strongly than it solvates Ag^+, relative to solvation of these ions by water ($\Delta G_{tr}(Cu^+) = -44$ kJ mol^{-1}, $\Delta G_{tr}(Ag^+) = -19$ kJ mol^{-1}),[5] we predict that *more than* half the solvation sites of 10^{-2} mol dm^{-3} Cu^+ are occupied by acetonitrile or 3-hydroxypropanenitrile in 15 mole % nitrile–water mixtures. This has important implications for the mobility of Cu^+ and Cu^{2+} ions during electrolysis, as discussed below.

(c) Mobility and Diffusion Coefficient of Cu^+ and Cu^{2+} Ions

Strehlow and Koepp showed that because Ag^+ has a solvation shell partly occupied by acetonitrile, the mobility of silver ions in dilute acetonitrile–water solutions is less than in water.[8] It is also less than that of ions like Na^+, Cu^{2+} and NO_3^-, whose solvation shells are occupied[5] only by water in acetonitrile–water or 3-hydroxypropanenitrile–water mixtures of high water content. Some conductances of ions in representative solvent mixtures are in Table 2 and the conductances of Cu^{2+}, Na^+, Ag^+ and Cu^+ in various acetonitrile–water and 3-hydroxypropanenitrile–water mixtures are shown in Fig. 1. The changes in the conductance of water-solvated Na^+ and Cu^{2+} are quite different from those of nitrile-solvated Ag^+ or Cu^+. Addition of small amounts (up to 10 mole %) of either acetonitrile or 3-hydroxypropanenitrile strongly reduces the mobility of Ag^+ or Cu^+ but not of Na^+ or Cu^{2+} in water (Fig. 1). Like $\lambda^\circ(Na^+)$, the mobility of Cu^{2+} and NO_3^- and presumably of H_3O^+ and SO_4^{2-} is little influenced by the presence of up to 10 mole % of organic nitrile in water (Table 2). The effect of the bulkier 3-hydroxypropanenitrile molecule and more viscous 3-hydroxypropanenitrile solvent on the mobility of Ag^+ and of Cu^+ is much greater than that of acetonitrile when added to water.

H_3O^+ and HSO_4^- are the predominant carriers of current in the 1–2 mol dm^{-3} H_2SO_4 and 0.5–1 mol dm^{-3} copper sulphate solutions used by us for electrolysis.

[8] Strehlow, H., and Koepp, H. M., *Z. Elektrochem.*, 1958, **62**, 373.

Electromigration of Cu^+ or Cu^{2+} is not significant, so that mass transfer of copper ions to the working electrodes depends on the rate of diffusion of Cu^+ or Cu^{2+} or in some cases of ion pairs like Cu,HSO_4^+. Clearly the large effect of organic nitriles on the mobility of Cu^+ in water is a factor which must be considered, when examining the electrolysis of $Cu_2SO_4/RCN/H_2O$ solutions.

Table 2. Equivalent conductances ($\lambda°$) of ions and viscosities (η) for nitrile-water mixtures at 25°
Values obtained in this work, unless otherwise stated

Sol-vent	$10^2\eta$ (kg m^{-1} s^{-1})	$\lambda°$ (mS m^2 mol^{-1})					
		Na$^+$	Ag$^+$	Cu$^+$	Cu^{2+}	SO$_4^{2-}$	NO$_3^-$
H$_2$O	9·05 ·	5·1	6·1[B]	6·2[D]	5·7	8·0	6·9
H$_2$O/MeCN[A]	9·5[D]	5·2	4·0[B]	3·6	5·3	8·0[E]	6·7[B]
H$_2$O/HOCH$_2$CH$_2$CN[A]	13·2	4·6	2·6	1·1	5·3[E]	8·0[E]	6·7[E]
MeCN	3·4[B]	7·7[C]	8·5[B]	6·5[C]	12·3[C]	—	10·6

[A] 0·1 mole fraction of nitrile in water.
[B] Strehlow, H., and Koepp, H. M., *Z. Elektrochem.*, 1958, **62**, 373.
[C] Mean value from those given in Siro, M., 'Physical Chemistry of Organic Solvent Systems' (Eds A. K. Covington and T. Dickinson) Ch. 5 (Plenum: New York 1973); Springer, C. H., Coetzee, J. F., and Kay, R. L., *J. Phys. Chem.*, 1969, **73**, 471; Yeager, H. L., and Kratochvil, B., *J. Phys. Chem.*, 1969, **73**, 1963.
[D] Extrapolated from measurements in dilute acetontrile-water, because Cu$^+$ disproportionates in water; extrapolation is guided by the behaviour of Ag$^+$ in water and in dilute acetonitrile-water.
[E] Estimated value, based on the assumption that there is negligible solvent effect on $\lambda°(SO_4^{2-})$ and $\lambda°(Cu^{2+})$ on transfer from water to 0·1 mole fraction nitrile-water, an assumption which is supported by the observed behaviour of Cu^{2+}, Na$^+$ and NO$_3^-$ in acetonitrile-water and water.
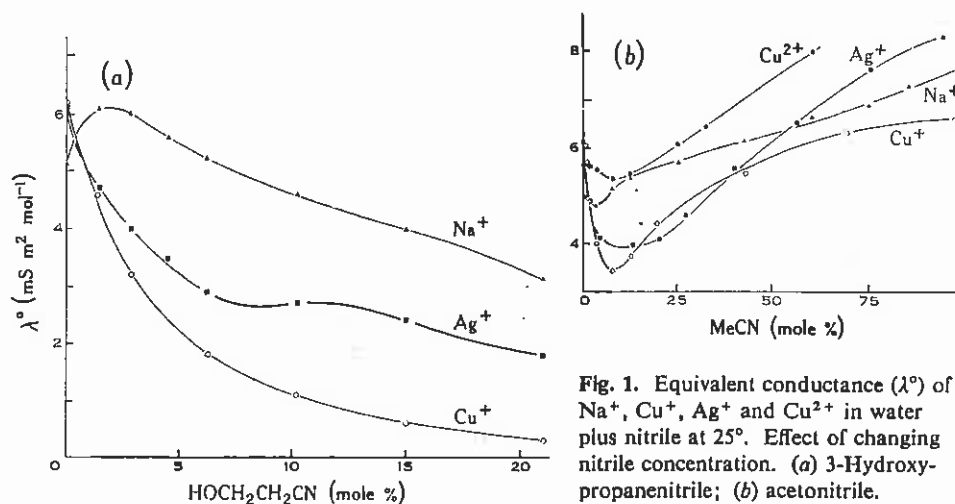

Fig. 1. Equivalent conductance ($\lambda°$) of Na$^+$, Cu$^+$, Ag$^+$ and Cu^{2+} in water plus nitrile at 25°. Effect of changing nitrile concentration. (a) 3-Hydroxy-propanenitrile; (b) acetonitrile.

The mobility of an ion is determined by its charge (z), its effective solvated radius (r), and the solution viscosity (η), as related through equation (2), in which A is a proportionality constant:[9]

$$\lambda° = Az/\eta r \qquad (2)$$

[9] Kortum, G., 'Treatise on Electrochemistry' (Elsevier: London 1965).

Viscosities of 3-hydroxypropanenitrile–water mixtures are in Table 3. Viscosities of acetonitrile–water mixtures were measured by Strehlow and Koepp.[8] Walden's rule (3) for a given ion in different solvents was formulated from equation (2) on the assumption that the radius of the ion was constant in the different solvents:

$$\lambda^\circ \eta = \text{constant} \qquad (3)$$

The concept of an unchanged solvodynamic unit is clearly inappropriate when comparing $\lambda^\circ(Cu^+)$ and $\lambda^\circ(Ag^+)$ in a nitrile–water mixture with their mobility in water.

Table 3. Viscosity and density of 3-hydroxypropanenitrile–water mixtures at 25°

Mole fraction of HOCH$_2$CH$_2$CN	0·000	0·028	0·062	0·102	0·208	0·442	1·000
Density (kg dm^{-3})	0·997	1·005	1·012	1·018	1·025	1·034	1·042
$10^2 \eta$ (kg m^{-1} s^{-1})	9·05	10·2	11·6	13·2	17·3	22·4	37·8

Fig. 2. Walden products ($\lambda^\circ \eta$) for Na$^+$, Cu$^+$, Ag$^+$ and Cu^{2+} (acetonitrile only) in water plus nitrile at 25°. Effect of changing nitrile concentration. (a) 3-Hydroxypropanenitrile; (b) acetonitrile.
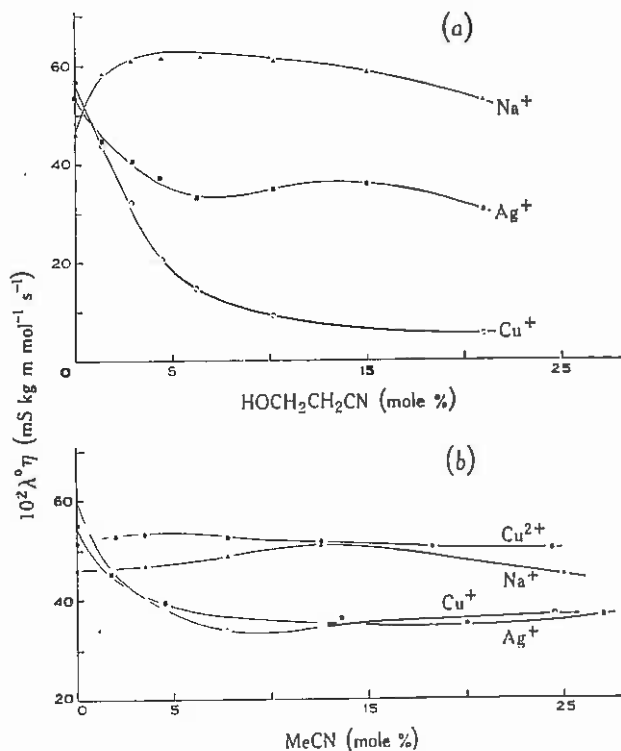
Equation (3) also assumes that the bulk viscosity is appropriate for the solvent in the region of the solvodynamic unit. A Walden plot for Cu^{2+}, Na$^+$, Cu$^+$ and Ag$^+$ ions in acetonitrile–water and for Na$^+$, Ag$^+$ and Cu$^+$ in 3-hydroxypropanenitrile–water mixtures at low ionic strength is shown in Fig. 2. With the exception of Cu^{2+} to some extent, Walden's rule is not obeyed, especially for dilute solutions of either nitrile in water. There is a sharp drop in the Walden product of Cu$^+$ and Ag$^+$ when a little of either organic nitrile is added to dilute solutions of AgNO$_3$ or CuNO$_3$ in water. The effect is greater with Cu$^+$ because of its stronger complex with

nitriles. The decrease in $\lambda°\eta$ is greater for Ag^+ and Cu^+ in the 3-hydroxypropane-nitrile which has larger molecules than does acetonitrile.

After the initial sharp drop in $\lambda°\eta$, the Walden product for Ag^+ and Cu^+ decreases gently over a large range of water–organic nitrile compositions (Fig. 2). The Walden product for sodium ions and, to a very small extent, Cu^{2+}, unlike Cu^+ and Ag^+, increases with the addition of a little acetonitrile. Perhaps this is because the water structure is broken by acetonitrile, lowering effectively the viscosity in the region of the water-solvated sodium ion.

With high proportions of acetonitrile, the conductance (Fig. 1) of Na^+ decreases to less than that of the smaller acetonitrile-solvated Ag^+ ion, as acetonitrile replaces water in the solvation shell of Na^+ also.[5] This is not observed for Cu^{2+} over the range studied, because Cu^{2+} has even less affinity for acetonitrile, relative to water, than has Na^+. The mobility of Na^+ and Ag^+ in various acetonitrile–water mixtures is quite consistent with the changes in composition of the solvation shells, as revealed by n.m.r. studies.[5]

It is clear from equation (2) and Table 2 that a small increase in the solution viscosity, a halving of the charge from Cu^{2+} to Cu^+ and a significant change in the composition and size of the solvation shell explain the over threefold greater mobility of Cu^{2+} in water over Cu^+ in 10% mole fraction acetonitrile–water and the 10-fold greater mobility over Cu^+ in 10% mole fraction 3-hydroxypropanenitrile–water. Substituting $\lambda°$ and the viscosity of Table 2 in equation (2) suggests that the radius of the acetonitrile-solvated Cu^+ ion is about 50% *greater* than that of water-solvated Cu^{2+} ion in 10 mole % acetonitrile–water or water. On the other hand, in pure water, the water-solvated Cu^+ has a radius which is about 10% *less* than that of the water-solvated Cu^{2+} ion in water.

(d) Limiting Current Densities and Copper Ion Mobility in Working Solutions

It follows from the mobilities of Cu^{2+} and Cu^+ and the relationship[9]

$$D = \lambda°RT/zF^2$$

that the diffusion coefficient D of Cu^+ in dilute solutions in 10 mole % (5 mol dm^{-3}) acetonitrile–water is about 66% and in 10 mole % 3-hydroxypropanenitrile is 20% of that for Cu^{2+} ion in water. This observation is of chemical interest, but the situation during electrolysis in concentrated sulphate media, containing sulphuric acid and acetonitrile or 3-hydroxypropanenitrile, is likely to be different, and this is the type of solution in which we are interested in this paper.

In concentrated solutions (0·5–1·0 mol dm^{-3}) containing significant proportions of H_2SO_4, the mobile species will include copper(II) ionic aggregates like Cu,HSO_4^+ and $Cu,(HSO_4)_2$. The corresponding copper(I) aggregates have less tendency to form because of the lower charge density of the Cu^+ compared with that of the Cu^{2+} ions. Such ionic aggregates are less mobile than their solvated Cu^{2+} and Cu^+ ions, so that in concentrated sulphate media, Cu^{2+} in water, and especially in nitrile–water mixtures of lower dielectric constant, might become less mobile than Cu^+ in acetonitrile–water. It is difficult to measure diffusion coefficients of copper ions by conductance in strongly acidic solutions, so to test ion-pairing effects in acidic sulphate media, we measured diffusion coefficients by $it^{1/2}$ measurements for linear diffusion

to a shielded platinum electrode.[9,10] Measurements were on 10^{-3} mol dm^{-3} solutions of copper sulphates containing $0 \cdot 1$ mol dm^{-3} H_2SO_4. The area of the electrode was evaluated by $it^{1/2}$ measurements on potassium ferrocyanide in 2 mol dm^{-3} KCl, for which the diffusion coefficient is known.[10] In acidic 30% v/v acetonitrile–water, $D(Cu^+)$ is $1 \cdot 34 \times 10^{-5}$ cm^2 s^{-1} (compare $9 \cdot 5 \times 10^{-6}$ cm^2 s^{-1} in dilute neutral solution) and $D(Cu^{2+})$ is $4 \cdot 8 \times 10^{-6}$ cm^2 s^{-1} (compare $1 \cdot 4 \times 10^{-5}$ in dilute neutral solution (Table 2)). In water containing $0 \cdot 1$ mol dm^{-3} H_2SO_4, $D(Cu^{2+})$ is $7 \cdot 1 \times 10^{-6}$ cm^2 s^{-1} and in pure water at infinite dilution, $D(Cu^{2+})$ is $1 \cdot 5 \times 10^{-5}$ cm^2 s^{-1}. Thus it appears that in acidic sulphate media at high ionic strength, the copper(I) ion in acetonitrile–water is of greater mobility than in dilute neutral solutions of nitrates and also of greater mobility than copper(II) ion as sulphate in acidic water or in acetonitrile–water. This contrasts with the situation for infinitely dilute solutions of nitrates in acetonitrile–water and 3-hydroxypropanenitrile–water, where, as noted, Cu^{2+} has a substantially greater diffusion coefficient than Cu^+.

The effective limiting current density (i_L/z, where z is the number of electrons involved) is directly proportional to the diffusion coefficient,[9] for the same thickness of diffusion layer. In view of the above discussion, it is not surprising that, contrary to predictions from Table 2, i_L/z for $0 \cdot 5$ mol dm^{-3} copper ions in 2 mol dm^{-3} H_2SO_4, at a copper cathode in a still solution, is greater for the more mobile copper ions of Cu_2SO_4/MeCN/H_2O than for $CuSO_4$ in strongly acidic water (Table 4).

However, in 3-hydroxypropanenitrile–water solutions, even in acidic sulphate media, the *very* low mobility of Cu^+ (Table 2) prevails and i_L/z for $0 \cdot 25$ mol dm^{-3} Cu_2SO_4 in 2 mol dm^{-3} H_2SO_4, $4 \cdot 1$ mol dm^{-3} 3-hydroxypropanenitrile–water, is less than i_L/z for $0 \cdot 5$ mol dm^{-3} $CuSO_4$ in water containing 2 mol dm^{-3} H_2SO_4.

Table 4. Effective limiting current densities i_L/z (mA cm^{-2}) at copper and graphite plate electrodes in still $CuSO_4/H_2O$, Cu_2SO_4/MeCN/H_2O and Cu_2SO_4/HOCH$_2$CH$_2$CN/H_2O solutions containing 2 mol dm^{-3} H_2SO_4 and $0 \cdot 47$ mol dm^{-3} copper ions at 25°

Solution	Copper cathode[A]	Soluble copper anode	Graphite anode[B]
$CuSO_4$			
$\quad$ H_2O	35	> 50	—
Cu_2SO_4			
$\quad$ 2 mol dm^{-3} MeCN	42	> 50	25
$\quad$ 6 mol dm^{-3} MeCN	36	> 50	20
$\quad$ $4 \cdot 1$ mol dm^{-3} HOCH$_2$CH$_2$CN	27	> 50	16

[A] Hydrogen was evolved at $0 \cdot 6$ V (n.h.e.).   [B] Oxygen was evolved at $1 \cdot 4$ V (n.h.e.).

The data in Table 4 for i_L/z are due not only to the differing mobilities of Cu^{2+} and Cu^+ in various solutions, but also to 'streaming effects' in the mixed solvent, as discussed later in this paper.

As noted in Table 4, the effective limiting cathodic current density for *equal* high concentrations of copper ions in strong sulphuric acid media is greater for Cu_2SO_4/MeCN/H_2O solutions than for $CuSO_4$/H_2O solutions. There is a further advantage, however, in that much more concentrated solutions of copper ions can be prepared with Cu_2SO_4/MeCN/H_2O (up to 3 mol dm^{-3} Cu^+) than with the less soluble $CuSO_4$,$5H_2O$ in water ($< 1 \cdot 5$ mol dm^{-3}) at the same temperature. Thus

[10] Stackelberg, M. von, Pilgram, M., and Toome, V., *Z. Elektrochem.*, 1953, 57, 342.

considerably higher effective cathodic limiting current densities than are shown by the differences in Table 4 are possible for electrolysis of $Cu_2SO_4/MeCN/H_2O$ when compared with near saturated $CuSO_4/H_2O$. As shown in Part I,[1] this gives the prospect of better copper cathode morphology at high effective current densities for $Cu_2SO_4/MeCN/H_2O$ than for $CuSO_4/H_2O$.

Table 4 also contains limiting anodic current densities at a carbon anode. They are considerably less than the cathodic limiting current densities for electrolysis of still $Cu_2SO_4/RCN/H_2O$ solutions and correspond to evolution of oxygen. The lower values are in part because the activity ratio Cu^{2+}/Cu^+ at the anode changes more than does the activity of Cu^+ for a given current density, but, as noted later, electron transfer at a carbon anode is slow and this too is a factor.

(e) Cell Voltages During Electrolysis in $Cu_2SO_4/RCN/H_2O$ and $CuSO_4/H_2O$ Solutions

In a working cell, the total cell voltage is made up of four contributions at each electrode.[9] These are the equilibrium potentials, the charge-transfer overpotentials, the ohmic polarization (*IR* drop), and the diffusion (or concentration) polarization in the solution. The voltages during electrolysis of copper(I) sulphate solutions in acidic nitrile–water mixtures, with both soluble and insoluble anodes, show some interesting effects.

Equilibrium Potentials

In electrolysis with a soluble copper anode, no matter what the copper salt as electrolyte, the equilibrium potentials at anode and cathode of course cancel and do not affect the total cell voltage. In electrolysis with an insoluble anode, the electrode processes are different, so equilibrium potentials are an important part of cell working voltages. In the electrowinning of copper from acidic aqueous copper(II) sulphate solutions, by use of an *insoluble* anode, the anodic reaction is the evolution of oxygen and cell voltages are high (2 V). In a $Cu_2SO_4/RCN/H_2O$ solution, the anodic reaction is oxidation of Cu^+ to Cu^{2+}. The equilibrium potentials for the oxidation of Cu^+ to Cu^{2+} in acetonitrile–water mixtures become more anodic and those for reduction of Cu^+ to copper become more cathodic with increased nitrile content (Table 1).[7] Thus the rest voltage in the cell

$$Pt|Cu_2SO_4, Cu_2SO_4|Cu \qquad\qquad (A)$$

increases with increasing proportion of organic nitrile. In solutions of about $0\cdot1$ mol dm^{-3} copper(I) sulphate, containing 1–2 mol dm^{-3} sulphuric acid, *c.* $0\cdot01$ mol dm^{-3} $CuSO_4$ and up to $0\cdot10$ mole fraction acetonitrile or 3-hydroxy-propanenitrile, the rest potential of cell (A) is less than $0\cdot5$ V, which is much less than that of cell (B) in water:

$$Pt|CuSO_4|Cu \qquad\qquad (B)$$

Of course, as electrolysis of $Cu_2SO_4/RCN/H_2O$ proceeds with an inert anode, the ratio of activities of copper(I) to copper(II) ions decreases and thus the rest potential increases slightly according to the usual Nernstian relationship[9]

$$RT/nF \ln[a(Cu^{2+})/a(Cu^+)]$$

Ohmic Polarization

The conductance of various concentrated solutions of $Cu_2SO_4/RCN/H_2O$ in the presence and absence of sulphuric acid has been measured at 25° and 50°, by means of an a.c. conductivity cell. Fig. 3 shows that in the presence of 2 mol dm^{-3} H_2SO_4, the presence of up to 250 g dm^{-3} (6 mol dm^{-3}) acetonitrile or 250 g dm^{-3} (3·5 mol dm^{-3}) 3-hydroxypropanenitrile produces only a small increase in the ohmic resistance of $Cu_2SO_4/RCN/H_2O$ solutions. Nitrile-rich solutions containing more than 6 mol dm^{-3} acetonitrile and solutions containing less (1 mol dm^{-3}) sulphuric acid have a noticeably greater resistance over the equivalent acidic aqueous solution. The contribution of ohmic polarization to the voltage of a working cell is much the same for the same *weight* composition of acetonitrile or 3-hydroxypropanenitrile. In summary, at the usual current densities, ohmic polarization due to the presence of the organic nitrile is not a significant factor in accounting for differences in cell voltages during electrolysis of acidic $CuSO_4/H_2O$ against acidic $Cu_2SO_4/RCN/H_2O$ electrolytes, containing up to 0·1 mole fraction RCN.
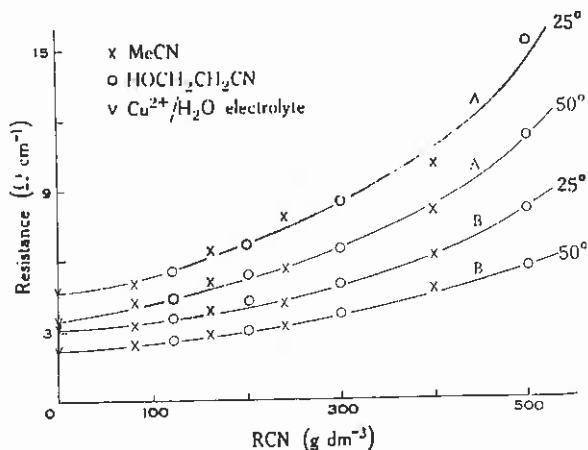

Fig. 3. Effect of nitrile on ohmic resistance of $Cu_2SO_4/RCN/H_2O$ electrolytes at temperatures shown. Cu^+ or Cu^{2+} 0·47 mol dm^{-3}; A, H_2SO_4 1 mol dm^{-3}; B, H_2SO_4 2 mol dm^{-3}.

Diffusion Overpotential

During electrolysis of simple aqueous electrolytes, the diffusion overpotential results from an alteration in the equilibrium electrode potential as the activities of the reactants near the electrode surface (i.e. in the diffusion layer) undergo a change. There is a limiting current density, where the concentration of reactant at the cathode surface falls to zero. In $Cu_2SO_4/RCN/H_2O$ solutions, this overpotential is interesting because diffusion of both the copper(I) ions and of the nitrile molecules must be considered. As copper(I) ions are reduced to copper at the cathode, or oxidized to copper(II) ions at an insoluble anode, free nitrile molecules are introduced into the diffusion layer making the mixture richer in nitrile. Conversely, as a soluble copper anode is oxidized to copper(I) ions, nitrile molecules are transported with the diffusing ion out of the diffusion layer. During electrolysis at an insoluble anode, diffusion overpotentials are likely to be higher than at a soluble copper anode because, for a given current density, the *ratio* of the activities of Cu^+/Cu^{2+} (which determines the equilibrium electrode potential) changes more than does the activity of Cu^+ (which determines the potential at copper). As noted in Table 1, the proportion of nitrile

at the electrode surface would have a significant effect on the equilibrium electrode potentials in the diffusion layer.

The difference in total polarization between a still and well stirred electrolyte is a valid and acceptable measure of the diffusion overpotential during the deposition of copper[9] and we have used it to distinguish diffusion overpotential, due to diffusion of ion and nitrile, from other types of polarization.
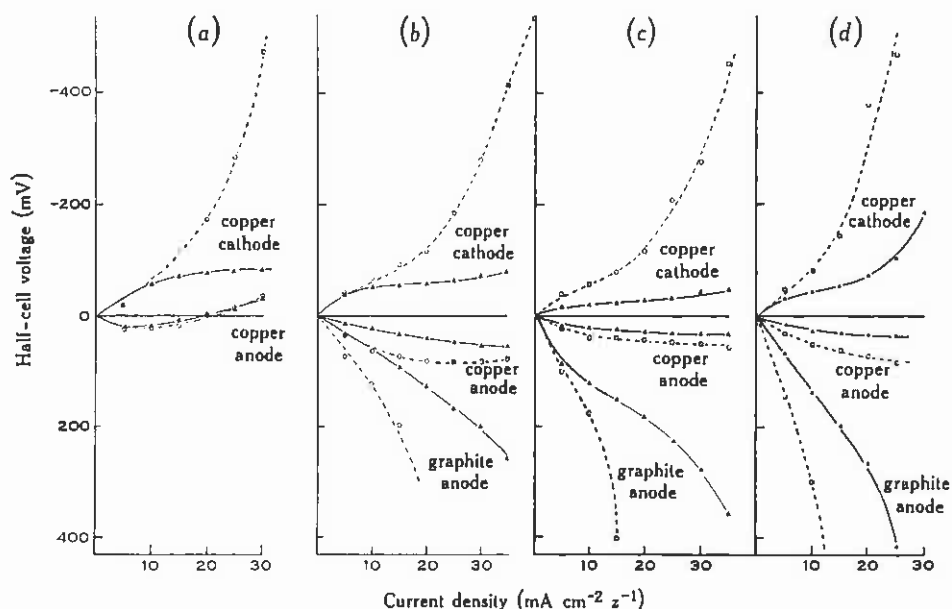

Fig. 4. Effect of current density (mA cm^{-2} z^{-1}; z = 1 for Cu^{+} and 2 for Cu^{2+}) on half-cell voltages (corrected for rest potential, cf. Table 1) in CuSO$_4$/H$_2$O and Cu$_2$SO$_4$/RCN/H$_2$O electrolytes at 25°: broken curves, still solutions; full curves, stirred solutions. (a) 0·47 mol dm^{-3} CuSO$_4$, 2 mol dm^{-3} H$_2$SO$_4$, no RCN; (b) 0·235 mol dm^{-3} Cu$_2$SO$_4$, 2 mol dm^{-3} H$_2$SO$_4$, 2 mol dm^{-3} MeCN; (c) 0·235 mol dm^{-3} Cu$_2$SO$_4$, 2 mol dm^{-3} H$_2$SO$_4$, 6 mol dm^{-3} MeCN; (d) 0·235 mol dm^{-3} Cu$_2$SO$_4$, 2 mol dm^{-3} H$_2$SO$_4$, 4·1 mol dm^{-3} HOCH$_2$CH$_2$CN.

As a preliminary evaluation and comparison, we measured working half-cell voltages at various effective current densities (i/z; z = 2 or 1) during electrolysis of Cu$_2$SO$_4$/RCN/H$_2$O and CuSO$_4$/H$_2$O electrolytes, using a copper cathode and both an insoluble graphite anode and a soluble copper anode in stirred and unstirred solutions. Each voltage was measured with reference to a standard calomel electrode placed centrally and exactly equidistant between a planar anode and cathode. The working half-cell voltages are plotted against effective current density in Fig. 4, after subtracting the rest potential of the cell (i.e. no current) and the ohmic polarization (Fig. 3). Thus Fig. 4 indicates the magnitude of the charge-transfer overpotential plus the diffusion overpotentials in a practical situation of the type described by Muir et al.[3,4] Rest potentials will, of course, vary if solutions with different concentrations of copper(i) and copper(ii) sulphate are used. We recognize that by modelling the commercial cells, i.e. by using planar electrodes in these experiments, only average current densities on the electrode surface can be recorded and that even in 'still' solutions, convection currents are induced near the electrode

surfaces. However, the results in Fig. 4 allow some interesting observations to be made when we compare electrolysis of Cu^+ and Cu^{2+} solutions, i.e. comparisons are at twice the current density for Cu^{2+} solutions as for Cu^+ solution. At high effective current densities, the cathodic diffusion overpotential is less in Cu_2SO_4 solutions containing acetonitrile than in purely aqueous $CuSO_4$ solutions. This effect is probably due to some 'stirring' of the 'still' solution due to density gradients at the electrode surface in the mixed solvent. Streaming effects are clearly visible at the vertical planar electrodes in the acetonitrile–water solutions at high current densities. A low-density acetonitrile-rich phase is produced at the cathode upward streaming and a dense water-rich phase is produced at the anode, during electrolysis of $Cu_2SO_4/MeCN/H_2O$ with a soluble copper anode. These streaming effects (solvent sorting) in acetonitrile–water solutions at high current densities also influence the effective limiting current densities of Table 4 for allegedly 'still' solutions of $Cu_2SO_4/RCN/H_2O$. They, along with the greater mobility of Cu^+ in concentrated sulphate solutions, may in part account for the higher effective cathode limiting current density of Cu_2SO_4 in 2 mol dm^{-3} MeCN/H_2O compared to $CuSO_4/H_2O$.

When 3-hydroxypropanenitrile is substituted for acetonitrile (Fig. 4d) the difference in half-cell cathodic voltage between still and stirred solutions at moderate current densities is much larger, in part because, as shown in Table 2, 3-hydroxypropane-nitrile-solvated Cu^+ ion is less mobile than acetonitrile-solvated Cu^+. Streaming effects at the electrodes are not seen in hydracrylonitrile solutions, presumably because the solvent is of comparable density to water (Table 3). The absence of stirring due to streaming also leads to a greater difference in the potential at a copper cathode between stirred and unstirred solutions.

The differences in potential at a copper cathode between stirred and unstirred solutions during electrolysis of $CuSO_4/H_2O$ and $Cu_2SO_4/MeCN/H_2O$ solutions are shown in Table 5.

Table 5. Differences in potential ΔE (mV) at a copper cathode between stirred and unstirred solutions during electrolysis of $CuSO_4/H_2O$ and $Cu_2SO_4/MeCN/H_2O$ solutions containing 2 mol dm^{-3} H_2SO_4 at 25°

Current density/z^A (mA cm^{-2})	5	10	15	20	25	30
ΔE (mV) for $CuSO_4/H_2O^B$	4	12	45	97	200	390
ΔE (mV) for $Cu_2SO_4/MeCN/H_2O^C$	25	36	57	89	196	331

^{A} $z = 1$ for Cu_2SO_4 and 2 for $CuSO_4$. ^{B} 0·47 mol dm^{-3} $CuSO_4$. ^{C} 0·235 mol dm^{-3} Cu_2SO_4 (i.e. 0·47 mol dm^{-3} Cu^+) and 6 mol dm^{-3} MeCN.

Charge-Transfer Overpotential

The charge-transfer overpotential is the extra potential which must be applied to an electrode to effect charge transfer from the electrode to the ion, or vice versa, and to overcome the activation energy for the anodic or cathodic reaction.

When diffusion overpotentials are minimized by stirring the electrolyte solutions, the remaining polarization (i.e. the difference between working and equilibrium potentials) is largely due to charge transfer and ohmic polarization.

In Fig. 4, the potentials for electrolysis of well stirred $CuSO_4/H_2O$ and $Cu_2SO_4/RCN/H_2O$ solutions at copper cathodes, copper anodes and graphite anodes are shown after subtraction of the ohmic polarization and the rest potential. The potentials closely approximate to the contribution due to charge transfer.

At a copper cathode and a soluble copper anode, the charge-transfer overpotential, for electrolysis of well stirred $CuSO_4/H_2O$ and $Cu_2SO_4/RCN/H_2O$ solutions, is small. At a copper cathode the overpotential is higher for electrolysis of $CuSO_4/H_2O$ than for $Cu_2SO_4/RCN/H_2O$. This is because the reduction of Cu^{2+} to Cu^+ in water is a relatively slow process[11] whereas reduction of Cu^+ to Cu in both water[11] and acetonitrile–water is fast. At very high current densities (>90 mA cm^{-2}) there is a significant charge-transfer overpotential for reduction of Cu^{2+} to Cu^+ in water, but not for Cu^+ to Cu.[11]

The most significant feature of Fig. 4 is the large charge-transfer overpotential and the low limiting current density (Table 4) observed at a carbon anode for the oxidation of Cu^+ to Cu^{2+} in nitrile–water solutions. The overpotential is directly related to the current density, i.e. to the rate of electrochemical oxidation. We find that the oxidation of Cu_2SO_4 in 6 mol dm^{-3} acetonitrile–water containing $0 \cdot 1$ mol dm^{-3} Na_2SO_4 at pH 3 at a platinum electrode has a rate constant of $1 \cdot 6 \pm 0 \cdot 4 \times 10^{-2}$ cm s^{-1}, while on glassy carbon the rate is much slower at $4 \cdot 0 \pm 0 \cdot 5 \times 10^{-4}$ cm s^{-1}. This compares, for example, with the rate constant of $4 \cdot 3 \times 10^{-3}$ cm s^{-1} for the oxidation of Fe^{2+} to Fe^{3+} at platinum in 1 mol dm^{-3} H_2SO_4 in water.[12]

Conclusions

The various polarization effects can be summarized as follows. The addition of nitriles to strongly acidified aqueous solutions has only a slight effect on the ohmic resistance of the electrolyte (Fig. 3). Nitriles are stable to the passage of current and do not appear to produce any detrimental effect on the physical and chemical quality of the copper deposited at the cathode. The main features which distinguish electrolysis in $CuSO_4/H_2O$ solutions from that in $Cu_2SO_4/RCN/H_2O$ solutions are the different anodic reactions at an insoluble anode, the differences in the charge ($+1$ and $+2$), and the different composition of the solvation shells of the solvated copper ions. Nitrile-solvated copper(I) ions are larger and less mobile than aquated copper(II) ions. The effect of this is masked by ion-pairing effects with Cu^{2+} in acidic sulphate media of high ionic strength, as used in electrolysis. Copper(I) ions carry a solvent shell of nitrile to the cathode and to an insoluble anode. This leads to a higher diffusion polarization at low current densities in cells containing $Cu_2SO_4/RCN/H_2O$, rather than $CuSO_4/H_2O$. Although the copper(I) ion is less mobile than Cu^{2+}, this is more than compensated for by the fact that only half the current density is required to deposit the same quantity of copper on the cathode from Cu^+ than from Cu^{2+}. Thus less power is consumed per mole of copper deposited, with the $Cu_2SO_4/MeCN/H_2O$ system than with the $CuSO_4/H_2O$ system. The overall cell voltage for electrorefining a soluble copper anode in $Cu_2SO_4/RCN/H_2O$ electrolytes is *less* than that in $CuSO_4/H_2O$ electrolytes, for the same rate of copper deposition at the cathode. The cathodic limiting current density is significantly less for $Cu_2SO_4/RCN/H_2O$ than for $CuSO_4/H_2O$. The anodic oxidation of Cu^+ to Cu^{2+} in water–nitrile mixtures at an insoluble anode take place at a low equilibrium potential, *v.* n.h.e., but the anodic reaction is slow and has a significant charge-

[11] Bockris, J. O'M., and Enyo, M., *Trans. Faraday Soc.*, 1962, 58, 1187; Bockris, J. O'M., and Mattisson, E., *Trans. Faraday Soc.*, 1959, 55, 1586.

[12] Galus, Z., and Adams, R. N., *J. Phys. Chem.*, 1963, 67, 866.

transfer overpotential which depends on the nature of the inert anode. There is a large diffusion polarization (stirring) effect at an inert anode. The limiting current density during electrolysis of $Cu_2SO_4/RCN/H_2O$ is determined by the anodic reaction at an insoluble graphite anode, rather than by the cathodic deposition of copper. Stirring in the region of an insoluble anode offers a much greater lowering of cell voltages than stirring in the region of the cathode. This allows cathodic copper deposition from a still solution, which is desirable, at quite high current densities, provided that there is stirring at the insoluble anode. Since no deposition or evolution of gas takes place at an insoluble anode and no slimes are produced, vigorous stirring is feasible during the electrowinning of copper from $Cu_2SO_4/RCN/H_2O$ solutions.

Acknowledgments