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The corrosion of copper in ethylene glycol–water mixtures containing chloride ions

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The anodic oxidation of copper at 25° C in 50% (w/w) ethylene glycol–water and in aqueous solutions has been studied by linear sweep voltammetry. The effect of chloride concentration at pH 0 and 3 has been explored. The results in both solvents follow a similar pattern. At pH 0 and in the absence of chloride, only one anodic peak is observed corresponding to the dissolution of copper metal as copper(II) ions. At intermediate chloride concentrations (0.01–0.03 M), two additional peaks are detected which have been attributed to the following reactions:

$$Cu + Cl^- \longrightarrow CuCl + e^-$$

$$CuCl \longrightarrow Cu^{2+} + Cl^- + e^-$$

When the chloride concentration is increased further, the three peaks gradually collapse back into one, corresponding to the dissolution of copper as a copper(I) chloro-complex. An additional peak appears at pH 3 which has been ascribed to the formation of copper(I) oxide. The results have been interpreted using E–pCl diagrams determined for the copper–chloride system in both 50% ethylene glycol–water and aqueous solutions. Further information has been obtained from rotating disc measurements and from microscopy. The relevance of these results to corrosion in automotive cooling systems is discussed.

1. Introduction

The aluminium and iron components of automotive cooling systems sometimes fail as a result of corrosion, a process which is greatly accelerated when copper is deposited on either of the metal surfaces [1]. The mechanism by which copper is deposited consists of two steps: in the first, copper from the radiator or gaskets is oxidized by oxygen dissolved in the coolant and stabilized in solution by some complexing agents; in the second, the copper complex ions, are displaced from solution by aluminium or iron. By this means, massive corrosion of a vehicle cooling system may be induced by a relatively minor corrosion of the copper components.

In principle, several copper complexing agents might be present in an automotive coolant. The most obvious of these is the chloride ion which stabilizes copper(I) and which is present in many water supplies [1, 2], sometimes in relatively high concentrations. Other possibilities are the breakdown products of ethylene glycol [3–6], the breakdown process itself being catalyzed by hot copper surfaces [3]. Finally, mention must be made of ammonia which can be formed by the reduction of nitrite [7], a good inhibitor of iron or aluminium corrosion.

In the study reported here, the effect of varying concentrations of chloride ion on the electrochemical oxidation of copper has been investigated in a 50% (w/w) mixture of ethylene glycol and water. These results are interpreted using an E–pCl diagram which was constructed from equilibrium measurements in the ethylene glycol–water mixture. Similar measurements were made in water for purposes of comparison.

So far as we have been able to establish, there are very few publications relating to the oxidation of copper in ethylene glycol–water mixtures containing chloride ions. Tsygankova *et al.* [8] investigated the oxidation in ethylene glycol with no added water and found that the surface became coated with copper(I) oxide. However, there is a vast literature [9–20] on the oxidation of copper in aqueous chloride solutions, usually for chloride concentrations in excess of 1 M.

2. Experimental details

Analytical grade reagents were used in all experiments without further purification. The water used in the preparation of solutions was purified in a Millipore Milli-Q System. All measurements were made in solutions whose ionic strength was approximately 1.0 M, either by using 1.0 M $HClO_4$ or 1.0 M $NaClO_4$, whose pH had been adjusted to 3 by the addition of $HClO_4$ acid. When necessary, the copper and chloride concentrations were determined volumetrically. All solutions, which were maintained at 25.0 ± 0.5° C, were

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de-aerated with high purity nitrogen gas for at least one hour prior to measurement, and during the measurement, an atmosphere of nitrogen gas was maintained over the solution.

The rotating disc equipment and electrochemical cells were as described earlier [21]. The gold electrode and gold ring-disc electrode were cleaned by abrasion on 1200 wet-and-dry paper, followed by careful washing in Millipore Milli-Q water. The electrochemical measurements were made using a PAR 173 Potentiostat and a PAR 175 Programmer, the voltammograms being recorded on a Houston 2000 x–y recorder. In the rotating ring-disc measurements, the ring potential was maintained by a Pine RD3 Potentiostat. All potentials were measured, and are reported relative to a silver/silver chloride electrode in a saturated sodium chloride solution (SSSE). This has a measured potential relative to the normal hydrogen electrode of 0.191 V.

The equilibrium lines on the E–pCl diagrams were determined in the following way. The Cu(II)/Cu line was located by measuring the potential of a copper electrode in a 0.01 M copper(II) solution containing no added chloride ion. The copper electrode was prepared by plating copper at a current density of $48\,\mathrm{A\,m^{-2}}$ onto a gold electrode rotating at 1000 rpm from a 0.4 M $CuSO_4$ in a 0.025 M H_2SO_4 solution for *ca.* 20 min. The CuCl/Cu, Cl^- line was determined by first plating a copper film onto a gold electrode as described above, and then oxidizing it electrochemically in a 0.03 M chloride solution to a point just before copper is passivated by CuCl (see Results and Discussion section). The potential of this Cu/CuCl electrode was then measured in solutions containing known concentrations of chloride ion.

In the potentiodynamic experiments, copper was first deposited onto a gold electrode rotating at 1600 rpm from a 0.01 M $Cu(ClO_4)_2$ solution containing a known concentration of chloride ion by sweeping the potential cathodically from the rest potential to -0.3 V. A linear potential sweep in the anodic direction was then recorded, usually at a sweep rate of $1\,\mathrm{mV\,s^{-1}}$ with potential limits of -0.3 V and $+0.6$ V. The potential sweep was then completed by scanning back to the rest potential. At this stage, the electrode was electrochemically stripped of any remaining copper, more chloride ion was added and the experiment repeated. The chloride concentration was progressively increased by the addition of a small but known amount of 4.0 M NaCl to the mixture. Because the volume changes are small, the change in chloride concentration can be readily calculated and controlled.

3. Results and discussion

3.1. *E–p*Cl *diagrams*

The construction of the E–pCl diagrams for 50% (w/w) ethylene glycol–water and for aqueous systems will be discussed first since these diagrams are useful in interpreting the potentiodynamic measurements.

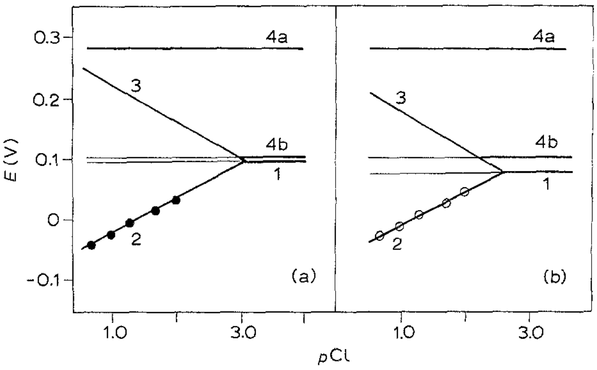

Fig. 1. E–pCl diagrams for Cu–Cl^- system in: (a) 50% ethylene glycol–water and (b) aqueous solutions, assuming a copper(II) concentration in solution of 0.01 M.

The experimental conditions chosen ($[Cu^{2+}] = 0.01$ M; ionic strength = 1.0 M) were the same as those used in the anodic dissolution studies. No corrections were made for activities or liquid junction potentials, and the free chloride concentration was assumed to be given by the total chloride concentration.

The equilibrium line corresponding to Reaction 1 on the

$$Cu^{2+} + 2e^- \rightleftharpoons Cu \qquad (1)$$

E–pCl diagram for the 50% ethylene glycol–water system (line 1, Fig. 1a) was located by measuring the potential of a copper plated gold electrode in a copper(II) solution containing no chloride. The potential readings were stable and the uncertainty in the measurements was less than ± 8 mV.

The line for Reaction 2 was similarly determined by

$$CuCl + e^- \rightleftharpoons Cu + Cl^- \qquad (2)$$

measuring the potential of a copper electrode coated with a porous layer of CuCl in solutions of various chloride concentrations. The plot of these points (line 2, in Fig. 1a) has a slope of 56 ± 4 mV per decade of $[Cl^-]$ with an apparent standard potential (value at $p\mathrm{Cl} = 0$) of -65 ± 12 mV. The magnitude of the slope is consistent with Reaction 2 for which a slope of 59.2 mV per decade of $[Cl^-]$ is expected. Had the soluble copper(I) chloro-complexes $CuCl_n^{1-n}$ (where $n > 1$) been formed, the slope of the equilibrium line would have been $59.2n$ mV per decade of $[Cl^-]$. From these measurements, there is therefore no evidence for the formation of any soluble copper(I) chloro-complex species up to $[Cl^-] = 0.01$ M. The Cu^{2+}, Cl^-/CuCl line 3 corresponding to the reaction

$$Cu^{2+} + Cl^- + e^- \rightleftharpoons CuCl \qquad (3)$$

was positioned using the fact that it must have a slope of 59.2 mV per decade of $[Cl^-]$, and that it must pass through the intersection of the Cu^{2+}/Cu and CuCl/Cu, Cl^- lines. The errors in the Cu^{2+}, Cl^-/CuCl line will therefore contain the errors in the other two lines and so its location in Fig. 1a will be less reliable.

The E–pCl diagram for copper in water was then constructed using the same approach, the results being drawn in Fig. 1b. The results agree with those values compiled by Pourbaix [22].

As may be expected, changing the solvent from 50% ethylene glycol–water to water leads to a shift in the equilibrium lines for the copper–chloride system. Overall, the E–pCl diagram for copper in 50% ethylene glycol–water in Fig. 1a, is moved to somewhat higher pCl values and potentials relative to the same diagram in water (Fig. 1b). The likely reason for this is that CuCl is less soluble in 50% ethylene glycol–water than in water.

In order to complete the two diagrams, the Cu_2O, H^+/Cu line was included using the literature value [22] for the reaction

$$Cu_2O + 2H^+ + 2e^- \rightleftharpoons 2Cu + H_2O \qquad (4)$$

Lines 4a and 4b correspond to Reaction 4 at pH 0 and 3, respectively, these two pH values being those used in the potentiodynamic experiments. It was assumed that the Cu_2O, H^+/Cu line has the same standard potential in both solvents. Although this assumption cannot be rigorously justified, it is in qualitative agreement with the potentiodynamic results described below.

3.2. *Anodic oxidation of copper in a 50% ethylene glycol–water mixture*

The anodic oxidation of an electrodeposited copper film in 50% ethylene glycol–water mixture containing 0.01 M Cu^{2+} and various chloride concentrations was studied potentiodynamically.

3.2.1. In the absence of chloride ion. The polarization curve in 1 M $HClO_4$ is composed of one sharp peak (peak I, Fig. 2a) which from coulometric measurement, must be due to the oxidation of copper to copper(II) (i.e. the reverse of Reaction 1). At pH 3, the peak becomes very much broader. Clearly, some additional reaction is proceeding which can be seen as a bulge on the anodic side of peak I (Fig. 2b). In addition, coulometric measurements during the plating and anodic stripping steps showed that, in contrast to the situation at pH 0, not all the copper had been removed. This suggested that some insoluble form of copper was present on the surface, blocking the dissolution reaction. The E–pCl diagram shows that the Cu_2O, H^+/Cu line is only 1 mV above the Cu^{2+}/Cu line at pH 3 but 179 mV at pH 0; so it is reasonable to suppose that Cu_2O is formed at pH 3 but not at pH 0.

Furthermore, the peak moves by *ca.* 40 mV in the anodic direction when the pH is increased from 0 to 3. The shift is probably due to a change in the liquid junction potential; a value calculated for the change in liquid junction potential from the Henderson equation [23] is in reasonable agreement with this view.

3.2.2. At intermediate chloride concentrations ($0.03\,M > [Cl^-] > 0.01\,M$).

(i) *Linear Sweep Voltammetry.* On addition of Cl^-, the main anodic peak I, shown in Fig. 2, diminishes in height, but its base thickens, and a subsidiary wave, more prominent at pH 3 than at pH 0, develops at a position just anodic of peak I. A further increase in $[Cl^-]$ results in the appearance of two more distinct peaks, one more negative to and one more positive to the original peak I, as shown in Fig. 3. These have been labelled as peaks II and III, respectively.

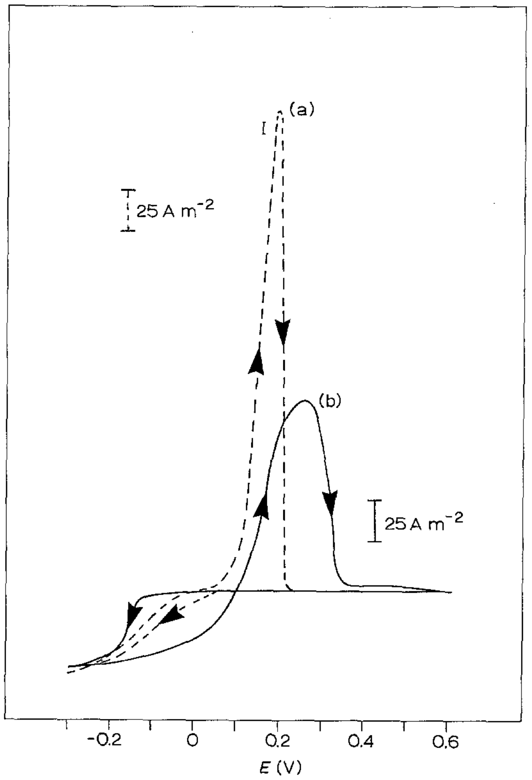

Fig. 2. A potentiodynamic polarization curve for Cu in 50% ethylene glycol–water at (a) pH 0 and (b) pH 3. Rotation speed 1600 rpm.

Peak II can be ascribed to the passivation of the copper surface by the formation of a solid film of

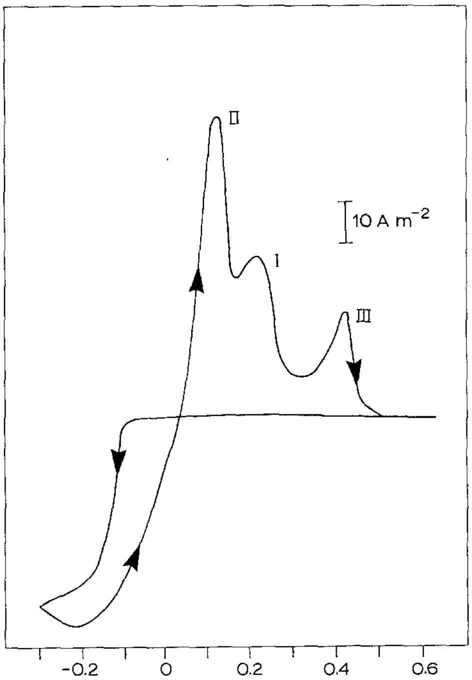

Fig. 3. A potentiodynamic polarization curve for Cu in 0.03 M Cl^- and 50% ethylene glycol–water at pH 3. Rotation speed 1600 rpm.

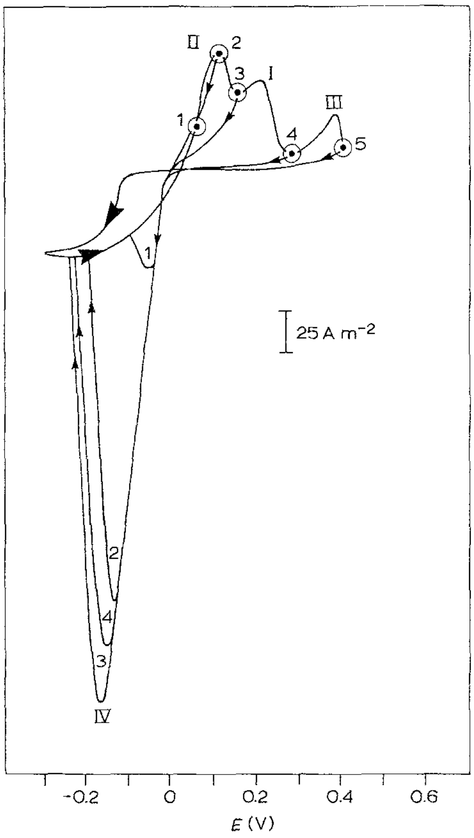

Fig. 4. The reduction peaks after reverse sweep in 0.03 M Cl^- and 50% ethylene glycol–water at pH 3, reverse sweep rate 10 mV s^{-1}, rotation speed 1600 rpm. Reduction peak was not observed when swept reversely after point 5.

CuCl (the reverse of Reaction 2). Several pieces of evidence point to this conclusion. Firstly, using an optical microscope, it could be seen that the copper surface was covered with a mass of white crystals which, for the reaction in water, have been identified by other workers such as CuCl [10, 24 and 25]. Secondly, the height and position of peak II depends very much on the chloride concentration. In particular, the nil current potential, which approximates the equilibrium or reversible potential for Reaction 2, is linearly dependent on pCl, the slope being 62 ± 6 mV per pCl unit, in accord with Equation 2. Also, the results obtained from solutions at pH 0 were comparable to those at pH 3, indicating that protons were not involved in the reaction.

As shown in Fig. 4, reversing the potential during or after the appearance of peak II (points 1, 2 or 3) led to reduction peak IV. According to Brossard [11], the corresponding peak in water is due to the reduction of CuCl but Crousier *et al.* [25] have attributed it to the reduction of $CuCl_2^-$. The possibility of the formation of $CuCl_2^-$ in the ethylene glycol–water mixture investigated here seems unlikely since, being a solution species, it would be spun off the disc surface and no reduction peak would result. In addition, peak IV is unusually sharp for a solution species. Coulometric measurements indicated that all of the anodically oxidized copper could be reduced if the reverse cathodic sweep was executed at a sufficiently high sweep rate. The reverse scan is 10 times faster than the forward scan in Fig. 4. This is not the case with low sweep rates, indicating that the material formed during the oxidation of peak II is reacting in some way before it can be reduced. This result is consistent with the hypothesis that peak II is due to the formation of CuCl which then dissolves in the chloride containing solution.

In contrast to peak II, the position of peak I is essentially independent of pCl, as one would expect for the dissolution of copper as copper(II). This also indicates that the formation of a Cu(II) chlorocomplex is not occurring. As for the case when chloride ion is absent, the shape of peak I is dependent on pH, being somewhat broader at pH 3 than at pH 0. This is again assigned to the additional step of copper(I) oxide formation according to Equation 4, passivating the surface.

Peak III in Fig. 3 was found to be somewhat variable, depending among other things, on the size of peak I, i.e. on the formation of copper(I) chloride. This being the case, peak III may be due to the oxidation of CuCl as given in Equation 5. This is in accord with the earlier proposal of Moreau [19] that CuCl is oxidized at higher potentials. On the other hand, it does not seem likely that peak III is due to the oxidation of copper(I) oxide since its peak potential is essentially independent of pH.

$$CuCl \longrightarrow Cu^{2+} + Cl^- + e^- \qquad (5)$$

To test for the involvement of CuCl in the oxidation reaction giving rise to peak III, a reverse scan was carried out starting from a potential just before and just after the appearance of peak III (points 4 and 5). As before, the reverse scan was rapid to minimize any CuCl dissolution. As can be seen in Fig. 4, a CuCl reduction peak (IV) is obtained when the potential is reversed just prior to, but not after, peak III. Peak III must therefore be due to the oxidation of CuCl. The oxidation of CuCl to copper(II) according to Equation 5 is entirely consistent with the E–pCl diagram for the system shown in Fig. 1. According to this diagram, for pCl values less than about 3.0, one would expect to see the sequence of reactions Cu → CuCl → Cu^{2+} as the potential is raised and lines 2 and 3 are crossed. In fact, one also sees the reaction Cu → Cu^{2+} corresponding to the light shaded portion of line 1 in Fig. 1a. It is apparent that under the conditions of the linear potential sweep experiment, the Cu/Cu^{2+} reaction is sufficiently fast relative to the Cu/CuCl/Cu^{2+} reactions for it to continue to be observed even at chloride concentrations where CuCl formation is favoured on thermodynamic grounds. It is perhaps surprising that copper dissolution continues to take place on a surface which is coated with CuCl. Thus, the CuCl coating must be partially porous.

Before considering the results of some rotating ring-disc electrode measurements, the effect on the linear potential sweep voltammograms of copper(II) in the reactant solution has been noted. The effect was determined by recording voltammograms using solutions containing no copper(II). In order to achieve this, the copper films had to be plated in another vessel and then transferred to the chloride-containing reactant solution. No discernable difference exists between the voltammograms recorded in the presence and absence of copper(II) so far as the position and shapes of the anodic peaks are concerned. However, differences between the amount of copper deposited and the total amount stripped anodically were detected coulometrically, even at pH 0 where copper(I) oxide should not be formed. These differences are believed to be due to some copper being dissolved by the reaction

$$\mathrm{Cu} + \mathrm{Cu}^{2+} + 2n\mathrm{Cl}^- \longrightarrow 2\mathrm{CuCl}_n^{1-n} \qquad (n \geq 2) \qquad (6)$$

Because the effect of copper(II) on the results is slight, most of the measurements were carried out with copper(II) in solution, the experimental procedure being much simpler in this case.

(ii) *Rotating ring-disc measurements.* For further information about the reactions corresponding to the various voltammetric peaks, rotating ring-disc measurements were made on the anodic dissolution of copper in a 50% ethylene glycol–water mixture containing 0.01 M copper(II) and 0.03 M chloride ion at pH 3. The current of the ring electrode, whose potential was set at 600 mV to oxidize any copper(I) passing its surface, was recorded against the disc potential as shown in Fig. 5. The corresponding disc voltammogram is also shown in Fig. 5.

A comparison of the ring current with the disc current in region A shows that the former is displaced to somewhat more negative potentials relative to the latter. Thus, there is an appreciable ring current when the disc current is zero and the ring current peaks at a more negative potential than the disc current. This is presumably a consequence of the formation of copper(I) by the chemical dissolution reaction, Equation 6, as well as the anodic oxidation of copper. Subsequent to the ring current maximum, there is a plateau (region B) in the production of copper(I). This corresponds to the diffusion limited dissolution of copper(I) chloride on the surface by chloride ions giving some copper(I) chloro-complex. As the rotation speed of the ring-disc electrode is increased, the plateau current also increases. Finally, in region C, there is a slight increase in ring current before the copper(I) production ceases when all of the copper film is stripped from the disc surface. The reason for this increase in copper(I) is not obvious. However, it may be associated with the direct oxidation of the copper film to copper(I) as the protective layer of copper(I) chloride is removed by oxidation.

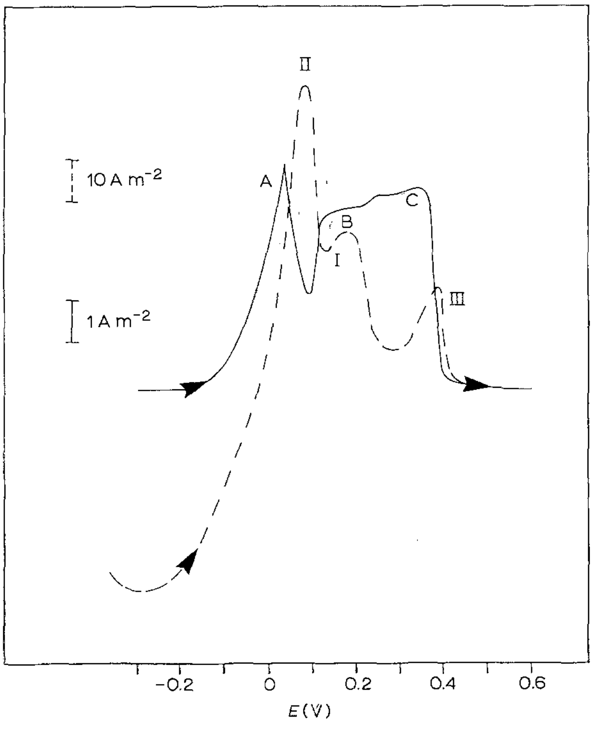

Fig. 5. The results of the rotating ring-disc electrode experiments for Cu(I) generated at a copper plated gold disc, presented as dashed curve and detected at a platinum ring, as solid curve. The ring was held at 600 mV (SSSE) and the disc was rotating at 1600 rpm. The solution is 0.01 M Cu^{2+} in 0.03 M Cl^- and 50% ethylene glycol–water at pH 3.

3.2.3. At high chloride concentrations

($0.1\,M > [Cl^-] > 0.05\,M$). When the chloride concentration was further increased, peak I diminished until it could no longer be distinguished and an additional feature, a bulge (peak V) in front of peak II, became apparent. This is shown in Fig. 6. The disappearance of peak I at a high enough chloride concentration is consistent with the *E*–*p*Cl diagram (Fig. 1a) which predicts that the direct oxidation of copper metal to copper(II) is replaced by the oxidation via CuCl at sufficiently high chloride concentrations.

However, the bulge just prior to peak II cannot be explained by the *E*–*p*Cl diagram. It was noted that the

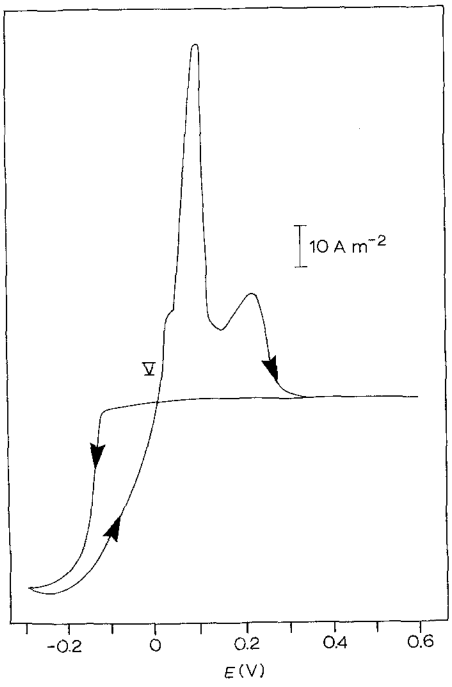

Fig. 6. A potentiodynamic polarization curve for copper in 0.05 M Cl^- and 50% ethylene glycol–water at pH 3. Rotation speed 1600 rpm.

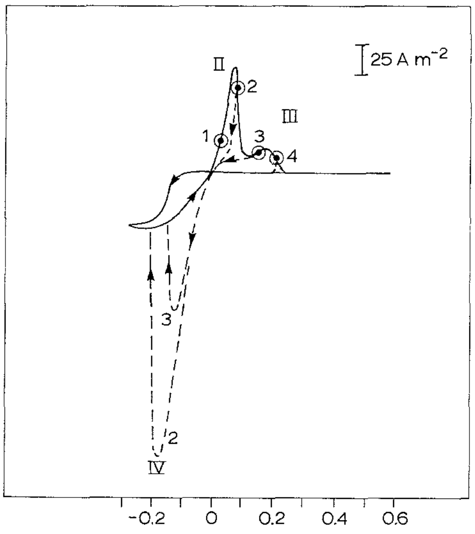

Fig. 7. The reduction peaks after reverse sweep in 0.06 M Cl^- and 50% ethylene glycol–water at pH 3, reverse sweep rate 10 mV s^{-1}, rotation speed 1600 rpm. Reduction peaks were not observed when swept reversely after points 1 and 4.

position of peak V is very dependent on the chloride concentration. A plot of the potential at zero current (i.e. between copper deposition and first stripping peak) against pCl is approximately linear, the slope being equal to 110 ± 20 mV per decade of $[Cl^-]$. This suggests that the dichlorocopper(I) complex is being formed according to the equation

$$Cu + 2Cl^- \longrightarrow CuCl_2^- + e^- \qquad (7)$$

Reverse potential scans for the system are shown in Fig. 7. When the potential sweep is reversed just into the bulge of peak V, no reduction peak is observed, as one would expect, since any soluble copper(I) species would be swept from the disc surface by the movement of the solution associated with the rotation of the disc.

The formation of the dichlorocopper(I) complex at these chloride concentrations is not expected on the basis of the E–pCl diagram shown in Fig. 1. However, this diagram refers to a copper concentration of 0.01 M and the copper(I) concentrations at the reacting disc surface are probably lower than this. Consequently, the equilibrium chloride concentration is reduced. This can be seen by writing the equilibrium equation for CuCl dissolution in the form

$$[Cl^-] = [CuCl_2^-]/K \qquad (8)$$

As shown in Fig. 7, reversing the scan just after peak II, i.e. at point 2, gave rise to the usual sharp CuCl reduction peak. No reduction peak was observed after peak III since, at these potentials, CuCl is oxidized through to soluble copper(II) which is swept from the surface.

3.2.4. *At very high chloride concentrations*

(*$[Cl^-] > 0.2\,M$*). The anodic dissolution of copper at very high chloride concentrations gave rise to a polarization curve consisting of a single peak which is situated *ca.* 150 mV more negative than peak I of Fig. 2. As other workers [10, 15, 17, 19, 26, and 27] have reported, the peak is probably due to the oxidation of copper to some copper(I) chloro-complex (Reaction 9) where $n \geqslant 2$ depending on the chloride concentration.

$$Cu + nCl^- \longrightarrow CuCl_n^{1-n} + e^- \qquad (9)$$

3.3. *Comparison of the anodic oxidation of copper in aqueous and in 50% ethylene glycol–water solutions*

The anodic oxidation of an electrodeposited copper film in aqueous solutions at pH 0 and 3 containing 0.01 M Cu^{2+} and various chloride concentrations is shown in the voltammograms of Figs. 8 and 9. It can be seen that the development of anodic peaks with increasing chloride concentration follows the same pattern as that of the 50% ethylene glycol–water system. Nevertheless, there are some significant differences between the two systems.

In the absence of chloride ions, the anodic peak associated with the oxidation of copper metal to copper(II) at pH 0 is the same in both water and 50% ethylene glycol–water. On the other hand, the anodic peak at pH 3 is much sharper in water than in 50% ethylene glycol–water. Thus, the formation of copper(I) oxide is less important in the former than in the latter.

As chloride ion is added to the aqueous system, the copper/copper(II) peak diminishes and is replaced by peaks due to other anodic reactions: the oxidation of copper to solid copper(I) chloride and the oxidation of copper(I) chloride to copper(II) in solution; copper(I) oxide is formed at pH 3 but not at pH 0. The trend in the development of the new anodic peaks in water is basically similar to that in 50% ethylene glycol–water (*cf.* Figs. 2, 3, and 6 and Figs 8 and 9). However, the formation of copper(I) chloride (peak II in Fig. 9) and the complete dissolution of copper as the dichlorocopper(I) complex takes place at much higher chloride concentrations in aqueous solution than in 50% ethylene glycol–water. Copper(I) chloride therefore is less soluble in 50% ethylene glycol–water than

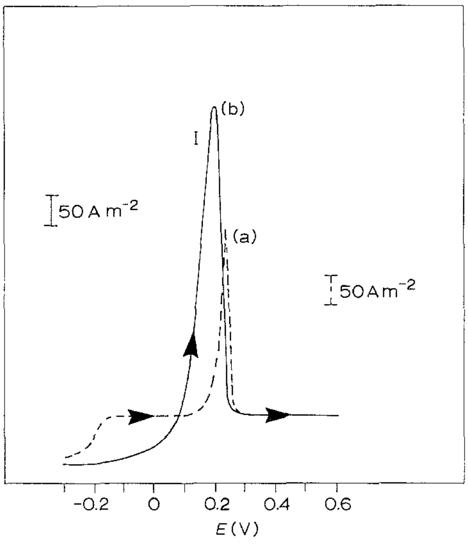

Fig. 8. A potentiodynamic polarization curve for copper in water at (a) pH 0 and (b) pH 3. Rotation speed 1600 rpm.

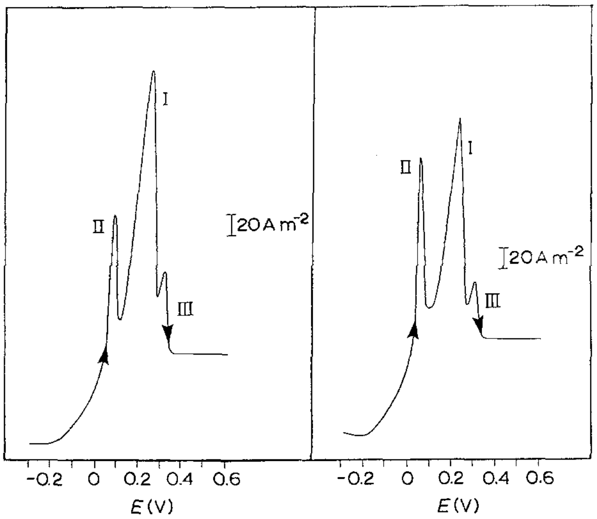

Fig. 9. An anodic polarization curve for copper in water with [Cl$^-$] of (a) 0.03 and (b) 0.06 M at pH 3. Rotation speed 1600 rpm.

in water alone. On the other hand, the dichlorocopper(I) complex is more stable in the ethylene glycol containing medium.

The results are consistent with the E–pCl diagrams. As shown in Fig. 1, the E–pCl diagram is shifted to higher pCl values when the solvent is changed from water to 50% ethylene glycol–water.

3.4. *Implications of the study for copper in an automotive cooling system*

The results of the oxidation of copper in both 50% ethylene glycol–water and aqueous solutions containing chloride ions suggest that ethylene glycol will probably inhibit the corrosion of the copper components of an automotive cooling system at room temperature. This is because protective films of copper(I) oxide and copper(I) chloride are more likely to be formed in 50% ethylene glycol–water than in aqueous, particularly at low chloride concentrations.

However, the conditions in a vehicle cooling system are conducive to the oxidation of ethylene glycol [4–6]. Breakdown products such as glycollic and formic acids are often present in coolants [5, 6] resulting in a lowering of the pH. Under these circumstances, the formation of protective films of copper(I) oxide is less likely and copper corrosion in the presence of chloride ions is favoured.

4. Conclusions

1. In the absence of chloride ions, copper is electrochemically oxidized to copper(II) in 50% ethylene glycol–water. If the pH is 3, this reaction is followed by passivation of the surface as a result of the formation of copper(I) oxide.

2. At intermediate chloride concentrations (0.03 M $>$ [Cl$^-$] $>$ 0.01 M), copper oxidation is a more complex process. As the potential is increased, copper metal is oxidized to copper(I) chloride and then copper(II) ions; this is followed by copper(I) oxide formation at pH 3 and the conversion of copper(I) chloride to copper(II).

3. At very high chloride concentrations ([Cl$^-$] $>$ 0.2 M), only one anodic peak is observed which can be ascribed to complexes of the type CuCl$_n^{1-n}$ where $n \geqslant 2$.

4. In 50% ethylene glycol–water, the oxidation of copper to copper(II) takes place at a higher potential than in aqueous solutions, but the formation of copper(I) chloride occurs at lower potential.

5. The anodic behaviour of copper in chloride ion containing solutions (either aqueous or 50% ethylene glycol–water) can be satisfactorily accounted for using E–pCl diagrams.

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