

Behaviour of poly(ethylene glycol) during electrodeposition of bright copper coatings in sulfuric acid electrolytes

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The interaction of poly(ethylene glycol) $M_n = 3000$ with copper I and II ions in aqueous-acidic media was studied by investigation of the specific electrical conductivity, optical density and the cyclic voltamperometric curves in Cu^+ and Cu^{2+} solutions. The results suggest the formation of complexes of the $\{\text{Cu}^+(\text{EO})_3 \cdot (x-1)\text{H}_2\text{O}\}$ and $\{\text{Cu}^{2+}(\text{EO})_4 \cdot (y-1)(\text{H}_2\text{O})_2\}$ types. In the case when $\{-\text{CH}_2\text{CH}_2\text{O}-\}_n$ and Cl^- are simultaneously present in the copper electrolyte, the possibility of simultaneous complex formation between both copper ions and ethylene oxide units, and copper ions and chloride ions is considered. The strong increase in copper electrodeposition overpotential after the addition of polyethers to the electrolytes containing brighteners is explained by the formation of these complexes.

1. Introduction

Poly(ethylene glycol) (PEG) and poly(propylene glycol) (PPG), as well as their block copolymers, combined with some dialkyl- or diaryldisulfides and saphronic dye derivatives are basic components of almost all contemporary electrolyte solutions for the deposition of bright copper coatings [1, 2]. However, their influence on the copper electrodeposition process is not clear.

It has been established that the addition of PEG or PPG to sulfuric acid electrolytes increases the overpotential of copper deposition [3]. Figure 1, for instance, shows copper electrodeposition (on a copper substrate) polarization curve in the presence of PEG of different concentrations which were potentiodynamically obtained. This effect, also established by other authors [4–6], is usually explained by the assumption that the polyether macromolecules are adsorbed on the growing surface, as a result of which the electrocrystallization process is blocked. Our investigations of the differential capacitance have shown that PEG (and PPG), adsorb to a relatively small extent on polycrystal [7] and monocrystal [8] copper surfaces respectively in the range of electrodeposition potentials (+300 to +100 mV vs NHE). This weak interaction is illustrated by the results represented on Fig. 2 (cf. [7] and [8]).

It has been shown [9] that even a low level of PEG adsorption is enough to block the active nucleation sites and an increase of copper deposition overpotential may be expected. In our opinion it is most unlikely that the high level of increased polarization is singularly due to this level of adsorption of the polymer on the metal coating surface. It may be anticipated that the influence of polyethers on the electrodeposition mechanism is of a much more complicated nature.

The presence of the ether linkages ($-\text{CH}_2-\text{CH}_2-\text{O}-$) is responsible for the unique properties of PEG (and PEO). The monomer unit contains one hydrophobic moiety $-\text{CH}_2-\text{CH}_2-$ and one hydrogen bonding site $-\text{O}-$. The amphiphilic character of PEO opens the possibility for particularly interesting specific interactions along the chain.

The presence of the electron-rich oxygen atoms in the backbone structure offers a site for coordination. PEO (PEG) effectively binds alkali and alkali-earth cations (s-metals) [10, 11] due to an interaction of the electron shells of oxygen and metal cations, which may also involve an additional ion-dipole mechanism. The anion, as a rule, plays a passive role but complicates (sterically and electrostatically) the interaction of the cation with the chain. Polyether complexes with some transition metals are also familiar [11–14]. On the basis of these data, there are good grounds to suppose that, besides its adsorption action on the copper surface, PEG may form complexes with Cu^+ and/or Cu^{2+} . The interaction of ethylene oxide ligands $(-\text{CH}_2-\text{CH}_2-\text{O}-)_n/-\text{EO}-/$ with copper ions impedes both their ionic transport in the overall volume of the electrolyte and their passage through the electrical double layer. Some authors suppose copper ion solvation by PEG due to pseudocrown ring formation by 5 or 6 ethylene oxide units, even in aqueous acidic media [15, 16].

Unlike the ions of the I and II main groups of the periodic table of the elements, copper ions are mild acids [17] and tend to interact with oxygen containing components to a lower extent. On the other hand, PPG and PEG are polymers with strong surface-active properties which allow the formation of monomolecular [4] or thicker layers [18] on the cathodic surface, or in its close vicinity. In that sense, a variation of a unifying idea is presented in [5] and, accordingly, a simultaneous action both of the

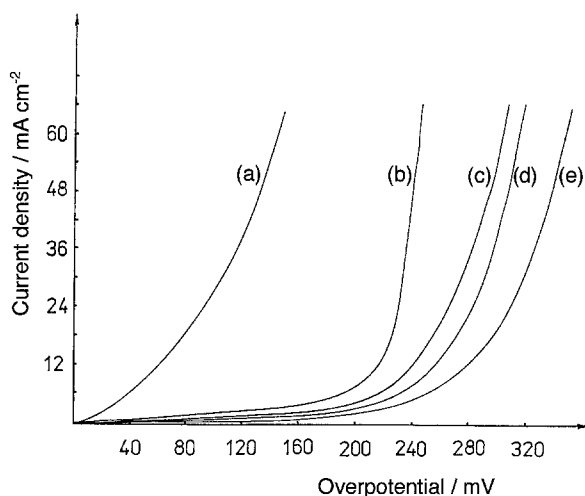


Fig. 1. Polarization curves of copper electrodeposition on a copper cathode in an electrolyte containing: (a) $220 \text{ g dm}^{-3} \text{ CuSO}_4 \cdot 5\text{H}_2\text{O}$, $60 \text{ g dm}^{-3} \text{ H}_2\text{SO}_4$, $0.09 \text{ g dm}^{-3} \text{ NaCl}$; (b) (a) + $0.5 \times 10^{-7} \text{ mol dm}^{-3} \text{ PEG}_{3000}$; (c) (a) + $0.5 \times 10^{-6} \text{ mol dm}^{-3} \text{ PEG}_{3000}$; (d) (a) + $1.3 \times 10^{-6} \text{ mol dm}^{-3} \text{ PEG}_{3000}$ and (e) (a) + $1.5 \times 10^{-5} \text{ mol dm}^{-3} \text{ PEG}_{3000}$.

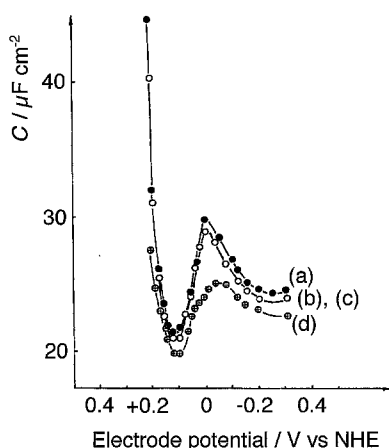
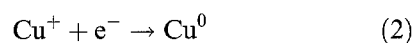
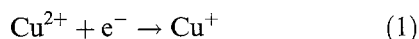


Fig. 2. Dependence of the differential capacity (C) of a polycrystalline copper electrode on the electrode potential in a basic 0.01 N KF electrolyte (curve (a)) and after the addition of: $1.3 \times 10^{-5} \text{ mol dm}^{-3} \text{ PEG}_{3000}$ (curve (b)); $1.3 \times 10^{-4} \text{ mol dm}^{-3} \text{ PEG}_{3000}$ (curve (c)); $1.3 \times 10^{-3} \text{ mol dm}^{-3} \text{ PEG}_{3000}$ (curve (d)). Curves (b) and curve (c) are the same.

adsorption and complex formation abilities of polymers is not excluded.

Investigating of polymer influence is also complicated by the complexity of the system used. As is well known, electrochemical reduction of copper ions in sulfuric acid electrolytes takes place in two stages [19–21]:



Additionally, the presence of chloride ions, which are an obligatory component of all bright copper-sulfuric acid electrolytes, leads to the formation of complex ions of the, CuCl^+ , CuCl_2^- , CuCl_3^- , CuCl_4^{2-} types [22–24]. This leads to complicated equilibrium processes with the participation of Cu^+ and Cu^{2+} on one hand, and complex ion and hydroxonium cations

on the other. Obviously, the diversity of these ion formations considerably complicates the investigation of the interaction mechanism with the polyether components.

The present investigation aims to study the behaviour of a polyether-copper salt in aqueous-acidic media by means of independent physico-chemical methods and to compare the results obtained to published data concerning the influence of polyethers on copper deposition overpotential changes [3] and those of the electrical double layer capacity [7, 8], which are considered to be qualitative and quantitative criteria for polyether adsorption on the metal surface.

2. Experimental details

The investigations of the interactions between PEG and Cu^+ , Cu^{2+} respectively, were carried out using three independent methods:

(i) Measurement of the specific conductivity (κ) changes of aqueous-acidic copper electrolyte solutions by means of conductometric titration: For this purpose, certain quantities of PEG, were added to Cu^+ and Cu^{2+} -containing solutions, after which measurements with an a.c./d.c. Wayne Kerr B 641 bridge at 1592 Hz frequency were made. Solution temperature during the measurements was kept in the $25 \pm 0.05^\circ \text{C}$ interval with the aid of two series of combined thermostats with a circulating agent—kerosene [25, 26]. The deviation of the measurements was 0.1%.

$\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ solutions of $1 \times 10^{-4} \text{ mol dm}^{-3}$ concentrations were studied. 1 to 6 –EO– units per copper atom were subsequently added in the form of PEG with molecular weight 3000 (Fluka).

(ii) Measurements of optical density (OD) changes of $1 \times 10^{-4} \text{ mol dm}^{-3}$ solutions of the above-mentioned salts after a preliminary addition of PEG 3000 or cross-linked PEO. The measurements were carried out in the u.v. range with a Specord u.v./v.i.s., Carl Zeiss Jena (Germany) spectrometer.

Crosslinked PEO (PEO-N) was obtained by γ -irradiation of 2% high molecular weight PEO water solutions, BADIMOL™ type, produced by Neochim – Dimitrograd, Bulgaria; $M_v = 2.5 \times 10^6$ in an inert atmosphere. The radiation source was ^{60}Co with a 270 krad h^{-1} power and an overall irradiation dose of 5 Mrad. The formed gel was repeatedly washed with distilled water after which it was lyophilized. Under the conditions described, the average length of the \bar{M}_c segments was about 3000 [27]. This method allows the chemical structure of crosslinked PEO to be, to a great extent, identical to that of linear PEG. Thus it may be considered that the character of PEG and PEO-N interaction with copper salts will be the same. PEO-N is a more convenient subject for investigation, as a double phase gel/solution system forms after its addition to the solution. As a result of this, having measured the concentration of the salt in the solution, the salt

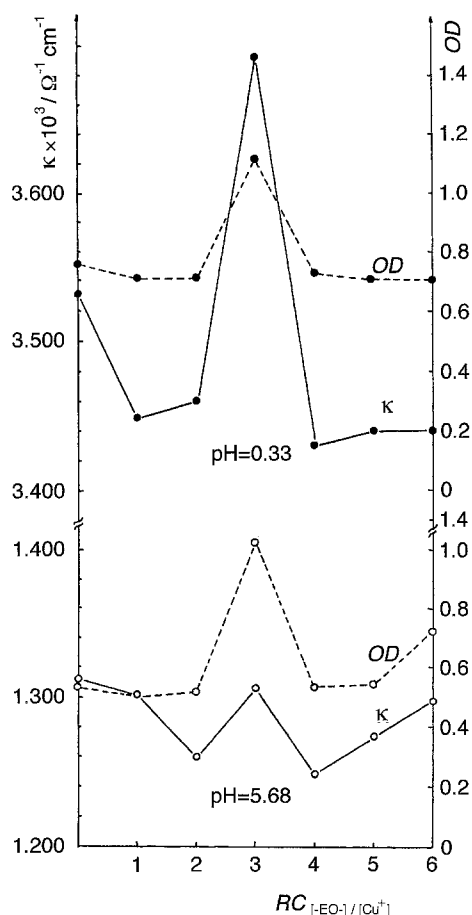


Fig. 3. Dependence of the specific electrical conductivity κ of 1×10^{-4} M $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ solutions at two different pH values; the concentration ratio (RC) of the ethylene oxide groups and the univalent copper ions ($\{-\text{EO}-\}/\{\text{Cu}^+\}$) varies from 1 to 6. Optical density (OD) changes of the same solution at $\lambda = 210$ nm are shown with dotted lines.

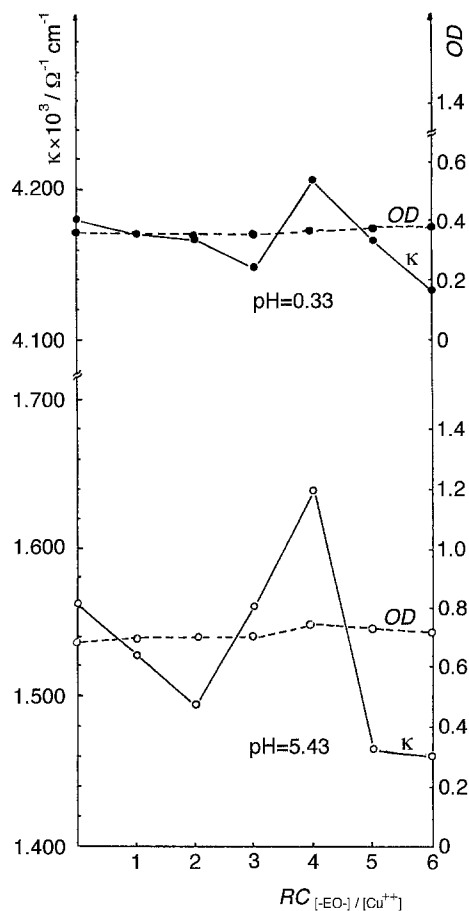


Fig. 4. Dependence of the specific electrical conductivity κ of 1×10^{-4} M $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions (at different pH values of the solutions) in which the concentration ratio (RC) of ethylene oxide units and bivalent copper ions ($\{-\text{EO}-\}/\{\text{Cu}^{2+}\}$) varies from 0 to 6. Optical density (OD) changes of the same solutions at $\lambda = 210$ nm are shown with dotted lines.

distribution coefficient between the gel phase and the solution may be determined as a basis of determination of the binding strength of the salt-ethylene oxide ligands.

(iii) Copper ion concentration measurements using a method similar to that suggested in [28], comprising a cyclic voltametric stripping analysis (CVS) technique: This method allows an exact quantitative measurement of the reduced copper ion concentration with respect to that of the dissolved copper atoms before and after the addition of PEG to the electrolyte.

The potentiodynamic sweep rate was 100 mV s^{-1} in the -0.7 to $+0.8 \text{ V}$ range (vs NHE) (potentiostat-galvanostat GWP 673 ZWG, Germany) on a platinum hemisphere cathode of 1.2 mm diameter with a 99.2% Pt counter electrode. A mercury sulfate reference electrode was used. The nearly equal quantity of current charge in the cathodic and anodic areas of the curve was automatically coulometrically registered.

The working electrolyte of 100 ml volume was saturated with purified argon for 40 min before the voltamperometric curves were made. The temperature of the electrolyte was 25°C . Stirring of the electrolyte was performed by an electromagnetic stirrer (400 rpm).

Voltamperometric investigations were carried out in basic electrolytes: 0.01 molar $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ solutions with

pH 0.33, to which certain quantities of PEG 3000 were added.

3. Results

3.1. Specific conductivity changes of Cu^+ and Cu^{2+} containing solutions after addition of PEG

The addition of definable amounts of PEG to the $1 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions leads to κ changes with the appearance of maxima when $-\text{EO}-/\text{Cu}^+ = 3$ (Fig. 3) and $-\text{EO}-/\text{Cu}^{2+} = 4$ (Fig. 4) ratios are reached. Further increases in the quantity of PEG added does not lead to changes in κ .

The appearance of extremums in such cases is considered to be connected with the formation of complexes of a donor/acceptor stoichiometric ratio equal to that or the ligand/metal ion. A drastic change of the conductivity of the system [29] is observed when the latter is reached.

3.2. Optical spectra changes of Cu^+ and Cu^{2+} solutions after addition of PEG or PEO-N

The changes in the u.v. spectra of $1 \times 10^{-4} \text{ mol dm}^{-3}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solutions in the

range 200 to 250 nm, after the subsequent addition of PEG 3000 portions at $-\text{EO}-/\text{Cu}^+$ or $-\text{EO}-/\text{Cu}^{2+}$ ratios varying from 0.5 to 5 were studied. It was established that, for all Cu_2Cl_2 solutions, the optical density value (OD) in the range of the spectral maximum OD increases considerably at a $-\text{EO}-/\text{Cu}^+$ ratio of 3. It is important to point out that this increase in the solution optical density correlates to the results of the measured conductivity change of the same solution after the addition of the same quantities of PEG (Fig. 3).

The analogous investigations of CuCl_2 containing solutions showed a much weaker change of optical density after the addition of PEG. Though not very well defined, a correlation between κ and OD changes (Fig. 4(b)) may be observed only at higher pH values (pH 5.43).

To obtain more precise information about the character of interaction in the $\text{Cu}^+/\text{HCl}/\text{PEO}/\text{H}_2\text{O}$ and $\text{Cu}^{2+}/\text{HCl}/\text{PEO}/\text{H}_2\text{O}$ systems, the complex formation between PEO-N and copper salt-hydrochloric acid solutions was studied. Since the system contains two phases: a swollen gel and acidic solution, the possible PEO with H^+ , Cu^+ (Cu^{2+}) complexes will be formed only in the gel phase. As a result of this, H^+ or Cu^+ (Cu^{2+}) concentration changes may be registered more easily. Obviously, concentration changes of ions in the liquid phase are, in this case, a direct consequence of the cation/PEO-N interactions.

Cu_2Cl_2 and CuCl_2 solutions of $1 \times 10^{-4} \text{ mol dm}^{-3}$ concentrations were used and 10, 20, 30, 40 and 50 mg PEO-N were added to 5 ml portions of each of the solutions, respectively. The solutions were left for 24 h in the dark at room temperature and the liquid phase u.v. spectrum was taken afterwards (Figs 5 and 6).

An increased water phase adsorption, compared to the basic solution before the addition of PEG, was established in the 200 to 260 nm interval. The increase was proportional to the added quantity of PEO-N. We suppose that the change of the maximum at about 210 nm is due to complex anion formation with a Cu^+ (Cu^{2+}) central atom, the 'ate' complexes: CuCl_2^- , CuCl_3^{2-} , CuCl_4^{3-} and CuCl_4^{2-} [22–24].

3.3. Voltamperometric determination of Cu^+ and Cu^{2+} concentration changes after the addition of PEG and/or Cl^-

As mentioned above, the CVS method, in the case of completely reproducible voltamperograms, makes possible the precise registration of electrochemical reaction changes in the cathodic and anodic areas determined by the influence of different organic additives [28]. Our investigations with the aid of CVS show a single peak in the anodic area corresponding to copper dissolution which results in the deposition of copper in the cathodic area. The practically equal current density during the cathodic and anodic processes, as well as the existence of a single peak in the cathodic area, suggests that the current density

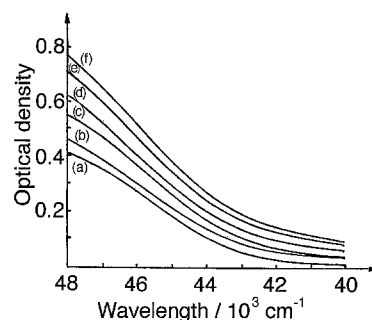


Fig. 5. Ultraviolet spectra of a $1 \times 10^{-4} \text{ M}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ solution (curve (a)) to 5 ml of which have been added 10 (curve (b)), 20 (curve (c)), 30 (curve (d)), 40 (curve (e)) and 50 mg (curve (f)) of crosslinked PEO. The spectra of the centrifuged liquid phase were taken after 24 h contact between the crosslinked PEO gel and univalent copper ions solution. Quartz cell width: 1 cm.

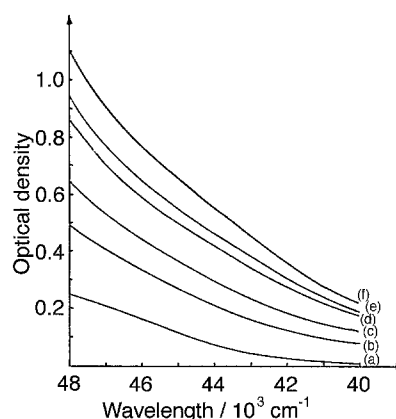


Fig. 6. Ultraviolet spectra of a $1 \times 10^{-4} \text{ M}$ $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ solution (curve (a)) to 5 ml of which have been added 10 (curve (b)), 20 (curve (c)), 30 (curve (d)), 40 (curve (e)) and 50 mg (curve (f)) of crosslinked PEO. The spectra of the centrifuged liquid phase were taken after a 24 h contact between the set PEO gel and the bivalent copper ions. Quartz cell width: 2 cm.

during the cathodic period is used singularly for the reduction of copper ions. The height and location changes of the voltamperograms maxima in the presence of PEG may be used for a qualitative, and in certain cases quantitative, estimation of the concentration change of free copper ions as a result of complex formation.

The changes in the voltamperograms obtained for a 0.01 mol dm^{-3} $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution (curve (a)) after the addition of: PEG at two different concentrations (curves (b) and (c)), and copper (I) and chloride ions (curves (d) and (e)) are shown in Fig. 7. The reduced height of the peaks in the anodic area when PEG is added suggests that the concentration of copper ions reducing in the cathodic area is decreased. This effect increases with the addition of Cu_2Cl_2 (Fig. 7, curves (c)–(e)). A similar effect is observed in cases of a reversed consequence of addition of PEG and Cu_2Cl_2 to the copper sulfate solution (Fig. 8). The well known [3, 30] weak depolarization effect (Fig. 2, curve (b)), illustrated by a peak increase in the anodic area is registered after the initial addition of Cl^- in the form of Cu_2Cl_2 . An increase in current density in the cathodic (anodic) areas occurs. Further addition of PEG leads to a twofold decrease in the quantity of

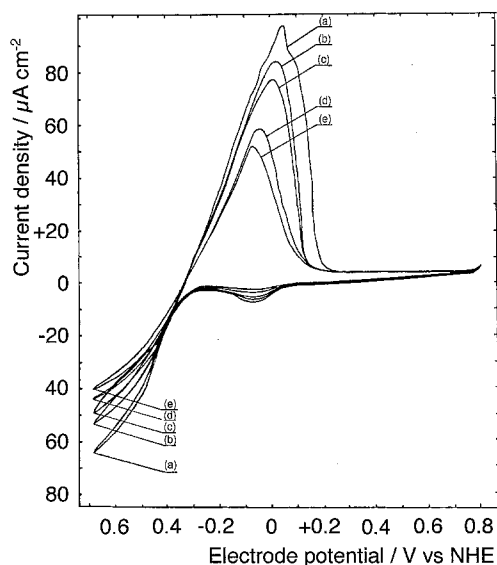


Fig. 7. Cyclic voltamperograms (scan rate: 100 mV s^{-1}) obtained using a platinum electrode in a $0.01 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution of pH 0.33 (curve (a)) to which has been added: $1.3 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (b)); $2.6 \times 10^{-6} \text{ mol dm}^{-3}$ PEG + $1 \times 10^{-6} \text{ mol dm}^{-3}$ Cu_2Cl_2 (curve (d)); $2.6 \times 10^{-6} \text{ mol dm}^{-3}$ PEG + $3 \times 10^{-6} \text{ mol dm}^{-3}$ Cu_2Cl_2 (curve (e)).

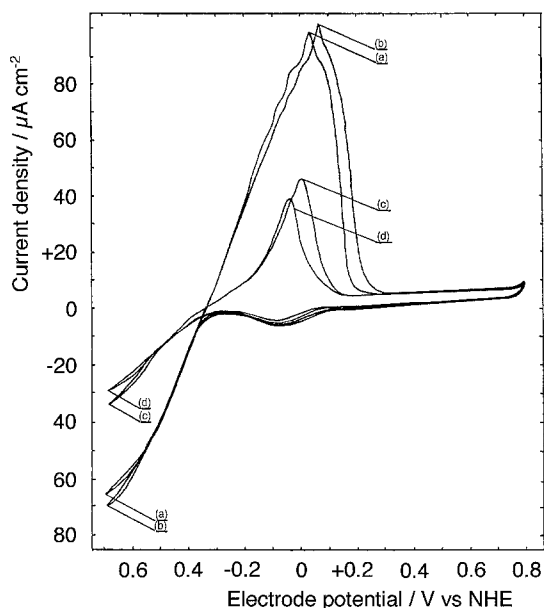


Fig. 8. Cyclic voltamperograms (scan rate: 100 mV s^{-1}) obtained using a platinum electrode in a $0.01 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution of pH 0.33 (curve (a)) to which has been added: $1 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ (curve (b)); $1 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ + $1.3 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (c)); $1 \times 10^{-5} \text{ mol dm}^{-3}$ $\text{Cu}_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ + $4 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (d)).

dissolved, with respect to deposited metal. Obviously, the addition of PEG leads to a considerable decrease in current density resulting from the diminished free copper ion concentration.

Copper (II) ion reduction is a two stage process (Equations 1 and 2). This is why, bearing in mind the results concerning κ and the optical spectra of Cu^+ in the presence of PEG, a voltamperometric study of the system was of interest. Voltamperograms for a solution containing Cu(I) ions only (0.01 mol dm^{-3} Cu_2Cl_2) are presented in Fig. 9. A

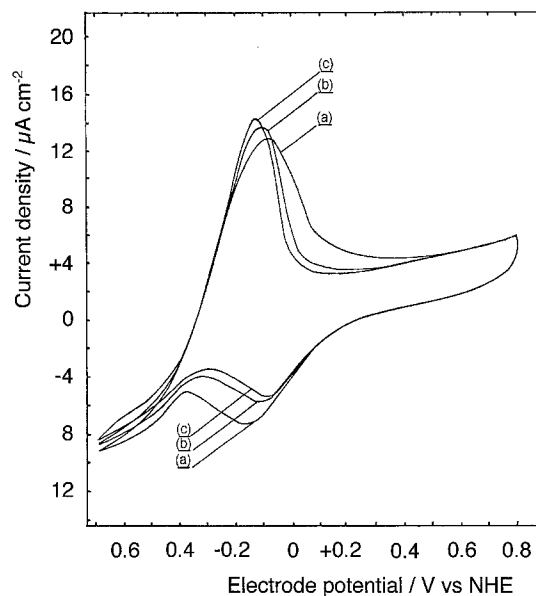


Fig. 9. Cyclic voltamperograms (scan rate: 100 mV s^{-1}) obtained using a platinum electrode in a $0.01 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution of pH 0.33 (curve (a)) to which has been added: $1.3 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (b)); $2.6 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (c)).

decrease in current density in the cathodic (and anodic) areas after the addition of PEG (Fig. 9, curves (b) and (c)) was also registered in this case.

The decrease in the charge under the cathodic/anodic peaks in the form of absolute values and percentage per part of the studied solution systems is presented in Table 1.

The results show that, besides the established decrease in the electrochemical reaction rate after the addition of PEG, two other effects occur: (i) the current density decrease after the addition of PEG is much greater after Cl^- is added; (ii) the maxima of the copper oxidation/reduction peaks change location with the addition of PEG, and to a greater extent in the presence of chloride ions.

The results presented on Fig. 10 are also significant. They were obtained for a practically equimolar ratio of Cu^{2+} , PEG ($-\{\text{EO}\}-$) and Cl^- concentrations. Curve (a) shows the pattern and location of the cathodic and anodic peaks for a $1 \times 10^{-4} \text{ mol dm}^{-3}$ CuCl_2 solution. Curve (b) is obtained after the addition of $2.66 \times 10^{-5} \text{ mol dm}^{-3}$ PEG, and curves (c) and (d) after the subsequent addition of $1 \times 10^{-4} \text{ mol dm}^{-3}$ KCl and $2.6 \times 10^{-4} \text{ mol dm}^{-3}$ PEG. As can be seen in Figs 9 and 10, parallel to the decrease in current (Table 1), a marked shift of the cathodic peaks in the positive direction, and of anodic peaks in the negative direction is observed. These two effects also suggest that a specific interaction between Cu^{2+} and Cu^+ on one hand, and PEG ethylene oxide units and Cl^- on the other, occurs after the addition of PEG. As a result, the concentration of Cu(I) and Cu(II) ions in the electrolyte diminishes and, subsequently, the electrochemical reaction rate and current density also decrease. The analogous results have been achieved by Mirkova and Rashkov studying the influence of PEG and Cl^- on the anodic behaviour of copper during electrorefining using a rotating disc electrode [31].

Table 1. Charge under cathodic/anodic peaks changes in Cu^+ and Cu^{2+} containing electrolytes after the addition of PEG and Cl^-

| Electrolyte composition | Additions of: | | | | |
|--|--|----------------------------------|----------------------------------|--|--|
| | 0.01 M $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ | $+1.3 \times 10^{-5}$ M PEG 3000 | $+2.6 \times 10^{-5}$ M PEG 3000 | $+1 \times 10^{-6}$ M Cu_2Cl_2 | $+3 \times 10^{-6}$ M Cu_2Cl_2 |
| Charge, $Q(\mu\text{C})$ during the cathodic/anodic period | 652 (100%) | 531 (81%) | 502 (78%) | 362 (56%) | 334 (51%) |
| Electrolyte composition | 0.01 M Cu_2Cl_2 | $+1.3 \times 10^{-5}$ M PEG 3000 | $+2.6 \times 10^{-5}$ M PEG 3000 | – | – |
| | Charge, $Q(\mu\text{C})$, during the cathodic/anodic period | 150 (100%) | 136 (91%) | 131 (87%) | – |
| Electrolyte composition | 1×10^{-4} M CuCl_2 | $+2.6 \times 10^{-5}$ M PEG 3000 | $+1 \times 10^{-4}$ M KCl | $+2.4 \times 10^{-4}$ M PEG 3000 | – |
| | Charge, $Q(\mu\text{C})$, during the cathodic/anodic period | 475 (100%) | 453 (95%) | 422 (93%) | 442 (93%) |

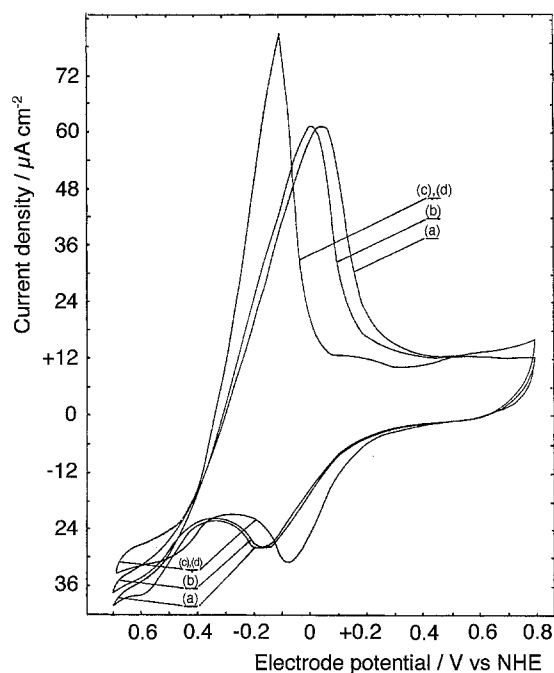


Fig. 10. Cyclic voltamperograms (scan rate: 100 mV s^{-1}) obtained using a platinum electrode in a $0.01 \text{ M CuSO}_4 \cdot 5\text{H}_2\text{O}$ solution of pH 0.33 (curve (a)) to which has been added: $2.6 \times 10^{-6} \text{ mol dm}^{-3}$ PEG (curve (b)); $2.6 \times 10^{-6} \text{ mol dm}^{-3}$ PEG $+1 \times 10^{-4} \text{ mol dm}^{-3}$ KCl (curve (c)); $2.55 \times 10^{-5} \text{ mol dm}^{-3}$ PEG $+1 \times 10^{-4} \text{ mol dm}^{-3}$ KCl (curve (d)). Curves (c) and (d) are the same.

4. Discussion

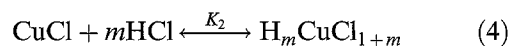
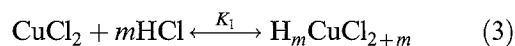
Studying the behaviour of PEG in a Cl^- and PEG containing copper sulfuric acid electrolyte [15, 32] Yokoi *et al.* suggest the following hypothesis: transition complexes, influencing the deposition reaction rates and copper dissolution, are formed in sulfuric acid electrolytes in the bulk electrolytes. Each Cu^+ orientates six electron pair donor oxygen atoms of the polyethylene oxide chains, that is, positively charged complexes of the $\{\text{Cu}^+(\text{EO})_6\}$ type are formed. In a layer near the cathodic surface they interact with the chloride ions adsorbed on the copper surface. The subsequent reduction of Cu^+ in the complexes is possible only after sufficiently negative cathodic potential values are reached.

The results obtained here are to a certain extent in accordance with these ideas. The decrease in current density in the presence of Cl^- is due: (i) to the possi-

bility of complex formation between Cu^+ and (EO) units; (ii) to the possibility of an interaction between these complexes and the specifically adsorbed chloride ions on the cathodic surface [15]; and (iii) to the possibility of an increased 'ate' complexes concentration of the CuCl_2^- , CuCl_3^- , CuCl^+ and CuCl_4^{2-} types, as a result of H^+ bonding with the oxygen atoms of the poly(ethylene oxide) chains which have an unshared electron pair. As a result of this, the inhibiting effect on the cathodic reaction increases. The established equivalent conductivity changes of $\text{Cu}^{2+}/\text{Cu}^+$ aqueous solutions after the addition of PEG are an indication of an interaction between copper ions and $-\text{EO}-$ units. The observed κ maxima at $\{-\text{EO}-\}/\{\text{Cu}^+\} = 3$ and $\{-\text{EO}-\}/\{\text{Cu}^{2+}\} = 4$ suggests that these ratios are connected to the stoichiometry of $-\text{EO}-$ ligands. The results also agree with other works [22, 33] concerning the coordination numbers of $\text{Cu}^+\{-\text{EO}-\}_3 \cdot \text{H}_2\text{O}$ and $\text{Cu}^{2+}\{-\text{EO}-\}_4 \cdot (\text{H}_2\text{O})_2$ types formed.

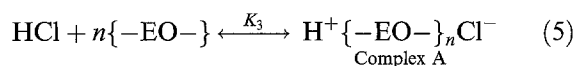
On the other hand, the u.v. spectra measurements for Cu_2Cl_2 and CuCl_2 hydrochloric acid solutions show that an increase in adsorption intensity in the 210 to 260 nm interval occurs after the addition of PEG.

This range is characteristic of the absorption of CuCl_2^- , CuCl_3^{2-} , CuCl^+ and CuCl_4^{2-} complex ions [33]. Obviously the addition of PEG causes the equilibrium reaction shift to the right in the direction of copper(I), and copper(II), acid formation:

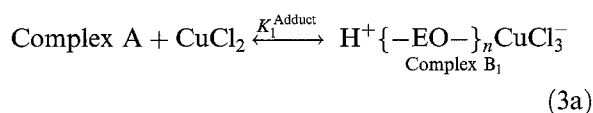


where $m = 1$ or 2 ,

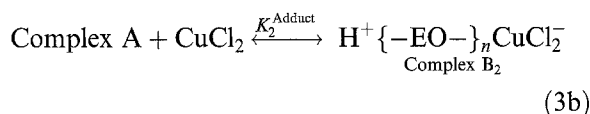
The most probable explanation is the fact that PEG interacts with the protons of acids [35]. The interaction of HCl may be presented as



Reaction 5 facilitates copper(I), or copper(II), anion formation:



where $K_1^{\text{adduct}} > K_1$, and



where $K_2^{\text{Adduct}} > K_2$.

When PEG is replaced by crosslinked PEO (PEO-N), two phases are formed: a swollen PEO-gel and a copper salt/water/hydrochloric acid solution. The PEO segments building up the PEO network form complexes with H^+ , and/or Cu^{n+} . It is well known that PEG interacts with the protons of acids [35]. Owing to the electrostatic potential, the Cl^- and CuCl_m^- anions migrate into the gel in such quantity as to be in exact equivalence to the fixed cations. The individual equilibrium exchange of ions between the cross linked PEO-N and the surrounding electrolyte closely resembles a Donnan membrane equilibrium [34], where the PEO gel acts as a membrane preventing the penetration of the fixed $\text{H}^+/\text{Cu}^{n+}/\text{PEO}$ complexes into the solution. As a result the concentration of the mobile ion species inside and outside the gel is different. Actually, with the concentration increase of the added PEO-N, a proportional absorption intensity increase in the 210 to 250 nm u.v. spectrum range is observed, which means that the concentration of complex copper anions in the solution increases.

Because the OD at 210 nm is assumed, as a measure for the concentration of $\text{Cu}(\text{I})$, and $\text{Cu}(\text{II})$, complex anions (CA) ($\text{CA} = \{\text{CuCl}_{m+2}\}_m^-$ or $\{\text{CuCl}_{m+1}\}_m^-$), the equation

$$\text{CA} = \text{constant}_1 \times OD \quad (6)$$

is satisfied. Combining equations 3 and 5, 4 and 5 leads to

$$\begin{aligned} \{\text{Complex B}\} &= K_m^{\text{Adduct}} \cdot K_3 \cdot \{\text{Cu}^{m+} \text{Cl}_m\} \\ &\times \{\text{HCl}\} \{-\text{EO}-\}^n \end{aligned} \quad (7)$$

As the concentrations of $\text{Cu}^{m+} \text{Cl}_m$ and HCl are high in comparison to complex B, then

$$\{\text{Complex B}\} = \text{constant}_2 \times \{-\text{EO}-\}^n \quad (7a)$$

Complex B contains $\{\text{CuCl}_{m+2}\}_m^-$ and $\{\text{CuCl}_{m+1}\}_m^-$ ions incapable of reacting with PEO segments as a result of which they distribute almost uniformly in the two phases due to an exchange with Cl^- ions. The additional formation of CA is due to the formation of complex B, so that

$$\{\text{CA}\} \approx \text{constant} \times \{\text{Complex B}\} = \text{constant} \times OD$$

The substitution of Complex B with the value of Equation 6 gives

$$\text{constant}_1 \times OD = \text{constant}_2 \times \{-\text{EO}-\}^n \quad (8)$$

or

$$OD = \text{constant}_3 \times \{-\text{EO}-\}^n \quad (9)$$

The mathematical processing of the experi-

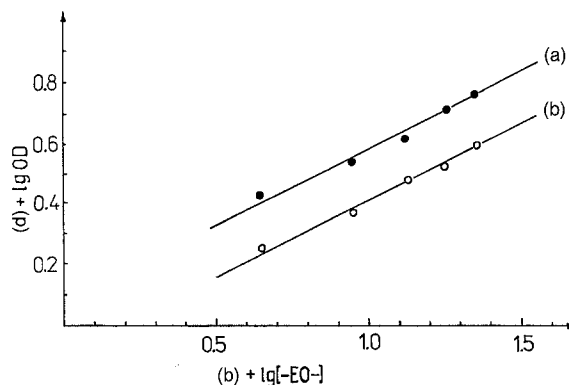


Fig. 11. Dependence of copper complex ion concentration ('ate'-complexes) in the solution, (as an optical density $OD_{210\text{nm}}$) against EO-units concentration in the swollen PEO-gel. Copper salt concentration: $1 \times 10^{-4} \text{ mol dm}^{-3}$. Curve (a): Cu^+ ; curve (b): Cu^{2+} .

mental results showed a linear dependence between $\log OD_{210\text{nm}}$ and $\log \{-\text{EO}-\}$ (Fig. 11).

In both the Cu_2Cl_2 and CuCl_2 cases the curve slope is equal to 1/2 which means that the stoichiometry of the interaction is: $\text{H}^+/\text{-EO-} = 2$, which is in accordance with other work [35].

$\{\text{CuCl}_{m+2}\}_m^-$ and $\{\text{CuCl}_{m+1}\}_m^-$ ions are incapable of reacting with PEG so that they distribute uniformly in the two phases as a result of an exchange with Cl^- ions.

The results for changes of κ and optical density of copper(I) and copper(II) aqueous-acidic solutions after the addition of PEG and PEO-N show that ethylene oxide units display complex formation properties both towards Cu^+ and Cu^{2+} , and the protons of the media. As a result of the $\text{-EO-}/\text{proton}$ interaction, noticeable changes in the stability constants of the existing copper(I) and copper (II) ions occur resulting in a concentration increase. These results show that the addition of Cl^- to the solutions of copper electrolytes leads to an increased concentration of complex ions of the CuCl_2 , CuCl_3^- , CuCl^+ and CuCl_4^{2-} types. This is in agreement with the voltamperometric investigations.

On the basis of the investigations made, the following mechanism of action of PEG in aqueous-acidic media containing chloride ions may be assumed:

4.1. Influence of PEG in the absence of Cl^-

In this case a relatively weak inhibition of the cathodic process is registered on the voltamperograms (Fig. 7, curves (b) and (c)). The lower reduction rate of copper ions in this case is probably due to the formation of complexes of the $\{\text{Cu}^+(\text{-EO-})_3 \cdot \text{H}_2\text{O}\}$ and $\{\text{Cu}^{2+}(\text{-EO-})_4 \cdot (\text{H}_2\text{O})_2\}$ types. As a result of this, the transportation of copper ions from the bulk electrolyte is impeded and the work for the discharge of the copper complex ion increases.

4.2. Influence of PEG in the presence of Cl^-

The explanation for the large increase in copper

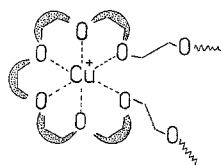


Fig. 12. Open chain ligands of PEG wrap around the Cu^{2+} ion forming pseudocrown moieties including Cu^+ .

deposition potential has been given by Yokoi *et al.* [15]. The open chain ligands of PEG are capable of wrapping around the Cu^{2+} ion with the formation of pseudocrown moieties including Cu^+ (Fig. 12).

As a result of their positive charge, these are attracted by the specifically negatively charged chloride ions adsorbed on the copper surface. At definite cathodic potential values, the Cu^+ -oxygen atoms bonds break and liberate the Cu^+ ions. The liberated PEG returns to the bulk electrolyte.

The pseudocrown helix structures between PEG and alkaline metals are established in nonaqueous media and solid phase [35]. The latest investigations [36, 37] show that the form and the structure of the ethylene oxide units are strongly influenced by the nature of the solvent.

In lipophilic media the oxygen atoms are pushed to the interior and oil-compatible $-\text{CH}_2$ -groups are directed outwards. In this case an electronegative cavity is formed which is suited to complexation of cations (Fig. 13(a)). In aqueous media the PEG segments are totally different, due to the possibility of the formation of hydrogen bonds between the electron donating oxygen atoms and solvent molecules. In this case the lipophilic $-\text{CH}_2$ -groups, by means of hydrophobic interaction, form the 'nucleus' of the segment, while the strongly polar oxygen atoms are directed towards the aqueous media (Fig. 13(b)).

On the basis of the considerable differences in the conformation interactions of PEG units in water and non-water media, pseudocrown formations following the Yokoi *et al.* model are not probable. We consider much more probable the scheme suggested by Suryanarayana *et al.* [38] according to which the copper ion coordinates just a single oxygen atom of the PEG unit, while the remaining three of five coordinations are occupied by already asymmetrically situated water molecules. The stoichiometry $-\text{EO}-/\text{Cu}^+ = 3$ and $-\text{EO}-/\text{Cu}^{2+} = 4$ indicates the $-\text{EO}-_n$ segment length including both the EO-unit, coordinates with Cu ions, and its neighbours. The results obtained in [38] are also in very good agreement with the investigations of Flodin *et al.* [39]. They assume an interaction between alkaline halides and PEG in aqueous media as a result of which an asymmetrical hydration both of the ionic solvation sphere and the so called 'structured' water, reacting with ether-oxygen atoms of the polymer chain, occur.

Obviously, in cases where complexes between Cu^+ , and/or Cu^{2+} , are formed, they are unstable for the following reasons: (i) the strong dipole character of

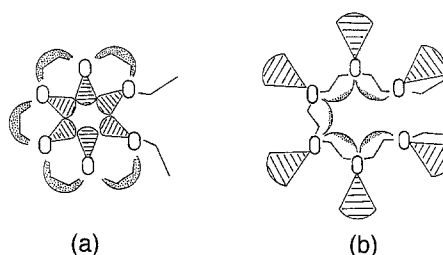


Fig. 13. Conformation changes of PEO segments depending on the character of the media: (a) in lipophilic solvents; and (b) in aqueous media.

water molecules, capable of competing with other ligands; and (ii) the absence of an appropriate polyether ring of a strictly defined geometry (radius) which would promote the stability of the complex.

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