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Absorption spectra of acidic Cu(II) solutions containing polyether laprol 2402 C

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Absorption spectra were obtained for solutions containing Cu(II), polyether laprol 2402 C and 0.6 M H_2SO_4 as a background electrolyte. They involve two main absorption bands falling into the visible and UV parts of spectra. The height of absorbance maxima observed at 800 and 236 nm was found to be in a linear dependence on Cu^{2+} and laprol concentrations respectively. These data may serve as measures of the indicated quantities. Examination of the spectroscopic data with regard to the laprol structure gives no evidence of the formation of sufficiently stable complexes between Cu^{2+} and laprol in strongly acidic media.

Key words: copper, polyether laprol, absorption spectra, complexes

INTRODUCTION

Much attention has been given recently to the development of industrial processes making it possible to obtain quality coatings of copper and its alloys. Plating baths used for this purpose usually contain polyethers such as polyethylene or polypropy-lene glycol (PEG and PPG respectively) in combination with other surface-active substances (SAS). Quite a comprehensive information on the electrochemical behaviour of such polyethers in Cu(II)-containing systems may be found in [1–3]. Despite a rather extensive literature on this subject, there is no general agreement among authors regarding the Cu(II) electroreduction in the presence of these SAS. Among different particles involved into charge transfer processes, Cu(II)–SAS complexes have been also discussed [1, 2], including also the formation of such substances as crown-compounds [4]. However, latest investigations [5–8] have shown that the form and structure of ethylene oxide units are strongly influenced by the nature of solvent. Though the pseudocrown helix structures between PEG and alkaline metals were established in nonaqueous media and solid phase [9], such formations in water solutions have been accepted as not probable [1]. More probable appears the scheme [10] according to which the copper ion coordinates just a single oxygen atom of the PEG unit, but such complexes seem to be rather unstable.

Recently, polyether laprol 2402 C has been applied as an effective component for bright bronze plating [11, 12]. However, voltammetric and impedance data [13–15] have shown a rather weak adsorption of laprol on a copper substrate when the solutions were carefully protected from chloride traces. It is common knowledge that Cl^- ions improve the anodic process and, therefore, are the necessary component of most plating baths. However, their role in complexation processes is not yet clear. This might be the reason why some of researchers [3] came to the conclusion that it is impossible to predict a correct mechanism for copper electrodeposition in the presence of PEG and chloride.

All the above problems concern the polyether laprol as well. In this connection, the investigations were carried out to reveal the possible interactions between Cu(II) the aforementioned substances. Analysis of absorption spectra was adopted for this purpose.

EXPERIMENTAL

The solutions under investigation contained 1–100 mM $CuSO_4$ (Mallinckrodt, USA, with chloride impurities less than 0.00005%), 0.6 M H_2SO_4 (analytical grade) and 5–30 g dm^{-3} laprol 2402 C (Russia). Trice-distilled water was used for the preparation of solutions.

The UV-visible spectra were recorded using a Perkin Elmer Lambda 35 UV/VS spectrometer in 1.0 cm path length quartz cells. Investigations were carried out at 20 °C.

RESULTS AND DISCUSSION

Laprol 2402C with the average molecular mass of 3200 may be treated as a block copolymer of PEG

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and PPG. Its approximate formula may be written as X-O-X, where X represents the chain

$$-(CH_2{-}CH{-}O)_p-[(CH_2{-}CH_2{-}O)_q-(CH_2{-}CH{-}O)]_m-H$$
$$\qquad\qquad\quad |\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad CH_3\qquad\qquad\qquad\qquad CH_3$$

with p = 10, q = 12, m = 1 or 2. As may be seen, coordination bonds between the metal ion and laprol might be formed through the unshared *p*-orbitals at oxygen atoms. A rough estimation shows that one mole of oxygen atoms resides in *ca* 50 g of this substance.

A consistent analysis of spectroscopic data requires the peculiar absorption bands of each component to be established primarily. Typical data obtained for $CuSO_4$ solutions containing 0.6 M H_2SO_4, using pure water as a "reference solution", are shown in Fig. 1. Such spectra include two maxima in the visible and UV regions.

One of them, observed at λ = 800 nm, may perfectly serve as a measure of Cu^{2+} concentration in the solution: the absorbance at this wavelength is in a linear dependence on [Cu^{2+}] (the inset in Fig. 1). However, this is not the case with the noisy maximum localized at *ca* 220 nm. It may be supposed that some other components (*e.g.* hydrosulphate ions) contribute to this region, but the conclusive clarification of the peak nature requires further investigations.

According to the similar data obtained for laprol solutions with background H_2SO_4, the main absorption occurs in the UV region (Fig. 2), but, again, the specific maxima observed at 190–200 nm do not characterize unambiguously the content of laprol in the solution. This seems to result from the superposition of absorption caused by several different components. However, data at somewhat higher wavelengths might be used for a rough estimation of laprol concentration due to the linear dependence of absorbance on laprol concentration (see inset in Fig. 2).

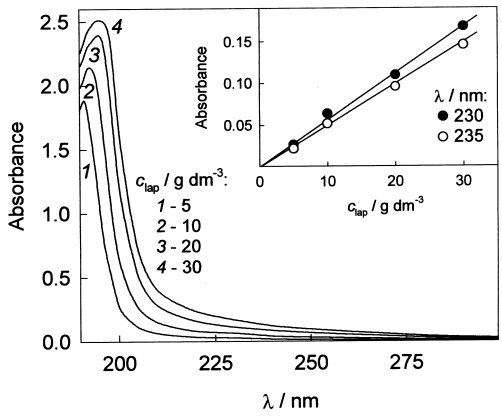

Fig. 2. Absorption spectra of laprol solutions recorded with regard to pure water. The absorbance at indicated λ *vs* laprol concentration is shown in the inset

Absorption spectra shown in Fig. 1 do not change when laprol is added to the extent of 20 g dm^{-3}. The data obtained both in the absence and presence of laprol actually coincide in the entire visible part of spectra. Minor deviations in the UV region are too small to be reliably established. However, the problems regarding the estimation of laprol concentration from spectrometric data work out, to a certain extent, when the reference solution containing Cu(II) is applied. Then, well-defined maxima appear in the UV spectra (Fig. 3), the height of which is proportional to the laprol concentration. At the same time, the slopes of linear dependences shown in Fig. 4 depend on Cu(II) concentration.

Similar data obtained at constant laprol concentrations are of different shape (Fig. 5). Absorbance

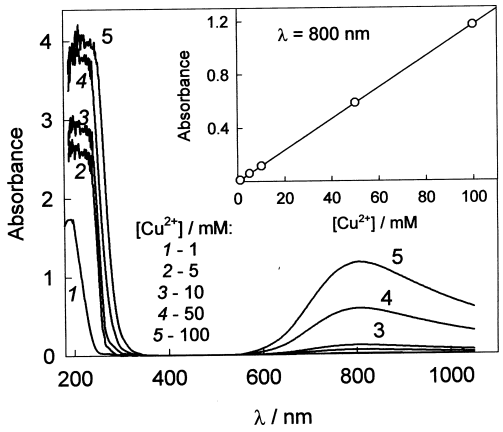

Fig. 1. Absorption spectra of Cu(II) solutions recorded with regard to pure water. The absorbance at λ = 800 nm *vs* Cu(II) concentration is shown in the inset

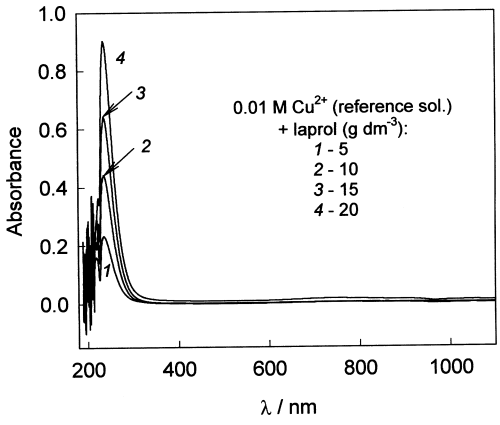

Fig. 3. Absorption spectra of 0.01 M Cu(II) solutions containing indicated amounts of laprol. Measurements were carried out with regard to 0.01 M Cu(II) solution

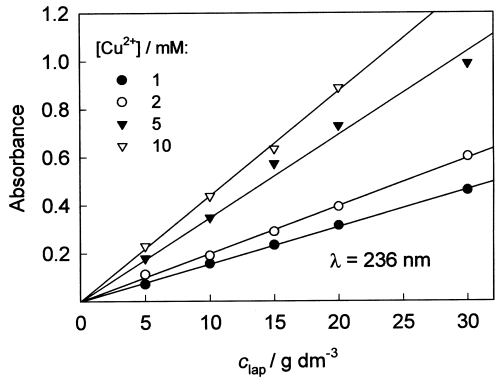

Fig. 4. Dependencies of absorption peak height on laprol concentration obtained for different [Cu^{2+}] indicated at the lines. Respective Cu(II)-containing solutions were used for reference

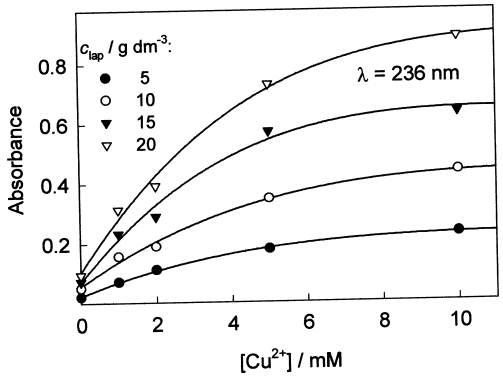

Fig. 5. Absorbance of solutions containing indicated constant amounts of laprol *vs* Cu^{2+} concentration. Respective Cu(II)-containing solutions were used for reference

of the solutions increases with the Cu^{2+} concentration approaching a certain limit.

To solve the problem on the complex formation between laprol and Cu^{2+} ions, some preliminary notes should be made. According to [10], the copper ion might coordinate just a single oxygen atom of the PEG unit, while the occupation of the remaining three or five coordinations by water molecules is preferable. With this assumption and the laprol structure in mind, the stoichiometric ratio of the oxygen and Cu^{2+} molar concentrations might be 4:1, which is equivalent, for example, to 2 g dm^{-3} of laprol in 0.01 M Cu(II) solution. Therefore, the data shown in Fig. 2 concern the solutions with a sufficiently large excess of laprol treated as a possible ligand. However, careful examinations of absorption spectra show no detectable decrease in Cu^{2+} concentration arising from laprol addition. Complexation effects should result in negative absorbance values at 800 nm, which, nevertheless, remain on the zero level. The most reliable interpretation of the experimental data should suppose that stable complexes between Cu^{2+} and laprol are not formed in strongly acidic media. The reasons for such behaviour seem to be the same as in the case of PEG [1], *viz.* the strongly dipole character of water molecules capable of competing with other ligands, and the absence of an appropriate polyether ring of a strictly defined geometry, which would promote the stability of the complex.

CONCLUSIONS

1. Absorption spectra of the solutions containing Cu(II), polyether laprol 2402 C and 0.6 M H_2SO_4 as a background electrolyte involve two main absorption bands falling into the visible and UV parts of spectra.

2. The height of absorbance maxima observed at 800 and 236 nm was found to be in a linear dependence on Cu^{2+} and laprol concentrations respectively. These data may serve as measures of the indicated quantities.

3. Examination of the spectroscopic data with regard to the laprol structure gives no evidence of the formation of sufficiently stable complexes between Cu^{2+} and laprol, which could be detected by the used technique.

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RŪGŠČIŲ Cu(II) TIRPALŲ, TURINČIŲ POLIETERIO LAPROLO 2402 C, ABSORBCINIAI SPEKTRAI

S a n t r a u k a

Išmatuoti tirpalų, turinčių Cu(II), polieterį laprolą 2402 C ir foninį 0,6 M H_2SO_4 elektrolitą, absorbcijos spektrai. Aptiktos dvi pagrindinės absorbcijos juostos, patenkančios į matomąją ir UV spektro sritis. Nustatyta, kad absorbcijos maksimumų, atitinkančių 800 ir 236 nm bangos ilgius, aukščiai yra tiesiai proporcingi Cu^{2+} ir laprolo koncentracijoms ir kad juos galima panaudoti nurodytų komponenčių kiekių matavimams. Spektroskopinių duomenų analizė, atlikta atsižvelgiant į laprolo struktūrą, nerodo, kad stipriai rūgščioje terpėje galėtų susidaryti pakankamai stabilūs Cu^{2+} ir laprolo kompleksai, kuriuos būtų galima aptikti panaudota metodika.