Cu(II) complex formation with pentaethylenehexamine: determination of stability constants by the ligand displacement method

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Cu(II) ions form 1 : 1 and 1 : 2 complexes with pentaethylenehexamine (penta) (pH 7), depending on penta excess. The spectrophotometric method of ligand displacement was applied for determining the stability constant of these complexes, using EDTA as a competitive ligand. The results are in agreement with the 1 : 1 and 1 : 2 stoichiometry of the complexes, namely Cupenta1+ and Cupenta2+, the stability constant logarithms being 21.3 and 29.5, respectively. The latter complex is one of the most stable known copper(II) complexes.

Key words: pentaethylenehexamine, copper(II), complex formation, stability constant

INTRODUCTION

Diamines, or higher amines, have found application as copper(II), cobalt(II) and cobalt(III) ligands in the novel systems of electroless copper deposition, in which Co(II) complexes act as reducing agents [1–12]. Firstly, ethylenediamine was documented as a proper ligand for such systems [1–5]. Later, it was shown that higher amines, such as propylenediamine [7] and diethylenetriamine [8–10, 13] give positive results, too. Probably, pentaethylenehexamine (penta) could also be applied as a Cu(II), Co(II) and Co(II) ligand in the systems for electroless copper deposition.

It is worth noting that in the case of ethylenediamine [5] and diethylenetriamine [13], detailed thermodynamic investigations were carried out, including calculations of Cu(II) and Co(II) complexation, the values of redox potentials of Co(III) / Co(II) and Cu(II) / Cu redox couples. The results of theoretical calculations were compared with the results obtained in real electroless deposition systems.

The thermodynamic calculations of such kind are very important for predicting the possibility of running Cu(II) reduction by Co(II) complexes with various polyamines and the use of such amines for electroless copper plating systems.

Summarizing, we did not find data on the complexation of Cu(II) ions in penta solutions, i.e. on the composition and stability of the complexes formed.

Therefore, this paper deals with a spectrophotometric study of complex formation with the aim to determine the composition and stability constants of Cu(II)–penta complexes, since preliminary experiments showed the possibility of the formation of such complexes.

EXPERIMENTAL

Analytical grade chemicals and bidistilled water were used to prepare the solutions. The solutions contained: copper sulphate pentahydrate CuSO₄ · 5H₂O 99% (Fluka); pentaethylenehexamine H₂N–CH₂–CH₂–NH–CH₂–CH₂–NH–CH₂–CH₂–NH–CH₂–CH₂–NH–CH₂–CH₂–NH₂ 90% (Aldrich); ethylenediaminetetraacetic acid EDTA 99% (Aldrich). The solution

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pH was adjusted by adding sulphuric acid H$_2$SO$_4$ 95% (PPH “Standard”, Poland). All experiments were carried out at 20 ± 1 °C.

Light absorption spectra were recorded using a Perkin Elmer Lambda 35 UV / VIS spectrometer at 20 °C in 1 cm-thick quartz cells. The optical blanc solution was pure water.

Measurements of the solution pH were carried out using a Toledo Mettler MP 220 pH-meter.

RESULTS AND DISCUSSION

A comparison of Cu(II) light absorption spectra in solutions of penta shows a rather complicated dependence on solution pH and, to a lesser extent, on the concentration of penta (Figs. 1–3).

According to spectrophotometric data, the complexation of Cu(II) with penta begins at pH higher than 2.
It may be noted that complicated spectral characteristics are connected with the distribution of penta in different forms – protonated and not, depending on solution pH (Fig. 4). Data on the values of protonization constants were taken from [14].

Light absorption spectra of Cu(II)–penta complexes almost coincide in the pH range from 6.0 to 9.0. The constancy of absorbance in a rather wide range of pH suggests formation of one kind of complex, e.g., a 1 : 1 Cu(II)–penta complex in the case of Fig. 1 (no excess of penta) and a 1 : 2 Cu(II)–penta complex in the case of Figs. 2 and 3 (excess of penta).

Additional experiments were made with the aim to test the validity of Beer’s law. Therefore, a series of spectra of solutions with a different Cu(II) concentration but a constant metal-to-ligand ratio were recorded (Fig. 5). The results show a linear dependence of absorbance on the concentration of complexes, the plots going through the origin of coordinates (Fig. 6). The obtained plots demonstrate the validity of Beer’s law for the system under investigation and the absence of dinuclear complex formation.
Under conditions of Beer’s law, the method of ligand displacement can be used to determine the stability constant of the complexes formed. In accordance with this method, the competitive ligand is supposed to form a Cu(II) complex compound with different optical properties; e.g., its light absorption maximum and/or molar extinction coefficient should differ quite a few from that of Cu(II)–*penta* complexes.

We selected as a competitive ligand EDTA (ethylenediaminetetraacetic acid), since it is known that at pH from ca. 4 to pH ca. 10 EDTA forms only one complex, namely CuY²⁻ (*Y*⁴⁻ is a fourfold deprotonated anion of EDTA) [15], the stability constant logarithm logγ¹⁺CuY²⁻ being 18.8 [16, 17]. Curves 9, 11 and 8 in Figs. 7, 8 and 9, respectively, represent the spectrum of CuY²⁻ at pH 7.0, showing the light absorption maximum at λ = 730 nm, the molar extinction coefficient (ε) being 92 mol⁻¹ l cm⁻¹.

Addition of EDTA into Cu(II)–*penta* solutions changes light absorption spectra, i.e., light absorbance decreases and light absorption maximum shifts to longer wavelengths with an increase in EDTA concentration (Figs. 7–9). Thus, the obtained spectra demonstrate the conversion of the Cu(II)–*penta* complex into the CuY²⁻ complex (Figs. 7–9).

When two complex compounds (in our case Cu*petra*²⁺ and CuY²⁻ (Fig. 7)) exist in equilibrium in a solution and their spectra differ, the concentrations of the complexes could be calculated from the experimental data obtained at different wavelengths by solving a system of equations:

\[
\begin{align*}
    c_{\text{Cu*petra*}^\text{2+}} &+ c_{\text{CuY}^\text{2-}} = [\text{Cu(II)}]_0 \\
    c_{\text{Cu*petra*}^\text{2+}} \cdot \varepsilon_{\text{Cu*petra*}^\text{2+}, \lambda} + c_{\text{CuY}^\text{2-}} \cdot \varepsilon_{\text{CuY}^\text{2-}, \lambda} & = A/\ell,
\end{align*}
\]

where \(c\) is the concentration (M) of the corresponding complexes, \([\text{Cu(II)}]_0\) is the total Cu(II) concentration (M), \(A\) is the light absorbance at wavelength \(\lambda\), \(\ell\) is the cell width (cm), \(\varepsilon\) shows the molar extinction coefficient values of the corresponding complexes at wavelength \(\lambda\) calculated according to

\[
\varepsilon_{\lambda} = A/\ell \cdot c \cdot (\text{mol}^{-1} \text{ cm}^{-1}).
\]

These results show that the quantities of the Cu*petra*²⁺ and CuY²⁻ complexes are...
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comparable only at ca. equal concentrations of the mentioned Cu(II) ligands. With the further increase in EDTA concentration, the content of the CuY³⁻ complex increases, and this complex predominates at a higher excess of EDTA (Table 1).

Knowing the concentrations of Cu(II) complexes present in the solution under investigation, the equilibrium concentrations of deprotonated ligand forms (Figs. 4 and 10, as well as detailed data of calculations, whereas the deprotonization constants of EDTA were taken from [16, 17]), the concentration of free copper(II) ions can be calculated. We assumed that EDTA and \( \text{penta} \) participate in complex formation in fully deprotonated forms, i.e. \( Y^{4-} \) and \( \text{penta} \).

The stability constant of \( \text{Cu(penta)}^{2+} \) complex,

\[
\beta = \frac{[\text{Cu(penta)}^{2+}]}{[\text{Cu(II)}] \cdot [\text{penta}]},
\]

was calculated using spectrophotometric data on Cu(II) distribution among the complexes (Table 1), whereas the concentration of free Cu(II) ions was taken from

\[
[\text{Cu(II)}] = \frac{[\text{Cu}Y^{2-}]}{\beta_{\text{CuY}^{2-}} \cdot [Y^{4-}]].
\]

Table 1. Data on equilibria in the Cu(II)–pentaethylenehexamine(penta)–EDTA system calculated from the spectrophotometric data of Fig. 7 (Cu(II)–penta molar ratio 1:1). \([\text{Cu}]_0 = 0.005 \text{ M; pH 7; 20 °C}\)

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* Averages of the values calculated at 550, 560, 570, 580, 590, 600, 610, 620, 630 nm wavelengths.

Fig. 9. Cu(II) light absorption spectra in pentaethylenehexamine (penta) solutions (1), EDTA (8) and their mixture (2–7). Solution composition (M): [Cu(II)] = 0.005; [penta] = 0.025; [EDTA]; 1 – 0, 2 – 0.001, 3 – 0.002, 4 – 0.003, 5 – 0.004, 6 – 0.005, 7 – 0.01, 8 – 0.005. Solution pH 7.0; 20 °C

Fig. 10. Distribution of protonated and deprotonated forms of EDTA (H₄Y⁴⁻) depending on pH
The results obtained at different EDTA concentrations correlate well, the mean value of log β_{Cu\text{penta}^{2+}} being 21.3 ± 0.4 (Table 1).

From the spectrometric data it was determined that the light absorption maximum of the complex compound under study is λ = 620 nm, the molar extinction coefficient (ε) being 167 mol⁻¹ l cm⁻¹.

The other experiments were performed at the same concentration of Cu(II), but at two (Fig. 8) or five (Fig. 9) times higher concentrations of penta, i.e. under conditions of 1 : 2 Cu(II)–penta complex predominating.

Since Beer's law is valid for the system under investigation (Figs. 5, 6), the procedure analogous to that described above was used to determine the stability of the Cu\text{penta}^{2+} complex. The following system of equations was solved:

\[
\begin{align*}
\text{c}_{\text{Cu\text{penta}^{2+}}} + c_{\text{Cu}^{2+}} &= [\text{Cu(II)}]^+ , \\
\text{c}_{\text{Cu\text{penta}^{2+}}} \cdot \varepsilon_{\text{Cu\text{penta}^{2+}}} + c_{\text{Cu}^{2+}} \cdot \varepsilon_{\text{Cu}^{2+}} &= A_{1}/l ,
\end{align*}
\]

The stability constant of Cu\text{penta}^{2+} complex,

\[
\beta = [\text{Cu\text{penta}^{2+}}] / [\text{Cu(II)}] \cdot [\text{penta}]^{2},
\]

was calculated using spectrophotometric data on Cu(II) distribution among the complexes (Tables 2 and 3), whereas the concentration of free Cu(II) ions was taken from Equation 4.

The results obtained at different concentrations of EDTA and penta correlate well, the value of log β_{Cu\text{penta}^{2+}} being 29.8 ± 0.5 (Table 2) (twofold excess of penta) and 29.2 ± 0.2 (Table 3) (fivefold excess of penta). The mean value of log β_{Cu\text{penta}^{2+}}, calculated from data obtained with both concentrations of penta, is 29.5 and coincides in margins of error.

From the spectrometric data it was determined that the light absorption maximum of the investigated complex compound is at λ = 630 nm, molar extinction coefficient (ε) being 186 mol⁻¹ l cm⁻¹.

It is worth noting that the 1 : 2 Cu(II)–penta complex is stronger than the 1 : 1 Cu(II)–penta complex and prevents formation of copper(II) hydroxide in strongly alkaline solutions under study conditions: no decomposition of this complex and formation of Cu(OH)₂ were observed at pH up to 13 and higher.

The results of the study show penta to be a chelating agent strong enough for binding Cu(II) ions in neutral and alkaline solutions. The newly obtained data on copper(II) and penta complexes show that the 1 : 2 Cu(II)–penta complex is among the most stable known copper(II) complexes and is in the same range with the very stable copper(II) complex with Quadrol (Q) – cf. log β_{Cu\text{Quadrol}^{2+}} = 29.5 with log β_{CuQ₂(OH)₂^{2+}} = 29.1 [18].

Table 2. Data on equilibria in the Cu(II)–pentaethylenehexamine(penta)–EDTA system calculated from the spectrophotometric data of Fig. 8 (Cu(II)–penta molar ratio 1 : 2). [Cu]₀ = 0.005 M; pH 7; 20 °C

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Mean: 29.8 ± 0.5

* Averages of the values calculated at 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700 nm wavelengths.

Table 3. Data on equilibria in the Cu(II)–pentaethylenehexamine(penta)–EDTA system calculated from the spectrophotometric data of Fig. 9 (Cu–penta molar ratio 1 : 5). [Cu]₀ = 0.005 M; pH 7; 20 °C

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Mean: 29.2 ± 0.2

* Averages of the values calculated at 550, 560, 570, 580, 590, 600, 610, 620, 630, 640, 650, 660, 670, 680, 690, 700 nm wavelengths.
CONCLUSIONS

1. Data of spectrophotometric investigations showed 1 : 1 and 1 : 2 complex formation of Cu(II) with pentaethylenehexamine (penta), depending on ligand concentration. The stability constant logarithms of Cupenta$^{2+}$ and Cupenta$^{2}_{2+}$ were found to be 21.3 and 29.5, respectively. Both complexes predominated in solutions with pH from 6 to ca. 10.

2. The Cupenta$^{2+}$ complex is stronger than the 1 : 1 Cu(II)–penta complex and prevented formation of copper(II) hydroxide in strongly alkaline solutions under study conditions: no decomposition of this complex and formation of Cu(OH)$_2$ were observed at pH up to 13.

3. The 1 : 2 Cu(II)–penta complex is among the most stable known copper(II) complexes and is in the same range with the very stable copper(II) complex with Quadrol (Q) – cf. log $\beta$ Cu$^{2+}$penta$^{2+} = 29.5$ with log $\beta$ Cu$^{2+}$Q$_2$(OH)$_2$$^{2+} = 29.1$.

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