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

Eugenijus Norkus[1]*,

Ina Stankevičienė,

Aldona Jagminienė,

Kęstutis Prušinskas

Department of Catalysis,
Institute of Chemistry,
Center for Physical
Sciences and Technology,
A. Goštauto 9,
LT-01108 Vilnius,
Lithuania

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 $\mathrm{Cu}penta^{2+}$ and $\mathrm{Cu}penta_2^{2+}$, 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.

Therfore, 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 $CuSO_4 \cdot 5H_2O$ 99% (Fluka); pentaethylenehexamine $H_2N{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH{-}CH_2{-}CH_2{-}NH_2$ 90% (Aldrich); ethylenediaminetetraacetic acid EDTA 99% (Aldrich). The solution

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* Corresponding author. E-mail: norkus@ktl.mii.lt

pH was adjusted by adding sulphuric acid H_2SO_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.

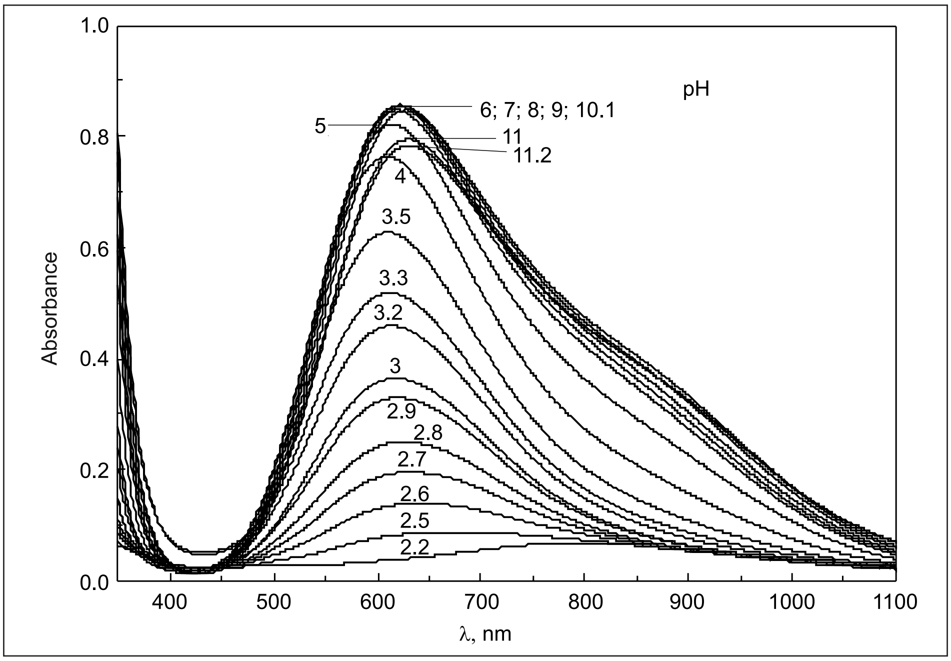

Fig. 1. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions with different pH. Solution composition (M): [Cu(II)]$_0$ – 0.005, [*penta*]$_0$ – 0.005. 20 °C

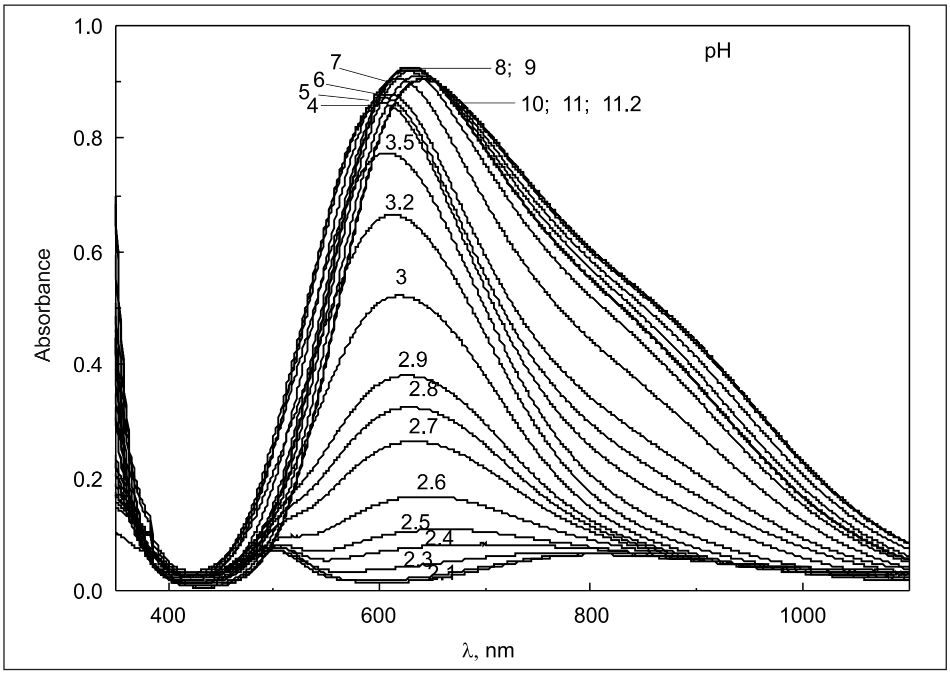

Fig. 2. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions with different pH. Solution composition (M): [Cu(II)]$_0$ – 0.005, [*penta*]$_0$ – 0.01. 20 °C

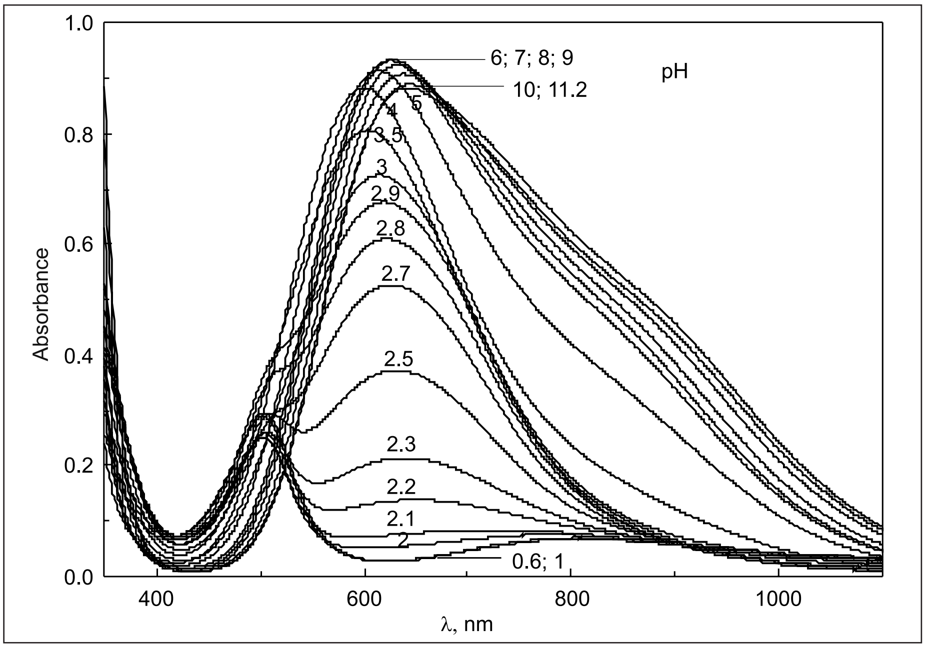

Fig. 3. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions with different pH. Solution composition (M): $[\mathrm{Cu(II)}]_0$ – 0.005, $[penta]_0$ – 0.025. 20 °C

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.

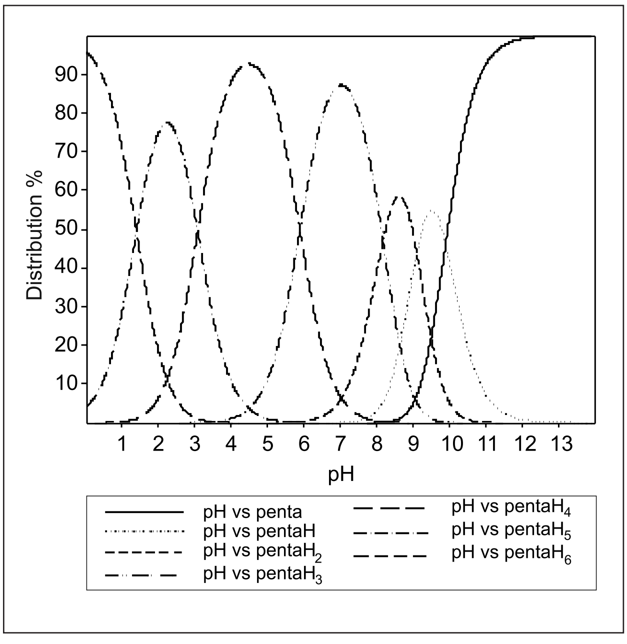

Fig. 4. Distribution of protonated and deprotonated forms of pentaethylenehexamine depending on pH

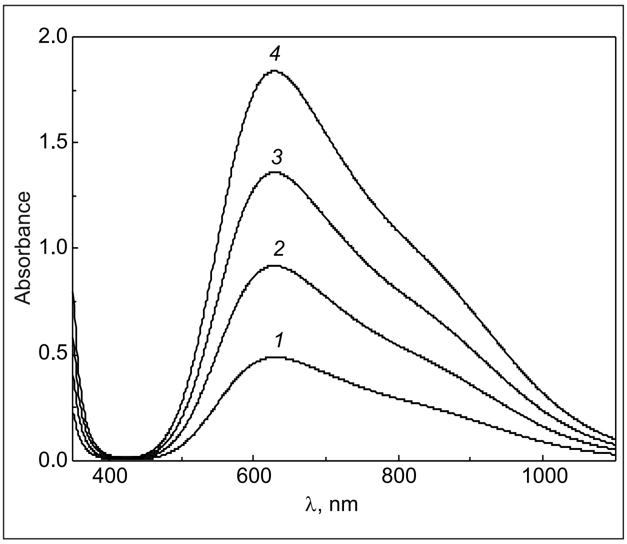

Fig. 5. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions. Solution composition (M): $[\mathrm{Cu(II)}]_0$: *1* – 0.0025, *2* – 0.005, *3* – 0.0075, *4* – 0.01, $[penta]_0$: *1* – 0.005, *2* – 0.01, *3* – 0.015, *4* – 0.02. Solution pH 7.0; 20 °C

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 $\mathrm{Cu}Y^{2-}$ (Y^{4-} is a fourfold deprotonated anion of EDTA) [15], the stability constant logarithm $\log\beta_{\mathrm{Cu}Y^{2-}}$ being 18.8 [16, 17]. Curves 9, 11 and 8 in Figs. 7, 8 and 9, respectively, represent the spectrum of $\mathrm{Cu}Y^{2-}$ at pH 7.0, showing the light absorption maximum at λ = 730 nm, the molar extinction coefficient (ε) being 92 $\mathrm{mol^{-1}\,l\,cm^{-1}}$.

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 $\mathrm{Cu}Y^{2-}$ complex (Figs. 7–9).

When two complex compounds (in our case $\mathrm{Cu}penta^{2+}$ and $\mathrm{Cu}Y^{2-}$ (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:

$$\begin{cases} c_{\mathrm{Cu}penta^{2+}} + c_{\mathrm{Cu}Y^{2-}} = [\mathrm{Cu(II)}]_0 \\ c_{\mathrm{Cu}penta^{2+}}\,\varepsilon_{\lambda_{i\,\mathrm{Cu}penta^{2+}}} + c_{\mathrm{Cu}Y^{2-}}\,\varepsilon_{\lambda_{i\,\mathrm{Cu}Y^{2-}}} = A_{\lambda_i}/l, \end{cases} \quad (1)$$

where c is the concentration (M) of the corresponding complexes, $[\mathrm{Cu(II)}]_0$ is the total Cu(II) concentration (M), $A_{\lambda i}$ is the light absorbance at wavelength λ_i, l is the cell width (cm), $\varepsilon_{\lambda i}$ shows the molar extinction coefficient values of the corresponding complexes at wavelength λ_i calculated according to

$$\varepsilon_{\lambda i} = A_{\lambda i} / cl \ (\mathrm{l\,mol^{-1}\,cm^{-1}}). \quad (2)$$

These results show that the quantities of the $\mathrm{Cu}penta^{2+}$ and $\mathrm{Cu}Y^{2-}$ complexes are

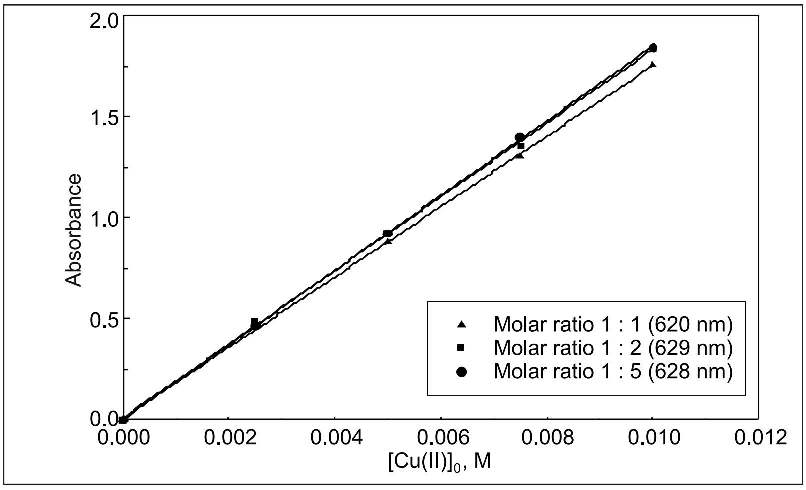

Fig. 6. Dependence of light absorbance on Cu(II) concentration in Cu(II) and *penta* solutions. pH 7.0; 20 °C

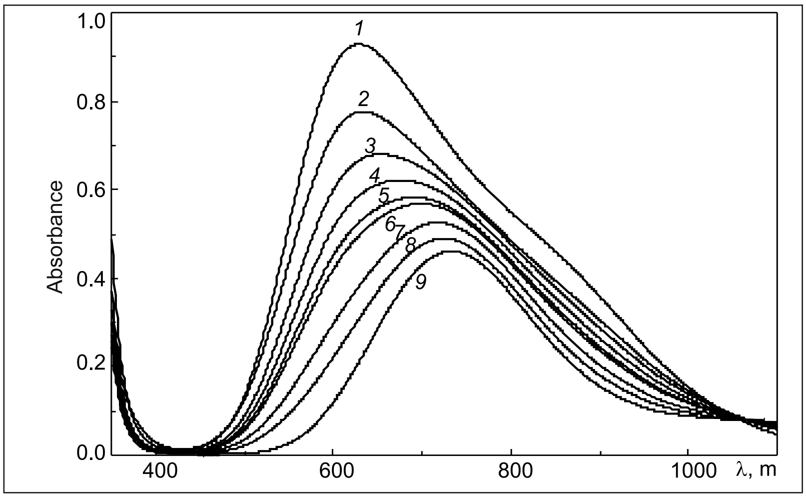

Fig. 7. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions (*1*), EDTA (*9*) and their mixture (*2–8*). Solution composition (M): $[\mathrm{Cu(II)}]_0$ – 0.005; $[penta]_0$ – 0.005; $[\mathrm{EDTA}]_0$: *1* – 0, *2* – 0.001, *3* – 0.002, *4* – 0.003, *5* – 0.004, *6* – 0.005, *7* – 0.01, *8* – 0.02, *9* – 0.005. Solution pH 7.0; 20 °C

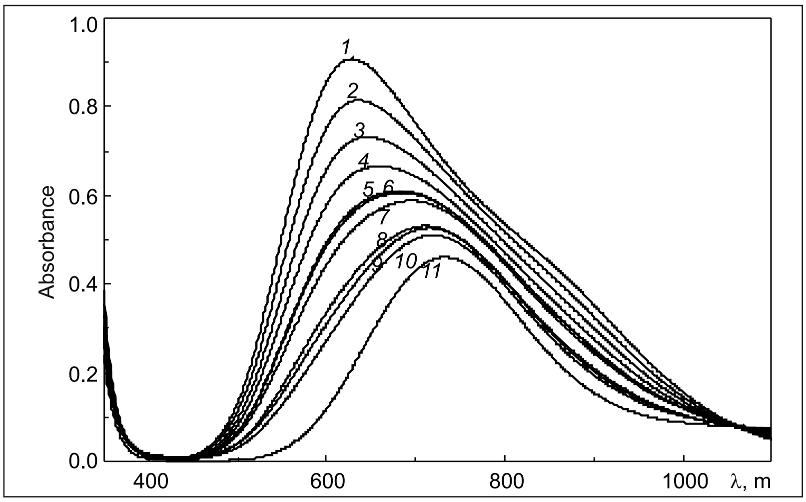

Fig. 8. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions (*1*), EDTA (*11*) and their mixture (*2–10*). Solution composition (M): $[\mathrm{Cu(II)}]_0$ – 0.005; $[penta]_0$ – 0.01; $[\mathrm{EDTA}]_0$: *1* – 0, *2* – 0.001, *3* – 0.002, *4* – 0.003, *5* – 0.004, *6* – 0.005, *7* – 0.007, *8* – 0.01, *9* – 0.008, *10* – 0.015, *11* – 0.005. Solution pH 7.0; 20 °C

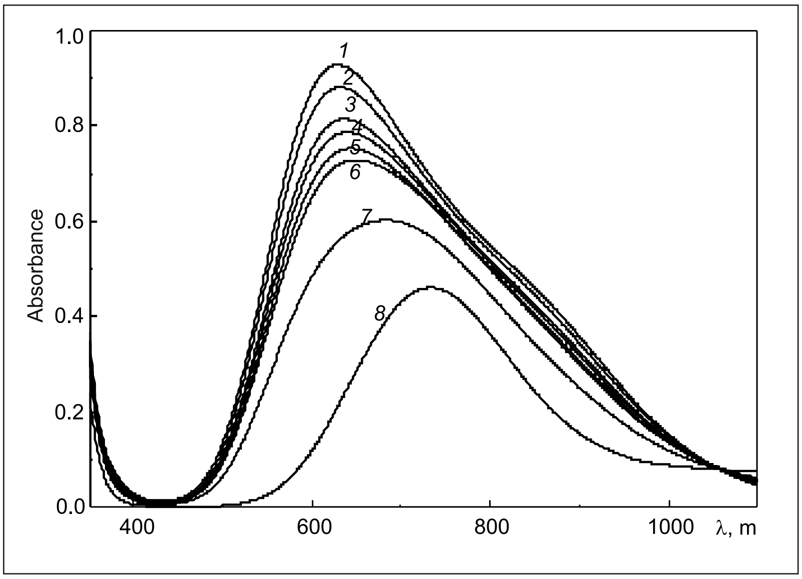

Fig. 9. Cu(II) light absorption spectra in pentaethylenehexamine (*penta*) solutions (*1*), EDTA (*8*) and their mixture (*2*–*7*). Solution composition (M): $[\mathrm{Cu(II)}]_0$ – 0.005; $[penta]_0$ – 0.025; $[\mathrm{EDTA}]_0$: *1* – 0, *2* – 0.001, *3* – 0.002, *4* – 0.003, *5* – 0.004, *6* – 0.005, *7* – 0.01, *8* – 0.005. Solution pH 7.0; 20 °C

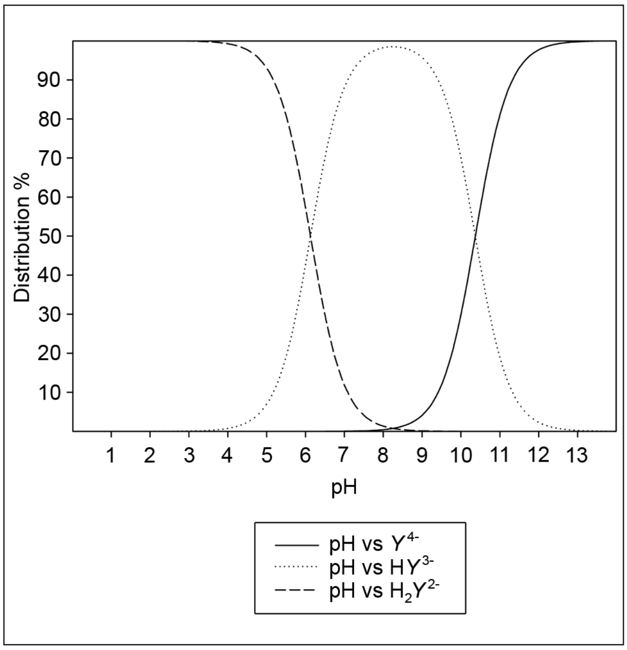

Fig. 10. Distribution of protonated and deprotonated forms of EDTA (H_4Y) depending on pH

comparable only at ca. equal concentrations of the mentioned Cu(II) ligands. With the further increase in EDTA concentration, the content of the $\mathrm{Cu}Y^{3-}$ 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 deprotanization constants of EDTA were taken from [16, 17]), the concentration of free copper(II) ions can be calculated. We assumed that EDTA and *penta* participate in complex formation in fully deprotonated forms, i. e. Y^{4-} and *penta*.

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

$$\beta = [\mathrm{Cu}penta^{2+}] / [\mathrm{Cu(II)}] \cdot [penta], \qquad (3)$$

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

$$[\mathrm{Cu(II)}] = [\mathrm{Cu}Y^{-}] / \beta_{\mathrm{Cu}Y2-} \cdot [Y^{4-}]. \qquad (4)$$

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). $[\mathrm{Cu}]_0 = 0.005$ M; pH 7; 20 °C**

$[\mathrm{EDTA}]_0$M	* $[\mathrm{Cu}Y^{2-}]$ M	*$[\mathrm{Cu}penta^{2}]$ M	$[penta]$ M	$[Y^{4-}]$ M	$[\mathrm{Cu}^{2+}]$ M	logβ$\mathrm{Cu}penta^{2+}$
0.001	0.000720821	0.004279179	4.66436E-10	1.04896E-07	2.30469E-15	21.8
0.002	0.001632483	0.003367517	1.05636E-09	1.38087E-07	3.03529E-15	21.2
0.003	0.002231435	0.002768565	1.44394E-09	2.88773E-07	1.29593E-15	21.2
0.004	0.002672859	0.002327141	1.72958E-09	4.98647E-07	8.60972E-16	21.2
0.005	0.002893948	0.002106052	1.87264E-09	7.91307E-07	5.82530E-16	21.3
0.010	0.003754949	0.001245051	2.42979E-09	2.34645E-06	2.53719E-16	21.3
0.020	0.004281696	0.000718304	2.77064E-09	5.90584E-06	1.14907E-16	21.4
						Mean: 21.3 ± 0.4

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

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). $[\mathrm{Cu}]_0$ = 0.005 M; pH 7; 20 °C**

$[\mathrm{EDTA}]_0$ M	* $[\mathrm{Cu}Y^{2-}]$ M	* $[\mathrm{Cu}penta_2^{2+}]$ M	[*penta*] M	$[Y^{4-}]$ M	$[\mathrm{Cu}^{2+}]$ M	$\log\beta\mathrm{Cu}penta_2^{2+}$
0.001	0.000713	0.004287	9.2285E-10	1.07806E-07	3.99849E-16	30.8
0.002	0.001339	0.003661	1.73349E-09	2.48189E-07	8.71659E-16	30.2
0.003	0.001882	0.003118	2.43502E-09	4.20247E-07	7.11202E-16	29.9
0.004	0.002495	0.002505	3.22845E-09	5.65627E-07	6.99437E-16	29.5
0.005	0.00244	0.00256	3.15828E-09	9.61728E-07	4.02244E-16	29.8
0.007	0.002758	0.002242	3.56905E-09	1.59393E-06	2.74326E-16	29.8
0.008	0.00366	0.00134	4.73669E-09	1.63067E-06	3.55967E-16	29.2
0.010	0.003501	0.001499	4.53091E-09	2.44187E-06	2.27274E-16	29.5
0.015	0.003918	0.001082	5.07094E-09	4.16374E-06	1.4918E-16	29.4
						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). $[\mathrm{Cu}]_0$ = 0.005 M; pH 7; 20 °C**

$[\mathrm{EDTA}]_0$ M	* $[\mathrm{Cu}Y^{2-}]$ M	* $[\mathrm{Cu}penta_2^{2+}]$ M	[*penta*] M	$[Y^{4-}]$ M	$[\mathrm{Cu}^{2+}]$ M	$\log\beta\mathrm{Cu}penta_2^{2+}$
0.001	0.000334	0.004666	1.01388E-08	2.50177E-07	2.11738E-16	29.3
0.002	0.000813	0.004187	1.07584E-08	4.4602E-07	2.88938E-16	29.1
0.003	0.001015	0.003985	1.102E-08	7.45812E-07	2.15807E-16	29.2
0.004	0.001272	0.003728	1.13519E-08	1.02517E-06	1.96626E-16	29.2
0.005	0.001459	0.003541	1.1595E-08	1.33032E-06	1.73985E-16	29.2
0.010	0.002593	0.002407	1.30628E-08	2.78285E-06	1.47706E-16	29.0
						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.

The results obtained at different EDTA concentrations correlate well, the mean value of $\log\beta\mathrm{Cu}penta^{2+}$ 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 $\lambda = 620$ nm, the molar extinction coefficient (ε) being 167 $\mathrm{mol^{-1}\,l\,cm^{-1}}$.

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 $\mathrm{Cu}penta_2^{2+}$ complex. The following system of equations was solved:

$$\begin{cases} c_{\mathrm{Cu}penta_2^{2+}} + c_{\mathrm{Cu}Y^{2-}} = [\mathrm{Cu(II)}]_0, \\ c_{\mathrm{Cu}penta_2^{2+}}\,\varepsilon_{\lambda_{i\,\mathrm{Cu}penta_2^{2+}}} + c_{\mathrm{Cu}Y^{2-}}\,\varepsilon_{\lambda_{i\,\mathrm{Cu}Y^{2-}}} = A_{\lambda_i}/l. \end{cases} \quad (5)$$

The stability constant of $\mathrm{Cu}penta_2^{2+}$ complex,

$$\beta = [\mathrm{Cu}penta_2^{2+}] \,/\, [\mathrm{Cu(II)}] \cdot [penta]^2, \quad (6)$$

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 $\log\beta\mathrm{Cu}penta_2^{2+}$ 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 $\log\beta\mathrm{Cu}penta_2^{2+}$, 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 $\lambda = 630$ nm, molar extinction coefficient (ε) being 186 $\mathrm{mol^{-1}\,l\,cm^{-1}}$.

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 $\mathrm{Cu(OH)_2}$ 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.* $\log\beta\mathrm{Cu}penta_2^{2+} = 29.5$ with $\log\beta\mathrm{Cu}Q_2(\mathrm{OH})_2^{2+} = 29.1$ [18].

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 Cu*penta*$^{2+}$ and Cu*penta*$_2^{2+}$ were found to be 21.3 and 29.5, respectively. Both complexes predominated in solutions with pH from 6 to ca. 10.

2. The Cu*penta*$_2^{2+}$ 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 $\mathrm{Cu(OH)_2}$ 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.* logβCu*penta*$_2^{2+}$ = 29.5 with logβCu*Q*$_2$(OH)$_2^{2+}$ = 29.1.

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Eugenijus Norkus, Ina Stankevičienė, Aldona Jagminienė, Kęstutis Prušinskas

Cu(II) KOMPLEKSŲ SUSIDARYMAS SU PENTAETILENHEKSAAMINU – PATVARUMO KONSTANTŲ NUSTATYMAS LIGANDO PAKEITIMO METODU

Santrauka

Cu(II) jonai, atsižvelgus į ligando perteklių, sudaro 1 : 1 ir 1 : 2 kompleksus su pentaetilenheksaaminu (*penta*) (pH 7). Minėtųjų kompleksų patvarumo konstantų verčių nustatymui buvo pritaikytas spektrofotometrinis ligando pakeitimo metodas, panaudojant EDTA kaip konkuruojantį ligandą. Gautieji rezultatai atitinka 1 : 1 ir 1 : 2 kompleksų stechiometriją, būtent Cu*penta*$^{2+}$ ir Cu*penta*$_2^{2+}$, o nustatytosios šių kompleksų patvarumo konstantų vertės yra atitinkamai lygios 21,3 ir 29,5. Pastarasis kompleksas yra vienas patvariausių žinomų vario(II) kompleksų.