
Speciation of transition metal ion complexes in alkaline solutions of alditols

2. Cu(II) complex formation with D-sorbitol

**Eugenijus Norkus* and
Jūratė Vaičiūnienė**

*Institute of Chemistry,
Laboratory of Catalysis
A. Goštauto 9,
LT-2600 Vilnius, Lithuania
E-mail: Norkus@ktl.mii.lt*

Jonas Reklaitis

*Lithuanian Customs Laboratory
Akademijos 7,
LT-2021 Vilnius, Lithuania*

Ernestas Gaidamauskas

*Faculty of Chemistry,
Vilnius University
Naugarduko 24,
LT-2006 Vilnius, Lithuania
E-mail:
ernestas.gaidamauskas@chf.vu.lt*

Debbie C. Crans

*Colorado State University,
Department of Chemistry
Fort Collins, CO 80523-1872, USA
E-mail: Crans@lamar.colostate.edu*

During investigation of the formation of Cu(II) complexes with D-sorbitol in alkaline solutions ($11.0 \leq \text{pH} \leq 14.0$) by means of direct current polarography and VIS-spectrophotometry ($20\text{ }^\circ\text{C}$, $I = 1.0$), the possibility of the formation of four complex compounds was shown. Under conditions of ligand lack the dinuclear complex Cu_2Sorb is formed ($\log \beta_{\text{Cu}_2\text{Sorb}} = 40.7 \pm 0.3$). Under conditions of ligand excess (10 times and higher), depending on pH and ligand concentration, three complex compounds are formed, namely $\text{CuSorb}(\text{OH})_2^{2-}$, $\text{CuSorb}_2(\text{OH})^{3-}$ and $\text{CuSorb}_2(\text{OH})_2^{4-}$ with the logarithms of stability constants 17.9 ± 0.3 , 20.1 ± 0.2 and 21.2 ± 0.2 , respectively. The diffusion coefficients and optical characteristics of the Cu(II)–D-sorbitol complex species were obtained.

Key words: copper(II), D-sorbitol, complex formation

INTRODUCTION

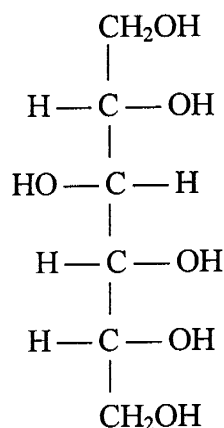
The complexes of polyols with different cations have a considerable biological, technological and analytical importance [1]. D-sorbitol (D-glucitol) represents an important stereoisomer of hexytol having the general formula of $\text{C}_6\text{H}_{14}\text{O}_6$ (Scheme).

It is generally agreed that D-sorbitol adopts a bent chain (sickle-shaped) conformation resulting in disruption of hydrogen bonding of the solvent in aqueous solutions [2].

The acidic behaviour (deprotonation) of D-sorbitol was investigated only in a few works suggesting deprotonation of one OH-group of polyol [3, 4]. The $\text{p}K_{\text{a}1}$ values obtained ($\text{p}K_{\text{a}1} = 13.14$ [3] and $\text{p}K_{\text{a}1} = 13.00 \pm 0.13$ [4]) show the deprotonation process occurring at rather high alkali concentration, but in the same pH range characteristic of stereoisomer of D-sorbitol, *e. g.* D-mannitol [5–8].

Complex formation equilibria between polyols and boric acid are used for separation and determination of polyols, *e. g.* D-sorbitol and xylitol, in multicomponent mixtures by isotachoelectrophoresis [9]. It was previously found that $\text{B}(\text{OH})_4^-$ forms 1 : 2

* Corresponding author.



Scheme 1. Fischer formula for D-sorbitol.

complexes with the double-deprotonated anion of D-sorbitol, the stability constant logarithm value being 4.5 [10].

Most of the not numerous data on the formation of D-sorbitol complexes with transition and heavy metal ions are qualitative, *i. e.* except the composition of the complexes formed, no information is presented about the stability constant values of the complexes and the complexation level of metal ions in D-sorbitol solutions.

The d.c.-polarographic behaviour of transition and heavy metal ions in alkaline solutions (1 mol/l KOH) of D-sorbitol (0.5 mol/l) is described in [11]. From the values of the half-wave potentials and the polarographic curves, authors found that many metal ions, such as Tl(I), Cu(II), Co(II), Mn(II), Pb(II), Zn(II), Cd(II), Fe(II), Sb(III), Fe(III), Bi(III), U(VI), V(V) and Cr(VI), yield well expressed, reproducible and well developed reduction waves which could be utilized for their polarographic determination. The anodic waves were observed for multivalent cations such as Mn(II), Fe(II), As(III) and Sb(III). The discussion about possible formation of metal ions hydroxy-complexes is absent in the present study, whereas hydroxy-complexes of Pb(II), Zn(II), Cu(II), etc. are well known [12–15]. Thus, no clear evidence of metal ions–D-sorbitol complex formation, except manganese(II)–D-sorbitol system (see below), is given in the study [11] mentioned.

In the same work, complex formation between manganese(II) and D-sorbitol was studied polarographically in detail, using the ligand displacement reaction between Mn(II)–EDTA complex and D-sorbitol in deaerated 1M KOH solutions. The Mn(II) : D-sorbitol ratio was found to be 1 : 2, the calculated stability constant being 1.94×10^{16} [11].

Other studies have also shown that the presence of D-sorbitol significantly increases the stability and solubility of the +2, +3 and +4 oxidation states of manganese in aqueous alkaline solution [16, 17].

Addition of D-sorbitol was shown to enhance the catalytic activity of manganese for the oxygen-alkali pulping process of paper manufacture due to an effective increase in the solubilization and activation of molecular oxygen by the manganese–D-sorbitol complexes [16].

Investigation of Pb(II) interaction with D-sorbitol in 1M NaOH solutions was carried out with the aid of Pb amalgam electrode [18]. The logarithm of the equilibrium constant of the reaction (where *L* is D-sorbitol):



was determined. The value of $\log K = 2.88$ shows a rather weak interaction of Pb(II) hydroxy-complex with D-sorbitol, but stronger than with D-mannitol ($\log K = 2.25$) [18].

Thin-layer ligand exchange chromatography [19] and microcalorimetry [20] were used for systematic studies of the stabilities of the complexes formed between alditols and lanthanide cations. Reactions of a series of trivalent lanthanide cations (La to Tb) with xylitol and D-sorbitol were studied, showing that the stability constants of the alditol complexes were the largest with Nd^{3+} and Sm^{3+} , all the stability constants calculated being smaller than 10^9 [20].

Complex formation of iron(III) with D-sorbitol was investigated in several studies. Complexes of Fe(III) with D-sorbitol in alkaline solutions have been investigated by EXAFS spectroscopy [21]. In the authors' opinion, the results obtained strongly support the formation of a mononuclear complex at pH 14, a dinuclear complex at pH 13 and oligonuclear species at pH 10–13 [21]. Polymeric Fe(III)–D-sorbitol complexes are also documented [22, 23].

When investigating the oxidation of D-sorbitol by Cr(VI), the EPR measurements showed that five- and six-coordinate oxo-Cr(V) intermediates with D-sorbitol were formed, with the alditols acting as bidentate ligands [24]. Cr(V) complexes were found to be stable enough to remain in solution for several days to months.

In a polarimetric study of the W^{VI} –D-sorbitol complexes, a mononuclear hydroxy-complex, $[\text{WO(OH)(C}_6\text{H}_{12}\text{O}_6)_2]^-$, was found at a higher pH (up to 11.5) and two dinuclear complexes at pH < 9.5 [25]. The values of the formation constants of the Mo^{VI} and W^{VI} complexes of various alditols obtained by potentiometry are summarized in [1]. From the data presented we can see that D-sorbitol complex is stronger with W^{VI} than with Mo^{VI} , the values of the formation constant logarithms being 19.26 and 16.90, respectively [26].

Although the ability of polyols to dissolve Cu(II) hydroxide in alkaline solutions has been known for many years, data on Cu(II) interaction with D-sorbitol are not numerous.

Hexadecanuclear Cu(II) complex with multideprotonated D-sorbitol was synthesized on concentrating aqueous solutions of the composition LiOH : Cu(OH)₂ : D-sorbitol in the molar ratio 1 : 2 : 1 in the form of monoclinic, blue crystals of the same stoichiometry [27]. In the compound obtained – Li₈[Cu₁₆(D-SorbH₋₆)₄(D-Sorb1,2,3,4H₋₄)₄ – half of the D-sorbitol ligands are completely deprotonated, and the other half of the D-sorbitol ligands are present as tetraanions, in which four neighbouring hydroxy-groups have been deprotonated [27]. The structure of the complex mentioned is discussed in the same work.

The possible structure of Cu(II) complex with D-sorbitol was discussed in [28]. With reference to ¹³C NMR signals broadening of C-1,2,3,4, author suggested dinuclear Cu(II) complex formation with one alditol molecule, D-sorbitol acting as a tetradentate ligand. On the grounds of chemical analysis data and EPR measurements, formation of similar dinuclear Cu(II) hydroxy-complex with deprotonated D-sorbitol of the formula Cu₂L(OH)Na · 6H₂O was suggested [29]. Light absorption maximum of the solutions of the latter compound at pH 11.7 was found to be at 642 nm. The EPR parameters of the Cu(II) complexes studied are presented [29].

Additionally, it should be mentioned that hexytols can be oxidized by molecular oxygen in aqueous alkaline solutions containing Cu(II) ions, the products formed at 50 °C in 0.5 mol/l NaOH being sodium formiate and glycolate [30]. Therefore, to exclude possibility such kind oxidation, the experiments in our work were carried out in ten minutes after mixing reactants, *e. g.* Cu(II) and D-sorbitol.

Data on the composition and stability of copper(II) complexes with D-sorbitol (especially under conditions of D-sorbitol excess) are not numerous, if any. Therefore the aims of the present study were a detailed investigation of Cu(II) complex formation with D-sorbitol in a wide pH range in solutions containing different concentrations of D-sorbitol and determination of the complexation level of copper(II) ions in alkaline solutions of D-sorbitol, as well as comparison of the results with those obtained for Cu(II)–D-mannitol system.

EXPERIMENTAL

Investigations were carried out by means of d.c.-polarography, vis-spectrophotometry, ¹³C NMR at 20 °C. The main experiments were performed at a constant ionic strength (*I* = 1.0; NaNO₃). Analytical

grade chemicals were used. The apparatus and methods are described in Part 1 [31] and elsewhere [32–35].

RESULTS AND DISCUSSION

Deprotonation of D-sorbitol in alkaline solutions. The ¹³C spectrum obtained in 0.3 mol/l D-sorbitol aqueous solution exhibits six signals at 63.0, 63.5, 70.2, 71.6, 71.8 and 73.6 ppm (Fig. 1, 0.005 mol/l NaOH, solution pH 11.33), which are readily assigned to C6, C1, C4, C2, C3 and C5 carbon atoms, respectively [36]. An increase of solution pH results in a downfield shift for all peaks, indicating deprotonation of all hydroxyl groups adjacent to carbon atoms. A significantly higher shift for C3 (2.8 ppm, when the total NaOH concentration increases from 0.005 M to 9.2 M), C2 (2.2 ppm), C4 (1.4 ppm) and C4 (1.1 ppm) carbon atoms than that for C5 (0.9 ppm) and C6 (0.6 ppm) carbons suggest that in 9.2 M NaOH solution hydroxyl groups adjacent to C2–C4 are deprotonated completely, while other hydroxyl groups are still protonated.

The method of calculations of p*K*_a values from NMR results is described in Part 1 [31]. A rough estimate shows that the p*K*_a value of OH-groups adjacent to C2–C3 carbons is equal approximately

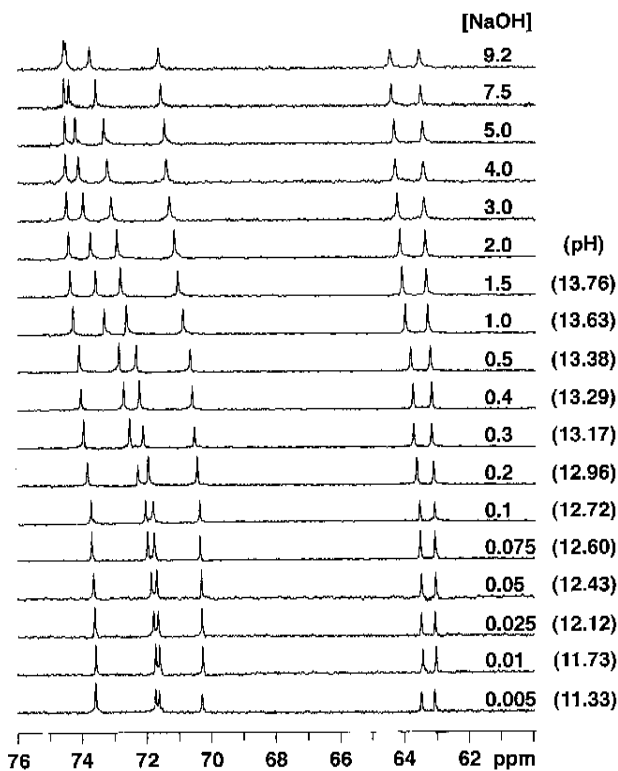


Fig. 1. ¹³C NMR spectra of D-sorbitol (0.3 mol/l) in aqueous NaOH solutions. The total NaOH concentration (mol/l) is shown for each spectrum. The pH values presented were measured experimentally. 20 °C

to 13.5 ± 0.3 , *i. e.* higher than the earlier determined values of pK_{a1} (13.1 [3] and 13.0 [4]). The difference between our results and the data presented in [3, 4] could be assigned to differences in temperature – our results were obtained for a temperature of 20 °C, whereas the values of 13.1 and 13.0 were obtained for solutions at 50 °C. It could be mentioned that according to NMR results, the pK_a values of OH-groups adjacent to C1 and C4 carbons are in the same order as for OH-groups adjacent to C2-C3 carbons of D-sorbitol, *i. e. ca.* 13.5.

Cu(II) complex formation with D-sorbitol under conditions of ligand lack. Copper(II) forms no complexes with D-sorbitol at $pH < 12$ in alkaline solutions, when the molar ratio of Cu(II) : D-sorbitol is 2:1. Formation of the $Cu(OH)_2$ precipitate is visually observed in the solution. At higher pH no precipitate is formed and the solution becomes blue in color, which is indicative of Cu(II) complex formation. Since copper(II) complexation begins at pH over 12.0 and $Cu(OH)_2$ precipitate is formed when Cu(II) : D-mannitol ratio exceeds 2:1, the results obtained can be accounted for by dinuclear Cu(II)–D-sorbitol complex formation with the deprotonated form of D-sorbitol ($pK_a = 13.5$, see above).

Light absorption spectra of dinuclear Cu(II)–D-sorbitol complex almost coincide in pH range (from 12.2 to 13.1), showing of formation a one-kind complex, *e. g.*, presumably a dinuclear Cu(II)–D-sorbitol complex Cu_2Sorb ($Sorb^{4-}$ is the anion of fourfold deprotonated D-sorbitol, presumably with deprotonated C1-C4 OH-groups). We presumed that D-sorbitol acts as a fourdentate ligand and the fourfold deprotonated D-sorbitol is involved in complex formation, since only deprotonated OH-groups can form sufficiently strong complexes in alkaline solutions [1, 37, 38]. Thus, the $pK_{a1,2,3,4}$ value highly approximately equals to 13.5 was used for calculations of equilibrium concentration of deprotonated anion of D-sorbitol.

Curve 1 in Fig. 2 represents the spectrum of Cu_2Sorb at pH 13.0, showing the light absorption

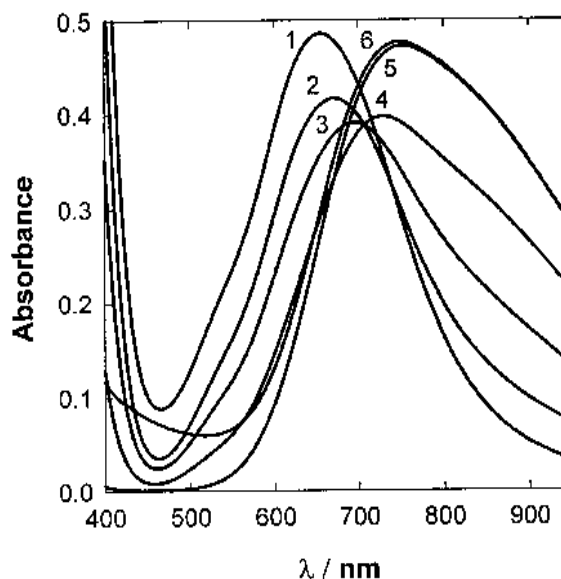


Fig. 2. Cu(II) light absorption spectra in alkaline solutions of D-sorbitol (1), EDTA (6) and their mixture (2–5). Solution composition (mol/l): $[Cu(II)]_0 = 0.010$; $[D-sorbitol]_0 = 0.005$; $[EDTA]_0$: 1 – 0, 2 – 0.005, 3 – 0.010, 4 – 0.020, 5 – 0.050, 6 – 0.020. Solution pH 13.00; 20 °C; $I = 1$

maximum at $\lambda = 655$ nm, the molar extinction coefficient (ϵ) being $97 \text{ mol}^{-1} \text{ l cm}^{-1}$.

Addition of EDTA into alkaline Cu(II)–D-sorbitol solution changes light absorption spectra, *i. e.* light absorbance decreases and light absorption maximum shifts to longer wavelengths with an increase in EDTA concentration up to 0.02 mol/l (Fig. 2). The resulting spectra demonstrate a conversion of Cu(II)–D-sorbitol complex into complex of $CuY(OH)^{3-}$ (Y^{4-} is the fourfold deprotonated anion of EDTA, pK_{a4} value being *ca.* 10.3 [12, 14]). Curve 6 in Fig. 2 represents the spectrum of $CuY(OH)^{3-}$ complex at pH 13.0.

When two complex compounds (in our case dinuclear Cu_2Sorb and $CuY(OH)^{3-}$) exist in equilibrium in the solution and their spectra differ, the concentrations of individual complexes can be calcu-

Table 1. Data on equilibria in the system Cu(II)–D-sorbitol(Sorb)–EDTA calculated from the spectrophotometric data of Fig. 1. $[Cu(II)]_0 = 0.010 \text{ mol/l}$, $[Sorb]_0 = 0.005 \text{ mol/l}$, pH 13.00

$[EDTA (H_4Y)]_0$, mol/l	$*[CuY(OH)^{3-}]$, mol/l	$*[Cu_2Sorb]$, mol/l	$[Y^{4-}]$, mol/l	$[Sorb]_0 - [Cu_2Sorb]$, mol/l	$[Sorb^-]$, mol/l	$\log[Cu(II)]$	$\log \beta_{Cu_2Sorb}$
0.005	0.0022	0.0039	0.0028	0.0011	0.00055	–20.13	41.1
0.010	0.0038	0.0031	0.0062	0.0019	0.00095	–20.24	41.0
0.020	0.0069	0.0016	0.0131	0.0034	0.0017	–20.31	40.6
0.050	0.0098	0.0001	0.0401	0.0049	0.00245	–20.63	39.9
							Mean: 40.7 ± 0.3

*Averages of the values calculated at 750, 800, 850 and 900 nm wavelengths.

lated from the experimental data obtained at different wavelengths according to [31].

The results obtained (Table 1) show that the quantities of Cu_2Sorb and $\text{CuY}(\text{OH})^{3-}$ complexes are comparable only at low concentrations of EDTA (up to 0.01 mol/l). With a further increase in EDTA concentration the amount of $\text{CuY}(\text{OH})^{3-}$ complex rises, and this complex predominates.

Knowing the concentrations of Cu(II) complexes existing in the solution under investigation, the equilibrium concentrations of deprotonated ligand forms and the concentration of free copper(II) ions can be calculated. Further the stability constant of Cu_2Sorb complex,

$$\beta = [\text{Cu}_2\text{Sorb}] / [\text{Cu}(\text{II})]^2 \cdot [\text{Sorb}^{4-}] \quad (2)$$

was calculated using the spectrophotometric data on Cu(II) distribution among the complexes (Table 1). The details of the calculation method are given in Part 1 [31].

The results obtained at different EDTA concentrations correlate well, the mean value of $\log \beta_{\text{Cu}_2\text{Sorb}}$ being 40.7 ± 0.3 (Table 1). It can be noted that the stability constants of dinuclear Cu(II) complexes with D-sorbitol and D-mannitol are almost the same and coincide in margins of error (*cf.* $\log \beta_{\text{Cu}_2\text{Man}} = 40.5 \pm 0.2$ [31]).

Cu(II) complex formation with D-sorbitol under conditions of ligand excess. No Cu(II)–D-sorbitol complex formation is observed at $\text{pH} < 10$, even if there is a considerable excess (1000 times) of D-sorbitol in the solution. Formation of the $\text{Cu}(\text{OH})_2$ precipitate is visually observed in the solution at $\text{pH} 8\text{--}10$, and there is actually no polarographic wave of Cu(II) reduction.

Single-stage quasi-reversible Cu(II) reduction waves are observed at higher pH ($\text{pH} > 11.0$). It was found that the limiting currents of Cu(II) reduction in alkaline solutions of D-sorbitol are diffusion-controlled – the limiting current dependence on the square root of the mercury column height is linear and the temperature coefficient of the limiting current is rather small and equals to *ca.* 1% per 1 °C (temperatures from 20 to 50 °C). It should be mentioned that at lower pH (from 11 to 12.5–13.2) and lower D-sorbitol concentrations (0.005 and 0.05 mol/l), the polarographic waves of Cu(II) reduction were two-stage (probably due the adsorption effects), therefore the values of the reversible half-wave potentials were not calculated and were not included in Fig. 3.

In the pH range from 11 to *ca.* 14 the polarographic waves of Cu(II) reduction in alkaline D-sorbitol solutions shift to more negative potentials (Fig. 3). This fact can be attributed to deprotonation of

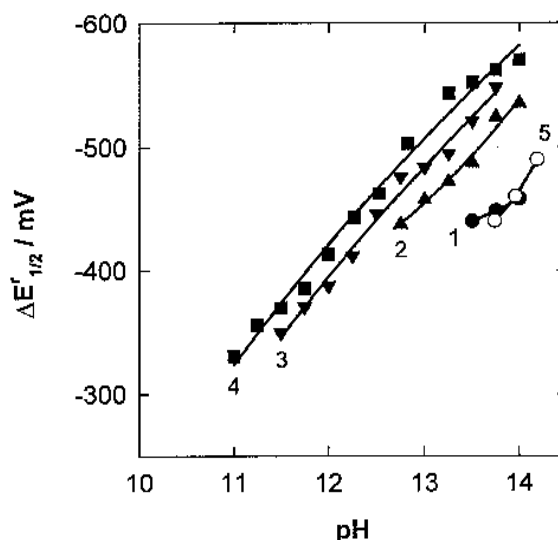


Fig. 3. Dependence of $\Delta E'_{1/2}$ of Cu(II) reduction on solution pH. Solution composition (mol/l): $[\text{Cu}(\text{II})]_0 - 0.0005$; $[\text{D-sorbitol}]_0$: ● – 0.005, ▲ – 0.05, ▼ – 0.2, ■ – 0.5, ○ – 0; 20 °C; $I = 1$

D-sorbitol in alkaline solutions and complex formation with Cu(II) ions. Thus, it is shown that undissociated D-sorbitol does not interact with Cu(II) ions, but the deprotonated D-sorbitol participates in complex formation with Cu(II) ions. The same tendency was observed when investigating Cu(II) complex formation with D-mannitol, another stereoisomer of D-sorbitol [31].

The slope of the half-wave potential shift depends on solution pH and D-sorbitol concentration (Fig. 3). At constant D-sorbitol concentrations (0.05–0.5 mol/l) the slope of the $\Delta E'_{1/2}$ dependences is equal to *ca.* 80–100 mV per pH unit, which for the single-stage two electron reduction of Cu(II) indicates coordination of Cu(II) with 3–4 ligand particles (presumably with D-sorbitol anion and OH^- ions). Since with increase in solution pH the activity of OH^- ions as well as the equilibrium concentration of the deprotonated form of D-sorbitol rise, the number of deprotonated D-sorbitol particles involved in complex formation can be determined from the slope of $\Delta E'_{1/2}$ on D-sorbitol concentration at constant pH values. The slopes equal to 35–70 mV were obtained with a tenfold increase in D-sorbitol concentration showing 1–2 anions of D-sorbitol taking part in complex formation.

Thus, the results showed the possible existence of Cu(II) complexes with two ligands – anions of D-sorbitol (analogous to D-mannitol [31], we suggest doubly deprotonated anion Sorb^{2-} , the $\text{p}K_a$ value being 13.5) and OH^- groups – with the general formula $\text{CuSorb}_n(\text{OH})_m^{2-2n-m}$, where $n = 1, 2$; $m = 1, 2, 3$; and $n + m = 3, 4$.

Calculations showed that all experimental data could be accounted for by presence in solution with pH 11–14 in appreciable concentrations of three kinds of complexes: $\text{CuSorb}(\text{OH})_2^{2-}$, $\text{CuSorb}_2(\text{OH})^{3-}$ and $\text{CuSorb}_2(\text{OH})_2^{4-}$ with the logarithms of stability constants 17.9 ± 0.3 , 20.1 ± 0.2 and 21.2 ± 0.2 , respectively. It should be noted that formation of tetrahydroxycuprate(II) – $\text{Cu}(\text{OH})_4^{2-}$ ($\log \beta_{\text{Cu}(\text{OH})_4^{2-}} = 15.5$ [15]) – was also considered in the calculations, and that the calculations showed no evidence of dinuclear Cu_2Sorb complex under conditions of a tenfold and higher excess of D-sorbitol in the solution. When comparing the results with these obtained for Cu(II)–D-mannitol system [31], we can conclude that the stability constant values of Cu(II) hydroxy-complexes containing two anions of D-sorbitol or D-mannitol are practically identical, *i. e.* coincide in margins of error. This fact is in agreement with data documented on the complexation of Cu(II) ions in alkaline solutions of L-tartrate and DL-tartrate, which showed practically no differences in Cu(II) complexation level in solutions of different tartrate stereoisomers whereas the spectral characteristics differed significantly [39].

The calculated distribution of Cu(II) among the complexes in alkaline solutions of D-sorbitol shows a complicated character of the complex equilibrium depending on solution pH and D-sorbitol concentration (Fig. 4 a–c). The results show that there is no region where the complex $\text{CuSorb}(\text{OH})_2^{2-}$, $\text{CuSorb}_2(\text{OH})^{3-}$ complex predominate at pH 11–12 in solutions containing thousandfold excess of D-sorbitol (Fig. 4c). The $\text{CuSorb}_2(\text{OH})_2^{4-}$ complex predominates in solutions at higher pH values (over 13.0) (Fig. 4a–c). It can be noted that calculations showed formation of appreciable amounts of $\text{Cu}(\text{OH})_4^{2-}$ at the highest pH studied and the lowest D-sorbitol concentrations used (Fig. 4a). This fact is in accordance with the data of Fig. 3, showing a possible transformation of Cu(II)–D-sorbitol complexes into $\text{Cu}(\text{OH})_4^{2-}$ under mentioned conditions (*cf.* curves 1 and 5 in Fig. 3).

Knowing Cu(II) distribution among the complexes with D-sorbitol and conditions of predominating of individual Cu(II)–D-sorbitol complexes, the diffusion coefficients of Cu(II) complex species were calculated from limiting current values of Cu(II) reduction (Table 2). The results, as in the case of

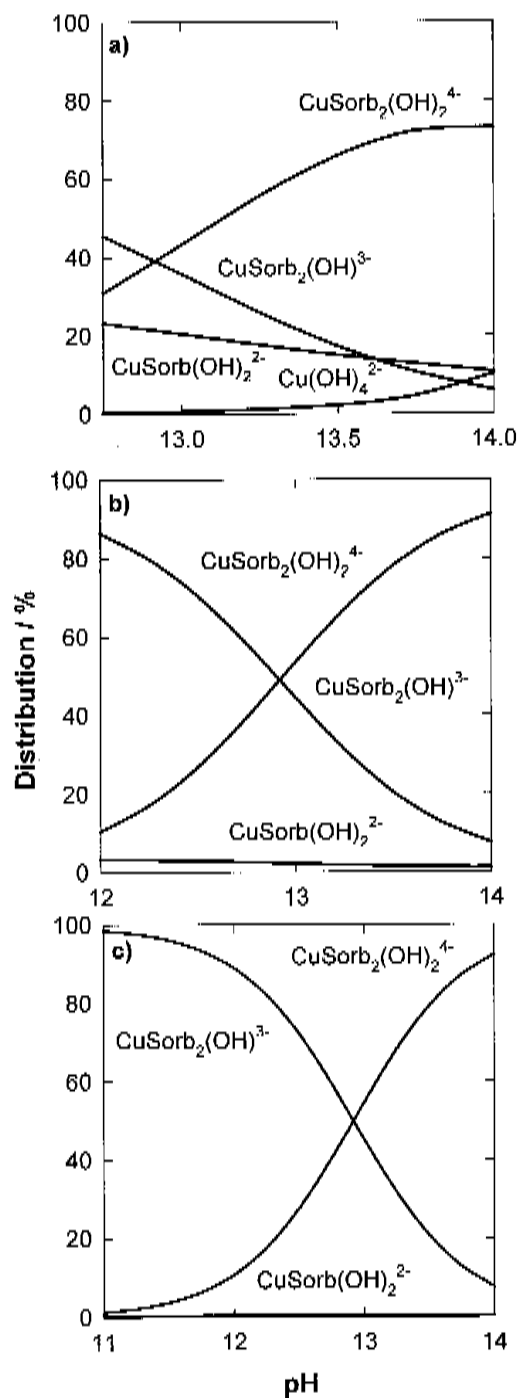


Fig. 4. Distribution of Cu(II) among the complexes in solutions containing (mol/l): $[\text{Cu}(\text{II})]_0 = 0.0005$; $[\text{D-sorbitol}]_0$: a) 0.005, b) 0.05, c) 0.5; 20 °C; $I = 1$ ($\log \beta_{\text{CuSorb}(\text{OH})_2^{2-}} = 17.9$, $\log \beta_{\text{CuSorb}_2(\text{OH})^{3-}} = 20.1$, $\log \beta_{\text{CuSorb}_2(\text{OH})_2^{4-}} = 21.2$, $\log \beta_{\text{Cu}(\text{OH})_4^{2-}} = 15.5$).

Table 2. Diffusion coefficient values of Cu(II) species with D-sorbitol calculated from polarographic data ($I = 1.0$; 20 °C)

Solution composition, mol/l	Predominating complex compound	$D \times 10^6, \text{cm}^2 \text{s}^{-1}$
$[\text{Cu}(\text{II})]_0 = 0.0005$, $[\text{Sorb}]_0 = 0.5$; pH 11.0	$\text{CuSorb}_2(\text{OH})^{3-}$	1.9
$[\text{Cu}(\text{II})]_0 = 0.0005$, $[\text{Sorb}]_0 = 0.2$; pH 14.0	$\text{CuSorb}_2(\text{OH})_2^{4-}$	1.6

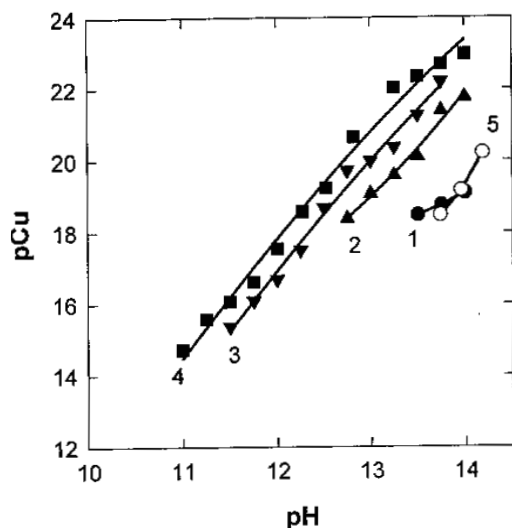


Fig. 5. Dependence of pCu on solution pH. Solution composition (mol/l): $[\text{Cu(II)}]_0 = 0.0005$; $[\text{D-sorbitol}]_0$: ● – 0.005, ▲ – 0.05, ▼ – 0.2, ■ – 0.5, ○ – 0; 20 °C; $I = 1$

Cu(II)-D-mannitol complexes, show a decrease in the diffusion coefficient value with an increase in the number of particles involved in complex composition. The values obtained are of the same order as those determined for Cu(II) complexes with D-mannitol [31].

The concentration of free (uncomplexed) Cu(II) ions calculated from $\Delta E_{1/2}^r$ values decreases with increase in D-sorbitol concentration and in solution pH, and ranges from *ca.* 10^{-14} to *ca.* 10^{-23} in the solutions investigated (Fig. 5), and is comparable with that obtained for Cu(II) in alkaline solutions of D-mannitol [31], glycerol or saccharose [40]. It can be noted that a comparison of complexation of Cu(II) ions in alkaline solutions of D-sorbitol with that in D-mannitol solutions in the same conditions shows Cu(II) complexation level being of the same order of magnitude.

A series of Cu(II) light absorption spectra were recorded in alkaline solutions of different pH containing 0.01 mol/l Cu(II) and different concentrations of D-sorbitol. The spectra obtained are complicated due to the presence in equilibrium of at least three kinds of Cu(II) complex species. The representative spectra are shown in Fig. 6.

On the grounds of the stability constants of Cu(II) complexes with D-sorbitol determined, the distribution of Cu(II) among the complexes for the spectrophotometric experiments was calculated and the conditions of predominating of individual Cu(II)-D-sorbitol complexes were found. The spectra of the solutions with predominating individual Cu(II)-D-sorbitol complexes are shown in Fig. 7. The values of the molar extinction coefficients of Cu(II)

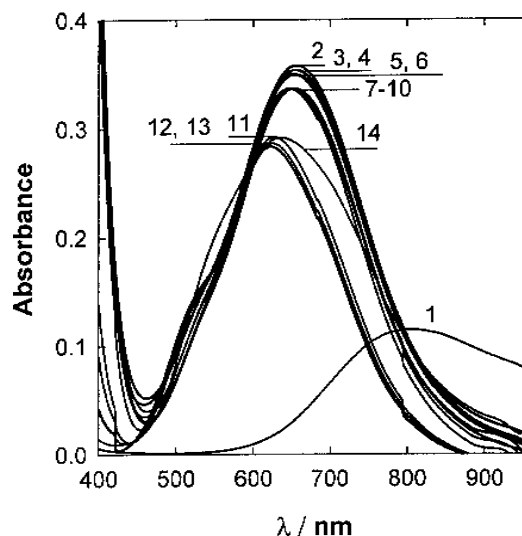


Fig. 6. Light absorption spectra of Cu(II)-D-sorbitol solutions containing (mol/l): $[\text{Cu(II)}]_0 = 0.01$; $[\text{D-sorbitol}]_0$: 2-13 – 0.1, 1 and 14 – 0.0. Solution pH: 1 – 4.00, 2 – 11.00, 3 – 11.25, 4 – 11.5; 5 – 11.75, 6 – 12.00, 7-10 – 12.25-13.00, 11 – 13.25, 12 – 13.50, 13 and 14 – 14.00; 20 °C; $I = 1$

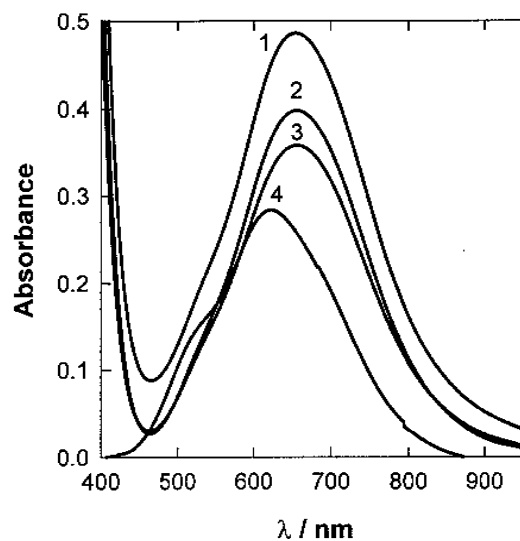


Fig. 7. Light absorption spectra of Cu(II)-D-sorbitol solutions with the dominating complexes: 1 – Cu_2Sorb (0.005 mol/l D-sorbitol; pH 13.00); 2 – $\text{CuSorb}(\text{OH})_2^{2-}$ (0.01 mol/l D-sorbitol; pH 12.00); 3 – $\text{CuSorb}_2(\text{OH})_3^{3-}$ (0.1 mol/l D-sorbitol; pH 11.00); 4 – $\text{CuSorb}_2(\text{OH})_4^{4-}$ (0.1 mol/l D-sorbitol; pH 14.00). $[\text{Cu(II)}]_0 = 0.01$ mol/l; 20 °C; $I = 1$

complexes with D-sorbitol were calculated and are presented in Table 3.

The spectral characteristics of Cu(II)-D-sorbitol complexes differ to some extent from those of Cu(II)-D-mannitol complexes presented in [31]. The values of the molar extinction coefficient of Cu(II)-D-sorbitol complexes are fractionally lower and the λ_{max} values are shifted to longer wavelengths by 5–

Table 3. Optical characteristics of Cu(II) complexes with D-sorbitol ($I = 1.0$; 20 °C)

Solution composition, mol/l	Predominating complex compound	λ , nm	ϵ , mol ⁻¹ l cm ⁻¹
[Cu(II)] ₀ – 0.01, [Sorb] ₀ – 0.005; pH 13.00	Cu ₂ Sorb	655	97
[Cu(II)] ₀ – 0.01, [Sorb] ₀ – 0.01; pH 11.97	CuSorb(OH) ₂ ²⁻	655	49
[Cu(II)] ₀ – 0.01, [Sorb] ₀ – 0.5; pH 11.25	CuSorb ₂ (OH) ³⁻	655	40
[Cu(II)] ₀ – 0.01, [Sorb] ₀ – 0.5; pH 13.75	CuSorb ₂ (OH) ₂ ⁴⁻	625	28

10 nm as compared to the values obtained for Cu(II)–D-mannitol complexes of the same composition. The results obtained are in accordance with earlier documented data on Cu(II) complex formation with a natural isomer of L-tartrate and racemic mixture of isomers, *i. e.* DL-tartrate, which showed a difference in the spectra of Cu(II) complexes with different tartrate stereoisomers [39].

CONCLUSIONS

1. Under conditions of ligand lack, copper(II) reacts with the anion of D-sorbitol in alkaline solutions ($12.2 \leq \text{pH} \leq 13.1$), forming a dinuclear 2:1 complex Cu₂Sorb with the stability constant logarithm value equal to 40.7 ± 0.3 and the molar extinction coefficient (ϵ) equal to 97 ($\lambda_{\text{max}} = 655 \text{ nm}$).

2. Under conditions of a tenfold or higher excess of D-sorbitol, in alkaline solutions ($11.0 \leq \text{pH} \leq 14.0$) the complex compounds CuSorb(OH)₂²⁻, CuSorb₂(OH)³⁻ and CuSorb₂(OH)₂⁴⁻ are formed, the logarithms of stability constants being 17.9 ± 0.3 , 20.1 ± 0.2 and 21.2 ± 0.2 , respectively.

3. The calculated diffusion coefficient values of CuSorb₂(OH)³⁻ and CuSorb₂(OH)₂⁴⁻ are $1.9 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$ and $1.6 \times 10^{-6} \text{ cm}^2 \text{ s}^{-1}$, respectively.

4. Comparison of complexation of Cu(II) ions in alkaline solutions of D-sorbitol with that in D-mannitol solutions in the same conditions shows the Cu(II) complexation level to be of the same order of magnitude.

5. The spectral characteristics determined show that the values of the molar extinction coefficient of Cu(II)–D-sorbitol complexes are fractionally lower and λ_{max} values are shifted to longer wavelengths by 5–10 nm as compared to the values obtained for Cu(II)–D-mannitol complexes of the same composition.

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References

1. J.-F. Verchère, S. Chapelle, F. Xin, and D. C. Crans, in *Progress in Inorganic Chemistry*, vol. 47, ed. K. D. Karlin, John Wiley & Sons, New York, 837 (1998).
2. F. Franks, J. Dadok, S. Ying, R. L. Kay, and J. R. Grigera, *J. Chem. Soc., Faraday Trans.*, **87**, 579 (1991).
3. P. Rys and H. Zollinger, *Helv. Chim. Acta*, **49**, 761 (1966).
4. P. Rys and H. Zollinger, *Helv. Chim. Acta*, **49**, 1406 (1966).
5. L. Michaelis, *Ber. Deutsch. Chem. Ges.*, **46**, 3683 (1913).
6. J. Murto, *Acta Chem. Scand.*, **18**, 1043 (1964).
7. M. Vicedomini, *Ann. Chim. (Rome)*, **71**, 213 (1981).
8. E. Bottari, D. Cellulosi, and M. R. Festa, *Talanta*, **50**, 993 (1999).
9. M. Pospisilova, M. Polasek, and V. Jokl, *J. Pharm. Biomed. Analysis*, **17**, 387 (1998).
10. V. A. Nazarenko and L. D. Ermak, *Zh. Neorg. Khim.*, **12**, 643 (1967).
11. B. L. Velikov and J. Doležal, *J. Electroanal. Chem.*, **71**, 91 (1976).
12. *Stability Constants of Metal-ion Complexes. Special Publication No 17*, Supplement No 1, eds. L. G. Sillen and A. E. Martell, Chemical Society, London, 1971.
13. *Stability Constants of Metal-ion Complexes. Part A: Inorganic Ligands*, ed. E. Högfeld, Pergamon Press, Oxford, 1982.
14. *Stability Constants of Metal-ion Complexes. Special Publication No 25*, Supplement No 1, eds. L. G. Sillen and A. E. Martell, Chemical Society, London, 1964.
15. E. Norkus and A. Vačkeliš, *Polyhedron*, **13**, 3041 (1994).
16. L. L. Landucci and N. Sanyer, *Tappi*, **57**, 97 (1974).
17. D. T. Richens, C. G. Smith, and D. T. Sawyer, *Inorg. Chem.*, **18**, 706 (1979).

18. M. Vicedomini, *Gazz. Chim. Ital.*, **98**, 1161 (1968).
19. Y. Israeli, J. P. Morel, and N. Morel-Desrosiers, *Carbohydr. Res.*, **263**, 25 (1994).
20. P. Rongčre, N. Morel-Desrosiers, and J. P. Morel, *J. Chem. Soc., Faraday Trans.*, **91**, 2771 (1995).
21. H. Winkler, W. Meyer, A. X. Trautwein, K. Hegetschweiler, and H. F. Nolting, *Physica B*, **209**, 733 (1995).
22. H. W. Rich, K. Hegetschweiler, H. M. Streit, I. Erni, and W. Schneider, *Inorg. Chim. Acta*, **187**, 9 (1991).
23. D. Chen, A. E. Martell, R. J. Motekaitis, S. Q. Niu, and D. McManus, *Inorg. Chim. Acta*, **293**, 206 (1999).
24. V. P. Roldan, V. A. Daier, B. Goodman, M. I. Santoro, J. C. Gonzalez, N. Calisto, S. R. Signorella, and L. F. Sala, *Helv. Chim. Acta*, **83**, 3211 (2000).
25. A. Cervilla, J. A. Ramirez, and A. Beltran-Porter, *Transition Met. Chem.*, **8**, 21 (1983).
26. M. Mikesova and M. Bartusek, *Coll. Czech. Chem. Commun.*, **43**, 1867 (1978).
27. P. Klüfers and J. Schuhmacher, *Angew. Chem.*, **34**, 2119 (1995).
28. S. J. Angyal, *Carbohydr. Res.*, **200**, 181 (1990).
29. L. Nagy, L. Zsikla, K. Burger, A. Rockenbauer, and J. T. Kiss, *J. Crystallogr. Spectrosc. Res.*, **19**, 911 (1989).
30. A. M. Sakharov, N. T. Silakhtaryan, and I. P. Skibida, *Kinet. Katal.*, **37**, 393 (1996).
31. E. Norkus, J. Vaičiūnienė, J. Reklaitis, E. Gaidamauskas, and D. C. Crans, *Chemija (Vilnius)*, in press.
32. E. Norkus and A. Vaškėlis, *Polyhedron*, **13**, 3041 (1994).
33. E. Norkus, A. Vaškėlis, I. Žakaitė, and J. Reklaitis, *Talanta*, **42**, 1701 (1995).
34. E. Norkus, A. Vaškėlis, and I. Žakaitė, *Talanta*, **43**, 465 (1996).
35. E. Norkus and R. Pauliukaitė, *Polish. J. Chem.*, **74**, 1231 (2000).
36. K. Bock and C. Pedersen, *Adv. Carbohydr. Chem. Biochem.*, **41**, 27 (1983).
37. K. Burger and L. Nagy, in *Biocoordination Chemistry: Coordination Equilibria in Biologically Active Systems*, ed. K. Burger, Ellis Horwood, Chichester, 236 (1990).
38. S. Yano, *Coord. Chem. Rev.*, **92**, 113 (1988).
39. E. Norkus, A. Vaškėlis, I. Žakaitė, and J. Reklaitis, *Chemija (Vilnius)*, N 2, 16 (1997).
40. E. Norkus, *State of Cu(II) Ions in Alkaline Solutions for Electroless Copper Plating*, PhD Theses, Institute of Chemistry and Chemical Technology, Vilnius, 1988.

E. Norkus, J. Vaičiūnienė, J. Reklaitis, Debbie C. Crans

PEREINAMŪJŲ METALŲ JONŲ KOMPLEKSINIŲ FORMŲ NUSTATYMAS ŠARMINIUOSE ALDITOLIŲ TIRPALUOSE

2. CU(II) KOMPLEKSAI SU D-SORBITOLIŲ

S a n t r a u k a

Nuolatinės srovės poliarografijos ir matomosios šviesos spektro dalies spektrofotometrijos metodais tiriant Cu(II) kompleksų susidarymą su D-sorbitoliu šarminėje terpėje ($11,0 \leq \text{pH} \leq 14,0$; $20\text{ }^\circ\text{C}$, $I = 1,0$), nustatyta, kad tirpaluose gali susidaryti keturių rūšių kompleksinės dalelės. Esant ligando trūkumui, susidaro dibranduolinis kompleksas Cu_2Sorb ($\log \beta_{\text{Cu}_2\text{Sorb}} = 40,7 \pm 0,3$). Kai tirpaluose yra dešimtubas ar didesnis ligando perteklius, priklausomai nuo tirpalo pH vertės ir ligando koncentracijos susidaro trys kompleksiniai junginiai – $\text{CuSorb}(\text{OH})_2^{2-}$, $\text{CuSorb}_2(\text{OH})_3^{3-}$ ir $\text{CuSorb}_2(\text{OH})_2^{4-}$, kurių patvarumo konstantų logaritmai lygūs atitinkamai $17,9 \pm 0,3$, $20,1 \pm 0,2$ ir $21,2 \pm 0,2$. Nustatyti kompleksinių dalelių difuzijos koeficientai bei optinės charakteristikos.