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The Spectrophotometry Determination of Chelate Complex: L-Ascorbic Acid with Cuprum (II) and Mercury (II) in Alkaline Solution

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Abstract

The aim of this paper is to present the chemical behaviour of cuprum (II) and mercury (II) in chelate complexes with L-ascorbic acid in alkaline solution. The results were interpreted by the spectroscopy method. Composition and total stability constants of the complexes were determined by the Jacymirski method. In solution in with pH = 9, H_2 Asc forms complexes of the type $[Me(Asc)_2]^{-2}$; Me : L = 1:2. The complexes are of medium stability.

Keywords: L-ascorbic acid, cuprum (II), mercury (II), spectrophotometry, chelate complex

Introduction

Our interest in L-ascorbic acid (H_2Asc) comes, despite its major biological role as vitamin C [1-4]. From that, studies of this interaction with metal ions are limited.

According to literature, the principal mechanism of this reaction is presented either as the oxidation of L-ascorbic acid to L-dehydroascorbic acid (Asc), via the free radical (HAsc*) from similarly to the reaction of H_2Asc with Cu(II) [5-8]:

$$H_2Asc + Cu(II) \leftrightarrow HAsc^* + Cu(I) + H^+$$
$$2HAsc^* \leftrightarrow H_2Asc + Asc$$

or by the formation of a complex [9, 10].

In recent years, particular attention has been paid to studies on the complexation of important bioelements with biologically active ligands **[11-13].** The presence of the dienol group (Fig. 1) in the molecule of the L-ascorbic acid allows us to assume possible complexation of the compounds with metal ions [10, 12-14].

Few authors have dealt with metal ascorbinate, and therefore, these complexes are not yet completely known. Relatively great attention has been paid to ascorbinate complexes of transition metals [9, 13-15] and lanthanide series [9]. This is associate probably with the role of cuprum and mercury in living organisms. The present study comprises investigation on ascorbinate complexes of Cu(II) and Hg(II) in alkaline solution.

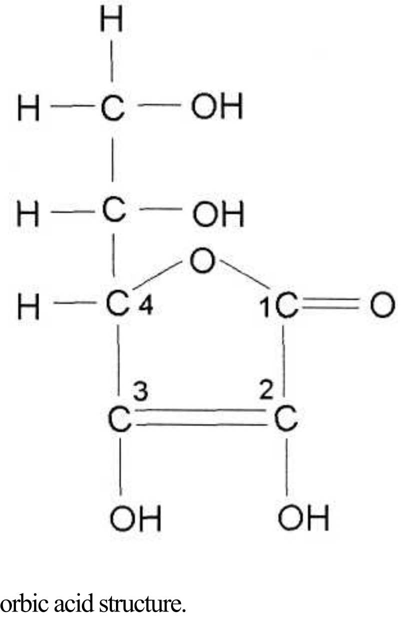


Fig. 1. L-ascorbic acid structure.

Experimental Procedures

Analar L-ascorbic acid manufactured by Fluka was used. The basic solutions of metal salts were used in the form of nitrates $Cu(NO_3)_2$ and $Hg(NO_3)_2$ analar grate of Gliwice. The pH value of the solutions investigated was adjusted with standard solutions of NaOH - Gliwice, prepared from analar reagents. Ionic strength was controlled with $NaNO_3$, analar grate Gliwice. L-ascorbic acid (vitamin C), $C_6H_8O_6$, H_2Asc reagent:

- stock solution with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was obtained by dissolving 0.176 g of the substance in a measuring flask of 100 cm^3 capacity.

Copper (II) nitrate (V), $Cu(NO_3)_2 \cdot 3H_2O$ reagent:

- stock solution with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was obtained by dissolving 0.242 g of the substance in a measuring flask of 100 cm^3 capacity.

Mercury(II) nitrate (V), $Hg(NO_3)_2 \cdot H_2O$ reagent:

- stock solution with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was obtained by dissolving 0.363 g of the substance in a measuring flask of 100 cm^3 capacity.

UV absorption spectra within the range of 190-350 cm^{-1} of aqueous solution of L-ascorbic acid with the concentration of $1 \cdot 10^{-4}$ mol/dm^3 were completed.

The following procedure was used: 1 cm^3 of the solution of L-ascorbic acid with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was added to a 100 cm^3 measuring flask and then it was made up to the mark with water.

UV absorption spectra of aqueous solution of L-dehydroascorbic acid within the range of 190-350 cm^{-1} were carried out.

The following procedure was used: 1 cm^3 of the solution of L-ascorbic acid with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was added to a 100 cm^3 measuring flask and was then made up to the mark with water. Then, the obtained solution was exposed to UV. After 24 hours the absorbency of the solution against water as reference material was measured.

In order to examine the influence of the medium on absorption of L-ascorbic acid, UV spectra within the range of 190-350 cm^{-1} in solutions at different pH were done. The examinations were done directly after blending and after 24 hours and exposure to UV.

The following procedure was used: 1 cm^3 of the solution of L-ascorbic acid with the concentration of $1 \cdot 10^{-2}$ mol/dm^3 was added to a 100 cm^3 measuring flask and then the solution of NaOH with proper concentration was added in such quantity that, after making up to the mark, pre-determined pH, e.g. pH = 9, could be obtained.

Solutions of NaOH or sodium base with suitable pH were used as reference material.

UV-VIS absorption spectra of aqueous solutions of copper and mercury within the range of 190-900 cm^{-1} were done to obtain the characteristics of copper and mercury.

The following procedure was used: in a 100 cm^2 measuring flask the solutions of the examined compounds with the concentration of $1 \cdot 10^{-2}$ were prepared by dissolving an appropriate weighed amount. Then, the absorbency of the solution against water was measured.

In order to investigate the influence of the medium on the shift of absorption maximum of examined metals, UV-VIS absorption spectra of the examined compounds within the range of 190-800 cm^{-1} in solutions with different pH values were done.

The following procedure was used: in a 100 cm^3 measuring flask the solution of the examined metal with the concentration of $1 \cdot 10^{-2}$ was prepared. Then the solution of sodium base with proper concentration was added. Suitable solutions of NaOH or sodium base with proper pH were used as reference material.

The solution containing L-ascorbic acid with lower concentration and sodium nitrate with concentrations equal to the examined solution were used as reference material.

UV spectra of L-ascorbic acid, its complex with cuprum (II) and mercury (II) and L-dehydroascorbic acid, in aqueous solution, were carried out with a CESIL INSTRUMENTS CE 8020 spectrophotometer.

Results and Discussion

I. Preliminary study

The mechanism of reaction L-ascorbic acid - metal is dependant on the pH of the reacting solution. It is known that the pH of solution strongly influences the spectrophotometric characteristic of L-ascorbic acid and metal ions [3, 4, 7]. In connection with this, the influence of pH on shape and positions of absorption bands of L-ascorbic acid, L-dehydroascorbic acid and metal ions was examined at the beginning of the work. For this purpose, the absorption

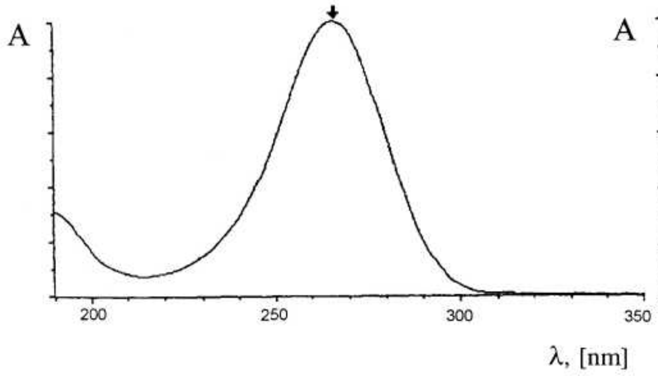


Fig. 2a. Spectrophotometry curve of L-ascorbic acid pH = 7.

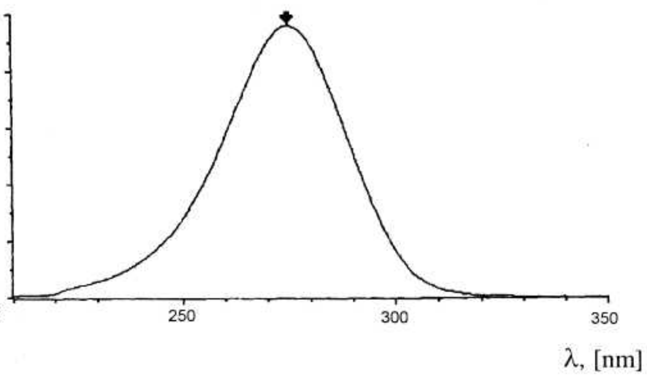


Fig. 2b. Spectrophotometry curve of L-ascorbic acid pH = 9.

Table 1.The λ_{max} values and molar absorption coefficients (ε) of H_2Asc solutions at different pH values.

pH	λ_{max}	ε[dm³ mol⁻¹ cm⁻¹]
7	266	$1.05 \cdot 10^4$
9	276	$1.81 \cdot 10^4$

spectra of aqueous solution of all reactants were recorded. The results are assembled in Tables 1-3.

It was observed that aqueous solutions of L-ascorbic acid with the concentration of 1 • 10^{-4} mol/dm^3 show very characteristic bands in UV spectrum, with maxims at 266 in neutral solution and 276 nm in alkaline solution (Table 1, Figs. 2a and 2b).

After that, it was noted that L-dehydroascorbic acid aqueous solution (at a concentration of 1 • 10^{-4} mol/dm^3), shows maximum absorption at λ_{max} = 300 nm. Next, the influence of the medium was examined. For that purpose the UV spectra of L-dehydroascorbic acid in solutions at different pH were done. Obtained λ_{max} (Fig. 3) and molar absorption coefficients are shown in Table 2.

The results of the examination show that pH has little influence on the location of L-dehydroascorbic acid signals.

In Table 3 and Fig. 4 we show aqueous solution with the concentration of 1 • 10^{-4} mol/dm^3 of various nitrates Cu(II) and Hg(II) at different pH.

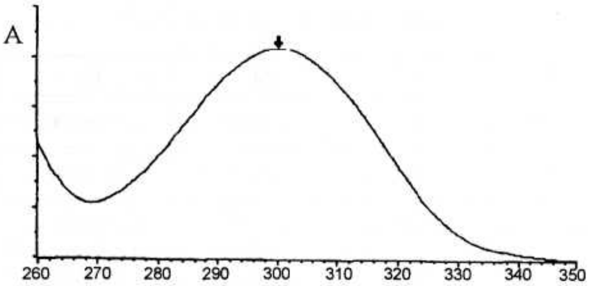


Fig. 3. Spectrophotometry curve of L-ascorbic acid pH = 9.

Table 2. The λ_{max} values and molar absorption coefficients (ε) of Asc solutions at different pH values.

pH	λ_{max} [nm]	ε[dm³ mol⁻¹ cm⁻¹]
7	300	$3.5 \cdot 10^3$
9	302	$3.4 \cdot 10^3$

Table 3. The λ_{max} values and molar absorption coefficients (ε) of various nitrates Cu(II) and Hg(II) solutions at different pH values.

Metal	pH	λ_{max} [nm]	ε [dm³ mol⁻¹ cm⁻¹]
Cu(II)	7	212	$2.75 \cdot 10^5$
	9	204	$1.29 \cdot 10^5$
Hg(II)	7	202	$4.04 \cdot 10^4$
	9	200	$3.43 \cdot 10^4$

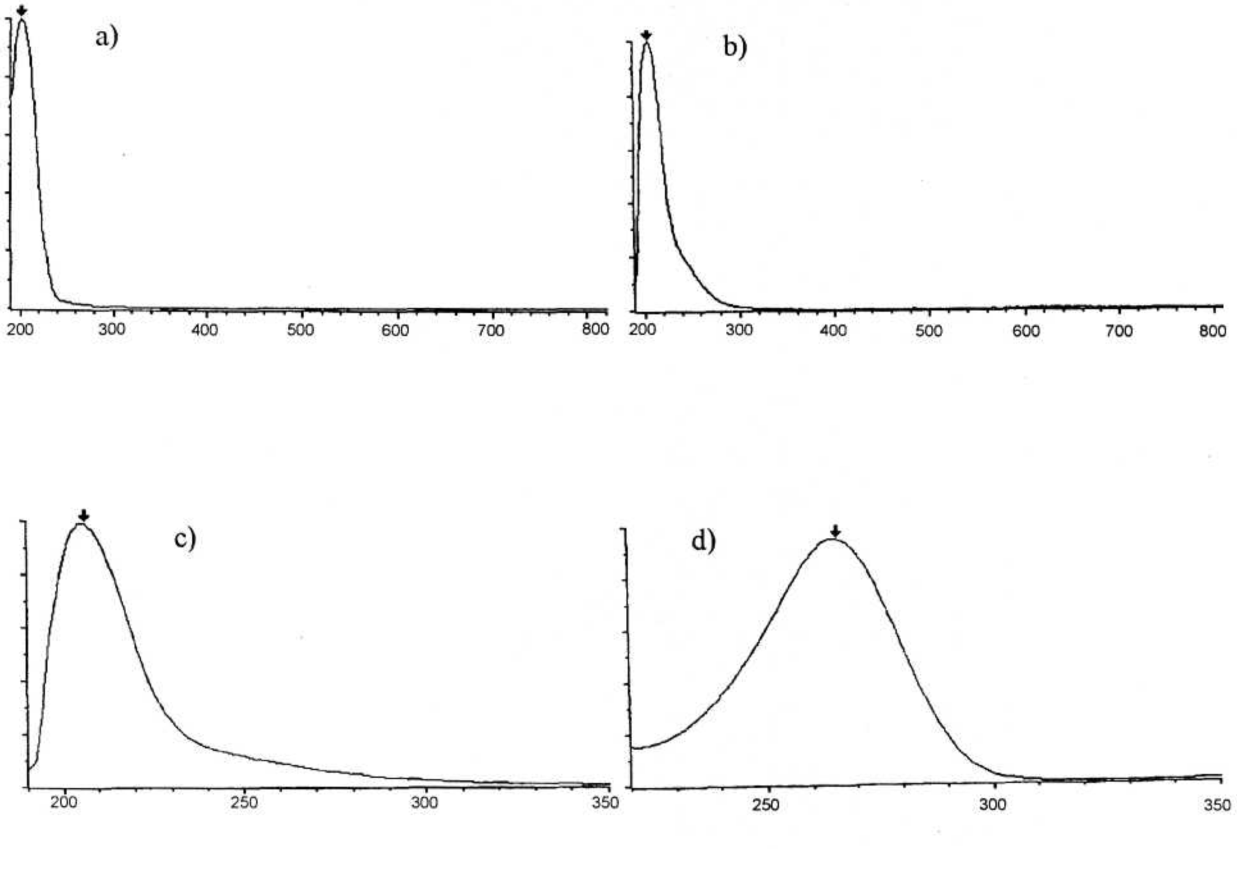


Fig. 4. Spectrophotometry curves of cuprum(II): a - pH = 7, b - pH = 9 and mercury(II): c - pH = 7, d - pH = 9.

Table 4. Some exemplary stability constants calculated using the Jacymirski method (e.g. L-ascorbic acid -cuprum (II)).

A	$\bar{\varepsilon}$	$\Delta\bar{\varepsilon}$	C_L	f_1	f_2	1/[L]	ϕ_1
0.155	25833	-116847	1.50E-06	-7.8E+10	2.62E+16	6.66E+05	-2.32E-02
0.162	27050	-115630	3.00E-06	-3.9E+10	2.62E+16	3.33E+05	-4.28E-02
0.167	27883	-114797	6.00E-06	-1.9E+10	1.64E+16	1.66E+05	-8.08E-02
0.180	29920	-112760	1.20E-05	-9.4E+09	8.99E+15	8.30E-04	-1.37E-01
0.194	32250	-110430	1.80E-05	-6.1E+09	6.17E+15	5.50E-04	-1.65E-01
0.206	34390	-108290	2.40E-05	-4.5E+09	4.70E+15	4.20E-04	-1.65E-01

Table 5. Some exemplary stability constants calculated with the Jacymirski method (e.g. L-ascorbic acid-mercury (II)).

A	$\bar{\varepsilon}$	$\Delta\bar{\varepsilon}$	C_L	f_1	f_2	1/[L]	ϕ_1
0.1305	3263	-15237	1.00E-05	-1.52E+09	9.25E+13	1.00E+05	-0.242
0.1586	3966	-14534	2.00E-05	-7.27E+08	7.86E+13	5.00E+04	-0.469
0.0204	510	-17990	4.00E-05	-4.50E+08	4.63E+13	2.50E+04	-1.080
0.2539	6348	-12152	8.00E-05	-1.52E+08	2.68E+13	1.25E-04	-1.600
0.4905	12263	-6237	1.20E-04	-5.27E+07	1.87E+13	8.33E-03	-1.920
0.6923	17307	-1193	1.60E-04	-7.46E+06	1.43E+13	6.25E-03	-2.140

Analyzing the absorption spectra of the above compounds at pH, one can conclude that the absorption maxima are practically equal at range 7-9.

II. The study of reaction of L-ascorbic acid - Cu(II) and L-ascorbic acid - Hg(II).

In solution L-ascorbic acid behaves as a weak dibasic acid, which dissociates in two steps. In the first step one hydrogen ion is released:

$$H_2Asc \leftrightarrow H^+ + Hasc^-$$

The corresponding ionization constant can be expressed as:

$$Hasc^- \leftrightarrow H^+ + Asc^{2-}$$

(using concentrations instead of activities). The value of the ionization constant for the stronger acid hydrogen has been determined by several authors. Most reliable values were obtained by Birch and Harris [7] ($K_1 = 6.77 \cdot 10^{-5}$, $pK_1 = 4.17$) and later by Ball [7]. In the text, Ball's data, e.g. $K_1 = 6.2 \cdot 10^{-5}$ ($pK_1 = 4.21$) will be employed as the ionization constant and its exponent, respectively, for the first dissociation step.

In the second dissociation step a further hydrogen ion is released. Birch and Harris obtained the value $K_2 = 2.69 \cdot 10^{-12}$ ($pK_2 = 11.57$).

The run of reaction L-ascorbic acid - metal ions was followed spectrophotometrically using the following proce-

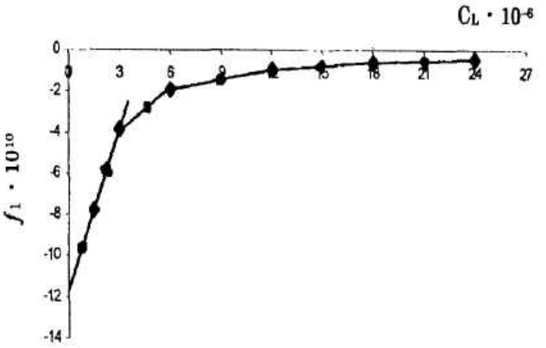


Fig. 5. Dependence of function f_1 on C_L; $a_1 = -11.726 \cdot 10^{10}$.

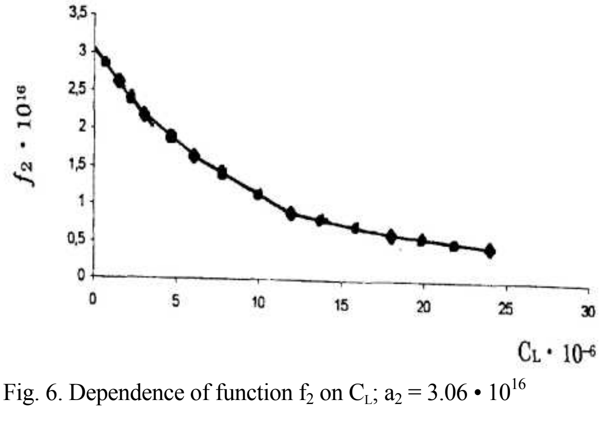


Fig. 6. Dependence of function f_2 on C_L; $a_2 = 3.06 \cdot 10^{16}$

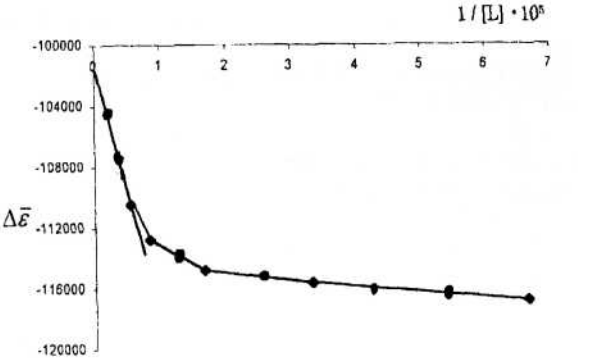


Fig. 7. Depencence of function Δε e on 1/[L].

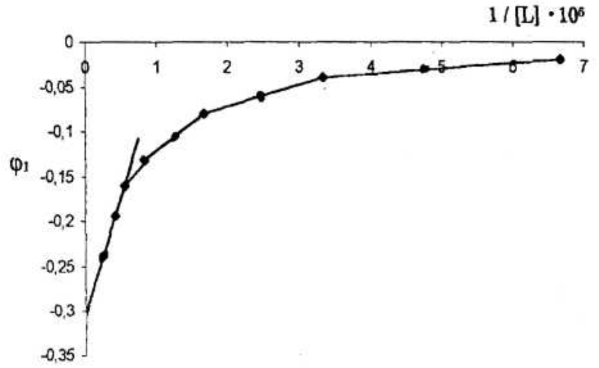


Fig. 8. Dependence of function φ1 on 1/[L].

dure. The 89 ml portion of 1 • 10^{-4} mol/dm^3 $Cu(NO_3)_2$ aqueous solution was placed into a 100 ml glass-tube. Next, the 10 ml of 1 • 10^{-2} mol/dm^3 aqueous solution of H_2Asc were added. The pH of reacting solution was adjusted using 1 • 10^{-2} mol/dm^3 NaOH. We have in solution Asc^{2-} ion, because the Asc^{-2} ion can only exist in alkaline medium. Then, the mixture was shaken vigorously and was recorded.

In alkaline medium at pH = 9 the following complexes are formed:

- cuprum (II) and L-ascorbic acid with maximum absorption at 206 nm, and
- mercury (II) and L-ascorbic acid with maximum absorption at 266 nm

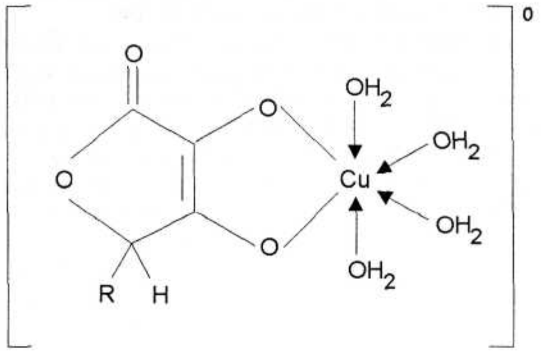
The stability constants was calculated using the of Jacymirski method [17, 18] (Tables 4, 5 and Figs. 5-8).

The stability constants calculated by the Jacymirski method show in Table 6.

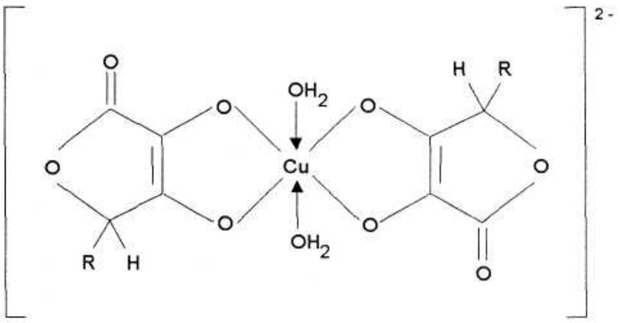
Table 6. The stability constant chelate complex.

Metal	β_1	β_2
Cu(II)	$2.52 \cdot 10^5$	$5.95 \cdot 10^9$
Hg(II)	$1.56 \cdot 10^4$	$4.60 \cdot 10^8$

From the spectrometric examination one may concluded that in the alkaline medium this ratio is 1:2. We suggested structure of chelate complex [15, 16] L-ascorbic acid : cuprum (II)



$[Cu(Asc)]^0$



and $[Cu(Asc)_2]^{2-}$

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