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, H₂Asc forms complexes of the type [Me(Asc)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 (H₂Asc) 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 H₂Asc with Cu(II) [5-8]:

\[ H₂Asc + Cu(II) \leftrightarrow HAsc* + Cu(I) + H^+ \]

\[ 2HAsc* \leftrightarrow H₂Asc + Asc \]

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 ascorbate 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 ascorbinat e 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(NO₃)₂ and Hg(NO₃)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 NaNO₃, analar grate Gliwice. L-ascorbic acid (vitamin C), C₆H₈O₆, H₂Asc reagent:
- stock solution with the concentration of 1 • 10⁻² mol/dm³ was obtained by dissolving 0.176 g of the substance in a measuring flask of 100 cm³ capacity.
- stock solution with the concentration of 1 • 10⁻² mol/dm³ was obtained by dissolving 0.242 g of the substance in a measuring flask of 100 cm³ capacity.
- stock solution with the concentration of 1 • 10⁻² mol/dm³ was obtained by dissolving 0.363 g of the substance in a measuring flask of 100 cm³ capacity.

UV absorption spectra within the range of 190-350 cm⁻¹ of aqueous solution of L-ascorbic acid with the concentration of 1 • 10⁻⁴ mol/dm³ were completed.

The following procedure was used: 1 cm³ of the solution of L-ascorbic acid with the concentration of 1 • 10⁻² mol/dm³ was added to a 100 cm³ 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 cm³ of the solution of L-ascorbic acid with the concentration of 1 • 10⁻² mol/dm³ was added to a 100 cm³ measuring flask and then it was made up to the mark with water.

In order to examine 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 cm³ measuring flask the solution of the examined compound with the concentration of 1 • 10⁻² was 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 cm³ measuring flask the solution of the examined metal with the concentration of 1 • 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.
The spectra of aqueous solutions 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 $1 \times 10^{-4}$ mol/dm$^3$ show very characteristic bands in UV spectrum, with maxima 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 $1 \times 10^{-4}$ mol/dm$^3$), shows maximum absorption at $\lambda_{\text{max}} = 300$ 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 $\lambda_{\text{max}}$ (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 $1 \times 10^{-5}$ mol/dm$^3$ of various nitrates Cu(II) and Hg(II) at different pH.

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**Table 1.** The $\lambda_{\text{max}}$ values and molar absorption coefficients ($\varepsilon$) of H$_2$Asc solutions at different pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>266</td>
<td>$1.05 \times 10^4$</td>
</tr>
<tr>
<td>9</td>
<td>276</td>
<td>$1.81 \times 10^4$</td>
</tr>
</tbody>
</table>

**Table 2.** The $\lambda_{\text{max}}$ values and molar absorption coefficients ($\varepsilon$) of Asc solutions at different pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>300</td>
<td>$3.5 \times 10^3$</td>
</tr>
<tr>
<td>9</td>
<td>302</td>
<td>$3.4 \times 10^3$</td>
</tr>
</tbody>
</table>

**Table 3.** The $\lambda_{\text{max}}$ values and molar absorption coefficients ($\varepsilon$) of various nitrates Cu(II) and Hg(II) solutions at different pH values.

<table>
<thead>
<tr>
<th>Metal</th>
<th>pH</th>
<th>$\lambda_{\text{max}}$ (nm)</th>
<th>$\varepsilon$ (dm$^3$ mol$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>7</td>
<td>212</td>
<td>$2.75 \times 10^5$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>204</td>
<td>$3.3 \times 10^5$</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>7</td>
<td>202</td>
<td>$4.04 \times 10^4$</td>
</tr>
<tr>
<td></td>
<td>9</td>
<td>200</td>
<td>$3.43 \times 10^4$</td>
</tr>
</tbody>
</table>

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

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

\[ \text{H}_2\text{Asc} \leftrightarrow \text{H}^+ + \text{Hasc}^- \]

The corresponding ionization constant can be expressed as:

\[ \text{Hasc}^- \leftrightarrow \text{H}^+ + \text{Asc}^{2-} \]

(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] \( (K_1 = 6.77 \times 10^{-5}, \ pK_1 = 4.17) \) and later by Ball [7]. In the text, Ball’s data, e.g. \( K_1 = 6.2 \times 10^{-5} \) \( (pK_1 = 4.21) \) 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 \( K_2 = 2.69 \times 10^{-12} \) \( (pK_2 = 11.57) \).

The run of reaction L-ascorbic acid - metal ions was followed spectrophotometrically using the following proce-
The 89 ml portion of $1 \cdot 10^{-4}$ mol/dm$^3$ Cu(NO$_3$)$_2$ aqueous solution was placed into a 100 ml glass-tube. Next, the 10 ml of $1 \cdot 10^{-2}$ mol/dm$^3$ aqueous solution of H$_2$Asc were added. The pH of reacting solution was adjusted using $1 \cdot 10^{-2}$ 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.

<table>
<thead>
<tr>
<th>Metal</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu(II)</td>
<td>$2.52 \cdot 10^9$</td>
<td>$5.95 \cdot 10^9$</td>
</tr>
<tr>
<td>Hg(II)</td>
<td>$1.56 \cdot 10^7$</td>
<td>$4.60 \cdot 10^7$</td>
</tr>
</tbody>
</table>

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)

References

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