

Complexes of bismuth(III) with ethylenediamine-*N,N'*-2,2'-di-(3-hydroxypropionic) acid

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Dedicated to Professor J. Majer, Corresponding Member of the Slovak Academy of Sciences, on his 50th birthday

The reaction of Bi(III) with ethylenediamine-*N,N'*-2,2'-di-(3-hydroxypropionic) acid was studied by spectrophotometric methods (curves of the dependences $A = f(\text{pH})$, molar ratios, graphic analysis, logarithmic analysis). The charge of the formed complexes was determined by the paper electrophoresis. Bi(III) forms a very stable complex BiL^+ with the studied agent ($\log \beta_1 = 19.02$) while in an alkaline medium before the total hydrolysis of Bi(III) some hydroxo complexes of the composition $\text{M} : \text{L} = 1 : 1$ are formed. The effect of different physical and chemical factors on the molar absorptivity coefficients was also followed with the prospect of a possible utilization of the BiL^+ complex for the determination of Bi(III).

Изучалась реакция Bi(III) с этилендиамин-*N,N'*-2,2'-ди-(3-оксипропионовой) кислотой спектрофотометрическими методами (с помощью зависимостей $A = f(\text{pH})$, молярных отношений, графического анализа, логарифмическим анализом). Заряд образовавшихся комплексов был определен методом электрофореза на бумаге. Bi(III) образует с приведенным реагентом очень стабильный комплекс с составом BiL^+ ($\log \beta_1 = 19,02$), причем в щелочной среде постепенно возникают оксидокомплексы с стехиометрическим составом $\text{M} : \text{L} = 1 : 1$ при полном гидролизе Bi(III). В работе также изучались физические и химические эффекты на молярный коэффициент абсорбции с целью использовать образование комплекса BiL^+ для спектрофотометрического определения Bi(III).

In one of our previous works [1] we studied the preparation of ethylenediamine-*N,N'*-2,2'-di-(3-hydroxypropionic) acid characterized by two carboxylic and alcoholic functional groups. In the quoted work, we also examined the complex formation properties of the agent with the group of alkaline earths ions and some bivalent ions of heavy metals. As a result, we derived the reaction mechanism and determined both the composition of the formed complexes and the reaction equilibria in solutions.

Abbreviation:

EDDHP ethylenediamine-*N,N'*-2,2'-di-(3-hydroxypropionic) acid.

Since the studied agent has been assumed to have a high complex formation affinity towards Bi(III), the subject of this work consisted in the study of their mutual reaction and the conditions under which it could be used for a spectrophotometric determination of Bi(III). This was accomplished by using the u.v. spectrophotometry. So far, other complexanes studied in a connection with Bi(III) have been EDTA [2–7] and in part also DCTA [5, 7] and NTA [8]. Generally, the authors studied the reaction mechanism and determined the stability constants. In some cases they report also partial results concerning the interference of some cations or anions [7–9] in the photometric determination of Bi(III) or in its determination by the spectrophotometric titration [9]. The reported results of the polarographic determination of the stability constants [3, 5] are rather scattered.

Experimental

Instruments, solutions, and chemicals

In the investigation, the following instruments were used: The recording spectrophotometer UNICAM SP-700 and the spectrophotometer UNICAM SP-500. (In the determination of the stability constants an attachment for measurements at the constant temperature was applied.) The deflection pH-meter Radiometer PHM 25 (± 0.01 pH unit) with a combined glass-calomel electrode GK 2301 C.

The solution of 0.1 M-Bi(ClO₄)₃ was prepared by dissolving the calculated amount of Bi₂O₃ in warmed up concentrated HClO₄ (dangerous!). The content of Bi(III) was determined gravimetrically as BiPO₄. Other solutions used were 0.1 M-NaOH, free of carbonates, 0.1–2 M-HClO₄ for the pH adjustments and 1 M-NaClO₄ for the ionic strength adjustments.

Absorption curves of the Bi(III)–EDDHP complexes

The Bi(III)–EDDHP complex formation was followed by the method of absorption curves [10]. Solutions with a tenfold excess of the agent and the equimolar solutions were measured. With respect to a fast establishment of the equilibrium, absorbances of the solutions were measured immediately after their preparation and blank solutions were used. The measurements were carried out from a strongly acidic up to alkaline pH. Values of pH < 1 were calculated from the HClO₄ concentration, while the needed activity coefficients were taken from literature [11].

Determination of the equilibria in solutions

The resulting absorption curves were evaluated as the dependences $A = f(\text{pH})$ at the wavelengths corresponding to the absorption maxima of the formed complexes. The $A = f(\text{pH})$ curves made it possible to determine the regions of the existence of the individual Bi(III)–EDDHP complexes. Their composition in the acidic region was examined by the method of molar ratios. The series of solutions with a constant metal concentration and increasing concentrations of the agent were measured. The ionic strength was adjusted to $I = 0.5$ (NaClO₄) and the absorbances of the prepared solutions were checked against blank solutions.

Stability constants were evaluated from the curves of the dependence $A = f(\text{pH})$ by means of a logarithmic analysis [12]. This analysis also verified the course of the cor-

responding reactions of the complex formation (the number of dissociated protons). The molar absorption coefficients of the complexes were obtained from the graphic analysis of the $A = f(\text{pH})$ curves; beside, they were calculated from the absorption curves at a sufficient excess of the agent. The stability constant of the first complex formed in the acidic region was also estimated by a method based on the determination of the complex and free metal concentrations in the pH region where a sufficient dissociation of the complex occurs [13, 14].

Paper electrophoresis

The method of the paper electrophoresis [15] was employed in order to determine the charges of the complexes of the Bi(III)—EDDHP system. The chromatographic paper Whatman 1 was saturated with a 10^{-3} M solution of EDDHP adjusted to the required pH with HClO_4 or NaOH . A drop of the solution containing 1×10^{-3} M-Bi(III) and 1×10^{-3} M-EDDHP was placed on the start. The electrophoresis was carried out at a potential gradient 10–12 V/cm for one hour.

Results and discussion

The course of absorption curves of the system Bi(III)—EDDHP measured in a series of the equimolar solutions (Fig. 1) as well as in solutions with a tenfold excess

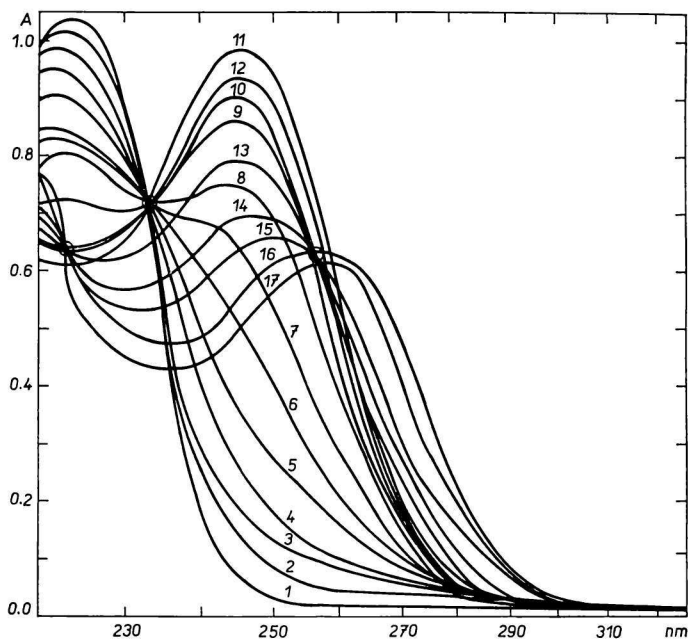


Fig. 1. Absorption curves of the Bi(III)—EDDHP complexes.

$c_M = 1.5 \times 10^{-4}$ M, $c_L = 1.5 \times 10^{-4}$ M, $l = 1.00$ cm, $I = 0.5$ (NaClO_4).

The corresponding pH: 1. 0.41; 2. 0.63; 3. 0.81; 4. 0.90; 5. 0.98; 6. 1.05; 7. 1.10; 8. 1.15; 9. 1.25; 10. 1.55; 11. 1.95–3.28; 12. 4.88; 13. 6.85; 14. 7.50; 15. 7.76; 16. 8.20; 17. 8.85.

of the agent corroborate a stepwise formation of the complexes with absorption maxima at λ 224, 245, and 260 nm. The absorption curves of solutions with equimolar concentrations of the components are evaluated in Fig. 2 as the dependences $A = f(\text{pH})$. The course of the curves suggests the formation of the first complex with an absorption maximum at λ 245 nm in a strongly acidic region (pH 0.4–1.2). All the absorption curves in the investigated region go through an isosbestic point at λ 233 nm, including the curves up to pH 3.28.

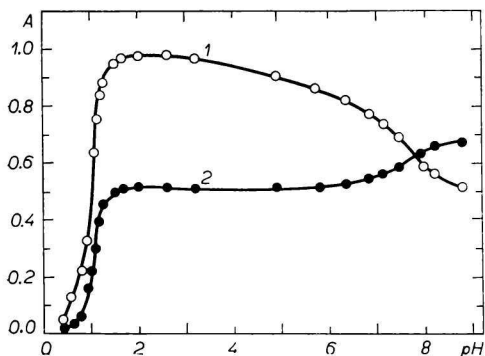


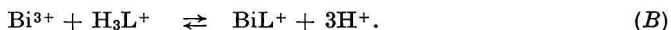
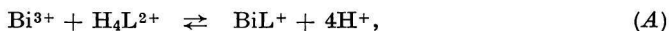
Fig. 2. Curves of the $A = f(\text{pH})$ dependence of the Bi(III)–EDDHP complexes, $c_M = c_L = 1.5 \times 10^{-4}$ M, $l = 1.00$ cm, $I = 0.5$ (NaClO₄).
1. $\lambda = 245$ nm; 2. $\lambda = 260$ nm.

The reaction mechanism of the complex formed in the mentioned strongly acidic region was determined on the basis of the logarithmic analysis. In the 0.4–1.2 pH region, the studied agent exists in the form of H_4L^{2+} and H_3L^+ species [1] which involves the necessity to include the corresponding dissociation constants of EDDHP into the relationships for the logarithmic analysis. These constants were taken from our previous work [1] and the logarithmic analysis was then carried out under the condition $c_M = c_L$, with the use of eqns (1) and (2)

$$\log \frac{A}{(\varepsilon_1 c_L - A)^2} = \log k + n(\text{pH}) - \log \varepsilon_1 - \log \left[1 + \frac{K_{a00}}{[\text{H}]} \right], \quad (1)$$

$$\log \frac{A}{(\varepsilon_1 c_L - A)^2} = \log k' + n(\text{pH}) - \log \varepsilon_1 - \log \left[1 + \frac{[\text{H}]}{K_{a00}} \right]. \quad (2)$$

The necessary molar absorption coefficients of the formed complex (ε_1) were determined from measurements of the solutions with a sufficient excess of the agent in the range of pH 1.8–2.5. The expression of the left hand side of eqn (1) or (2) was plotted against pH (Fig. 3) and the slope of this linear dependence yielded the number of protons released on the reaction. From this graphical evaluation we obtained the slope $n = 4.05$ and $n = 2.95$ for eqn (1) and (2), respectively. The results corroborate that two reactions, (A) and (B), occur simultaneously in the studied pH region



The formation of the complex BiL^+ was confirmed by the course of the Job curve of isomolar solutions as well as by the spectrophotometric titration. The result for

the composition of the reaction product was $M:L = 1:1$ in both the cases. The charge of the formed complex was confirmed by the electrophoretic mobility; in the range of $\text{pH } 2-3.5$ it took a constant value $U = +0.50$. With respect to the assumed molecular weight of the complex ($M = 443.42$) this corresponds to the charge $z = +1$ [16].

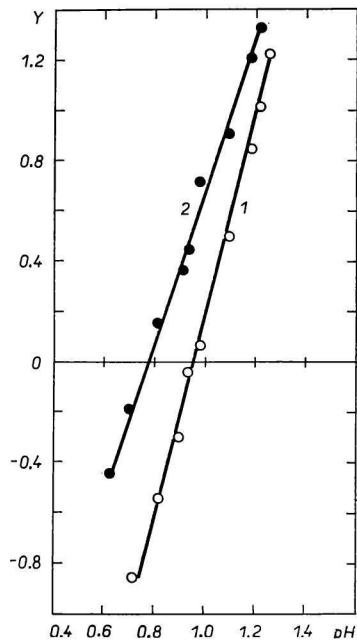


Fig. 3. Logarithmic analysis of the $A = f(\text{pH})$ curves in the region of $\text{pH } 0.6-1.2$.

$c_M = c_L = 1.5 \times 10^{-4}$, $l = 1.00$ cm, $\lambda = 245$ nm. Y is defined by the left side of eqns (1) and (2) for lines 1 and 2, respectively.

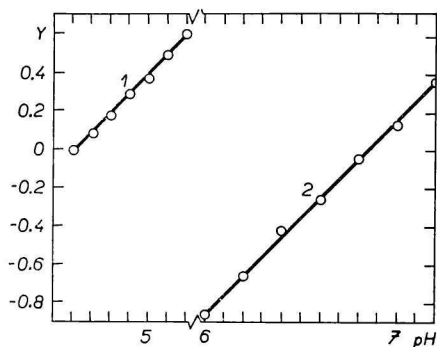


Fig. 4. Logarithmic analysis of the $A = f(\text{pH})$ curves at higher pH .

$c_M = 4 \times 10^{-5}$ M, $c_L = 4 \times 10^{-4}$ M, $l = 1.00$ cm, $\lambda = 270$ nm. Y is defined by eqn (7). The ranges of pH : 1. 4.6-5.2; 2. 6.2-7.2.

For the complex BiL^+ , the equilibrium constant was calculated from a logarithmic analysis (Fig. 3) according to eqns (1) and (2) under the following conditions

$$\log \frac{A}{(\epsilon_1 c_L - A)^2} + \log \left(1 + \frac{K_{a00}}{[\text{H}]} \right) = Y = 0, \quad (3)$$

$$\log \frac{A}{(\epsilon_1 c_L - A)^2} + \log \left(1 + \frac{[\text{H}]}{K_{a00}} \right) = Y = 0. \quad (4)$$

The stability constant was calculated from eqn (5)

$$\log \beta_1 = \log k + \text{p}K_{a00} + \text{p}K_{a0} + \text{p}K_{a1} + \text{p}K_{a2}. \quad (5)$$

The stability constant of the studied BiL^+ complex was also evaluated from the $A = f(\text{pH})$ curve according to *Hughes* and *Martell* [13]. The generalized relationships for the calculations are given in our previous work [14].

Besides of the complex BiL^+ formed in a strongly acidic medium, we also examined the reaction product arising in the pH region from 4 to 9 (Fig. 2). At first, we analyzed graphically the $A = f(\text{pH})$ curve in this region. The results revealed that the mentioned segment of the $A = f(\text{pH})$ curve involves the formation of three partial products, each of them being formed with a release of one proton. The linear course of all three segments of the curve is expressed by eqn (6)

$$A = \varepsilon_2 c_M - (A - \varepsilon_1 c_M) [\text{H}]^n / K_d. \quad (6)$$

The corresponding molar absorption coefficients listed in Table 1 were obtained graphically by means of eqn (6). The number of the released protons was confirmed by a logarithmic analysis using eqn (7)

$$\log \frac{A - \varepsilon_1 c_M}{\varepsilon_2 c_M - A} = \log K_d + n(\text{pH}). \quad (7)$$

The slope of both the linear dependences ($n = 0.98$ and 1.08) confirmed a reaction mechanism where the release of one proton takes place in each step (Fig. 4)

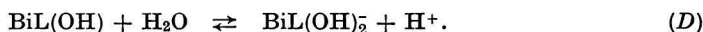
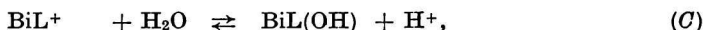


Table 1

Molar absorption coefficients of the $\text{Bi}(\text{III})$ —EDDHP complexes

Complex	λ , nm	pH	ε , $\text{cm}^3 \text{m}^{-1} \text{mol}^{-1}$
BiL^+	245	0.5–3.1	6360
$\text{BiL}(\text{OH})$	270	4.6–5.2	1770
$\text{BiL}(\text{OH})_2$	270	5.9–7.2	3320

Besides of the reaction mechanism described by the schemes (C) and (D), we still cannot exclude the formation of the complexes BiL and BiL^- , accompanied by a dissociation of protons from alcoholic groups. However, the reaction mechanism resulting in the formation of the hydroxo complexes shown in schemes (C) and (D) is more probable since at pH above 9 the solution becomes turbid and a precipitation of $\text{Bi}(\text{OH})_3$ occurs. This is also supported by the determined electrophoretic mobility which is reduced to zero in the range of pH from 4 to 10 (Table 2).

With regard to the formation of a very stable complex of $\text{Bi}(\text{III})$ with EDDHP which is characterized by a marked absorption maximum, we tried to utilize the formation of this complex for the determination of $\text{Bi}(\text{III})$. For this reason we examined the effect of several cations and anions ($\text{Cd}(\text{II})$, $\text{Pb}(\text{II})$, $\text{Zn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, $\text{Cu}(\text{II})$, $\text{Al}(\text{III})$, Cl^- , SO_4^{2-} , NO_3^-) upon the molar absorption coefficients. The interference was found in the case of $\text{Cu}(\text{II})$, if present in a higher concentration than equimolar, and $\text{Al}(\text{III})$ in a greater than a fivefold excess.

Table 2

Dissociation constants of EDDHP, stability constants and equilibrium constants of the Bi(III)–EDDHP complexes

Equilibrium	Constant	log of the constant
$[\text{H}_3\text{L}][\text{H}]/[\text{H}_4\text{L}]$	K_{a00}	-1.6 [1]
$[\text{H}_2\text{L}][\text{H}]/[\text{H}_3\text{L}]$	K_{a0}	-2.1 [1]
$[\text{HL}][\text{H}]/[\text{H}_2\text{L}]$	K_{a1}	-6.07 [1]
$[\text{L}][\text{H}]/[\text{HL}]$	K_{a2}	-9.20 [1]
$[\text{BiL}]/[\text{Bi}][\text{H}_4\text{L}]$	β_1	19.02 ^a 19.10 ^b 18.99 ^a
$[\text{BiL}(\text{OH})]/[\text{BiL}][\text{OH}]$	$k_{1\text{OH}}$	9.34
$[\text{BiL}(\text{OH})_2]/[\text{BiL}(\text{OH})][\text{OH}]$	$k_{2\text{OH}}$	7.09

a) Stability constant from logarithmic analysis.

b) Stability constant calculated from $A = f(\text{pH})$.

The influence of some other physicochemical parameters, such as temperature, the ionic strength, and the excess of the agent, on the absorbance of the BiL^+ complex was also followed. The optimum conditions for the determination of Bi(III) were found to be at 20–30°C, the ionic strength 0.1–0.5 and between a 10 to 20-fold excess of the agent in 0.5–4 cm cells. In contrary to NTA and DCTA, the reaction of Bi(III) with EDDHP takes place immediately and the formed complex is stable for several days. The determination can be performed with solutions with a content of Bi(III) $\geq 0.6 \mu\text{g/ml}$.

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