New Complexanes. XXI*.
Complex-forming Properties of the
N,N-Bis(2-hydroxyethyl)aminomethylphosphonic Acid

R. KARLÍČEK, J. MAJER and J. POLAKOVIČOVÁ

*Department of Analytical Chemistry, Faculty of Pharmacy, Komenský University,
Bratislava 1*

Acid-base properties of N,N-bis(2-hydroxyethyl)aminomethylphosphonic acid have been studied by potentiometric titration. Thus the values $pK_{a1} = 4.98$ and $pK_{a2} = 9.46$ have been found ($I = 0.1$ NaClO$_4$, 20°C). The regions of existence, the composition, equilibrium constants, and stability constants of the chelates with some heavy metals have been defined spectrophotometrically. It has been found that only complexes having the composition $M : L = 1 : 1$ but with different charges are formed from Cu(II) and Fe(III). On the other hand, Ni(II) may also form a complex with the composition $M : L = 1 : 2$. The complex-forming properties are also compared to those of N,N-bis(2-hydroxyethyl)glycine.

In analytical chemistry, the attention is paid to the preparation and application of new types of the chelating agents recently. In particular, the aminopolycarboxylic acids in which the rests of sulfonic or phosphonic acids substitute partially or fully for the carboxylic groups arouse a great interest. In the field involving the research of this new class of chelate-forming agents containing one or more aminomethyl-phosphonic groups, a great number of the substances derived especially from nitri-lotriacetic acid [1—4] and ethylenediaminetetraacetic acid [5—8] has been studied as yet. The results of these investigations indicate that the phosphonic group takes part in the coordination of metallic ion provided its position in molecule is sterically favourable for the formation of a chelate ring.

In this study, the acid-base and complex-forming properties of a substance derived from N,N-bis(2-hydroxyethyl)glycine namely N,N-bis(2-hydroxyethyl)amino-methylphosphonic acid have been investigated. To determine the composition and stability constants of the complexes, the following relationships were analysed graphically: the absorption curves of the solutions containing complexes with an excess of agent as well as of the equimolar solutions $A = f(pH)$, c_M and $c_L = $ const; $A = f(c_L)$, c_M and pH = const [9]; the *Job* curves of isomolar solutions [10]. The molar absorptivities of individual complexes were obtained by twofold approximation of the relationship

---

$$\frac{c_M}{(A - A_0)} = \frac{1}{\varepsilon_1} + \frac{1}{(c_L - \alpha)} \qquad (1)$$

where $\alpha = (A - A_0)/(\varepsilon_1 - \varepsilon_0)$ and $A_0 = \varepsilon_0\, c_M$.

The calculated values of molar absorptivities were used for the logarithmic relationships by means of which the equilibrium constants were computed. The slopes of logarithmic transformations served for the determination of the protons split off during the formation of complex. By using the same transformations under condition $\log f'(A) = 0$, the values of the equilibrium as well as of the stability constants were calculated [11, 12]. The number of the ligand particles bonded in the complex was determined by the *Asmus*'s transformation of the relationship $A = f(c_L)$ [13].

Experimental

Chemicals and equipment

N,N-Bis(2-hydroxyethyl)aminomethylphosphonic acid was prepared from diethanolamine and chlormethylphosphoric acid [14]. The substance was isolated in the form of the pentahydrate of disodium salt.

For $C_5H_{12}NO_5PNa_2 \cdot 5H_2O$ (333.19) calculated: 18.03% C, 6.05% H, 5.75% N; found: 18.13% C, 6.20% H, 5.61% N.

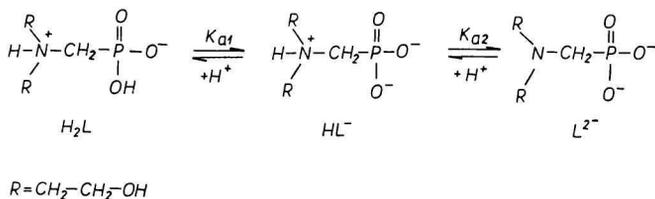The anhydrous salt was obtained by drying at 120°C. The aqueous solutions of disodium salts of BHAMP are stable.

The standard 0.1 M solutions of $Cu(ClO_4)_2$, $Ni(ClO_4)_2$, and $Fe(ClO_4)_3$ were prepared from corresponding perchlorates of anal. grade. The accurate concentrations were determined by complexometric titrations and corresponding factors were adjusted to $f = 1.000$. The adjustment of pH in solutions was made either by means of 0.1 M-NaOH or by means of 0.1 M-HClO$_4$. The adjustment of ionic strength was performed with 1 M-NaClO$_4$.

The spectrophotometric measurement was made by using the spectrophotometer Unicam SP 500 and SP 700 with quartz cells. The vacuum tube pH-meter PHM, Radiometer Co., with the glass electrode G-202B and saturated calomel electrode was used to pH-measurement.

Results and Discussion

Both dissociation constants of N,N-bis(2-hydroxyethyl)aminomethylphosphonic acid were determined by potentiometric titration of its solution in redistilled water with carbonate-free 0.1 M-NaOH in double-jacket vessel with thermostatic control (20 ± 0.2°C) under stirring with nitrogen flow. On the basis of the experimental pH values obtained in buffered regions of several titrations, the average values of the dissociation constants presented in Table 1 were calculated according to expressions valid for the dissociation of weak acids.

Like with other α-aminomethylphosphonic acids, the existence of the dipolar ion in which a proton is bonded to a quaternary nitrogen must be assumed. During the dissociation of this acid the first proton is split off from the negative phosphonic group $-PO_3H^-$ while second one comes from the quaternary nitrogen (Scheme 1).

$$
\begin{array}{ccccc}
\overset{R}{\underset{R}{\overset{|}{H-\overset{+}{N}-}}}CH_2-\overset{\overset{O}{\|}}{\underset{OH}{P}}-O^- & \underset{+H^+}{\overset{K_{a1}}{\rightleftharpoons}} & \overset{R}{\underset{R}{\overset{|}{H-\overset{+}{N}-}}}CH_2-\overset{\overset{O}{\|}}{\underset{O^-}{P}}-O^- & \underset{+H^+}{\overset{K_{a2}}{\rightleftharpoons}} & \overset{R}{\underset{R}{\overset{|}{N-}}}CH_2-\overset{\overset{O}{\|}}{\underset{O^-}{P}}-O^- \\
H_2L & & HL^- & & L^{2-}
\end{array}
$$

$$R = CH_2-CH_2-OH$$

The dissociation constants of the agent under investigation differ quite considerably from those of the substance without hydroxyl groups, *i.e.* diethylamino-methylphosphonic acid (Table 2) [4]. It cannot be interpreted only by an acidifying effect of hydroxyl groups. In particular, the considerable difference in pK_{a2} values cannot be caused only by different temperature (25°C), ionic strength ($I = 1$), and electrolyte used (KNO_3). Similarly, a very high value for the constant of proton dissociation from the quaternary nitrogen was found by above authors [4] in the case of nitrilotris(methylphosphonic) acid ($pK_{an} = 12.34$) although it ought to be considerable lower ($pK_{an} = 10.9$) according to other authors [3] and analogy with similar α-aminomethylphosphonic acids.

Table 1

Survey of the individual constants

Equilibrium	Constant	log const
$[HL][H]/[H_2L]$	K_{a1}	-4.98
$[L][H]/[HL]$	K_{a2}	-9.46
$[CuHL][H]/[Cu][H_2L]$	k_{1H}	$-1.51^a;\ -1.62^b$
$[CuHL]/[Cu][HL]$	β_{1H}	3.43
$[CuL][H]^2/[Cu][H_2L]$	k_{12}	$-4.94^c;\ -4.90^a;\ -4.91^b$
$[CuL]/[Cu][L]$	β_1	9.52
$[Cu(OH)L]/[CuL][OH]$	$k_{1\ OH}$	6.92
$[Cu(OH)L]/[Cu][L][OH]$	$\beta_{1\ OH}$	16.44
$[NiL][H]/[Ni][HL]$	k_{11}	-2.77
$[NiL][H]^2/[Ni][H_2L]$	k_{12}	-7.57
$[NiL]/[Ni][L]$	β_1	$6.69;\ 6.87$
$[NiL_2][H]/[NiL][HL]$	k_{21}	-6.78
$[NiL_2]/[NiL][L]$	K_2	2.68
$[NiL_2]/[Ni][L]^2$	β_2	9.46
$[Fe(OH)HL][H]/[Fe][OH][H_2L]$	k_{1H}	14.21
$[Fe(OH)HL]/[Fe][OH][HL]$	β_{1H}	19.19
$[Fe(OH)L][H]/[Fe(OH)HL]$	K_{Ka1}	-4.28
$[Fe(OH)L]/[Fe][OH][L]$	$\beta_{1\ OH}$	24.36
$[Fe(OH)L][H]^2/[Fe(OH)L]$	k	-13.67^d
$[Fe(OH)_3L]/[Fe(OH)L][OH]^2$	$k_{3\ OH}$	14.21
$[Fe(OH)_3L]/[Fe][OH]^3[L]$	$\beta_{3\ OH}$	38.6

a) $c_L/c_M = 4$; $\log c_L = -2.16$; b) $c_L/c_M = 10$; $\log c_L = -1.72$; c) $c_L = c_M$; $\log c_L = -2.70$; d) loss of the protons from the hydroxyethyl groups of agent.

Table 2

Comparison of the complex-forming properties of BHAMP, BHG, and DEAMP

Complex	Constant	log const		
		BHAMP[a]	BHG[b]	DEAMP[c]
H_2L	K_{a1}	4,98	1.68	5,79
HL	K_{a2}	9.46	8.14	12.32
CuL	β_1	9.52	8.37	
NiL	β_1	6.78	6.50	
NiL_2	K_2	2.68	4.40[d]	
Fe(OH)L	$\beta_{1\ OH}$	24.36		
$Fe(OH)_2L$	$\beta_{2\ OH}$		30.1	
$Fe(OH)_3L$	$\beta_{3\ OH}$	38.6	36.7	

a) 20°C, $I = 0.1$ NaClO$_4$; *b*) 20°C, $I = 0.1$ NaClO$_4$ [17]; *c*) 25°C, $I = 1.0$ KNO$_3$ [4]; *d*) 30°C, $I = 0.1$ KCl [18].

Equilibria in the solutions of Cu(II) BHAMP complexes

The $A-$pH plots of the solutions with an excess of agent indicate the formation of three complexes while the ascending branches of these curves are distinctly separated from each other by an horizontal section (Fig. 1, curve *1*).

Continuous variation: The position of maxima of the Job curves for isomolar solutions at pH 5.5 (Fig. 2, curves *1* and *2*) is near the value $x = 0.5$ and does not change over the range from 725 to 900 nm. The curves for solutions with pH 9.5 also show a maximum at $x = 0.5$ what corresponds to a formation of complexes having the
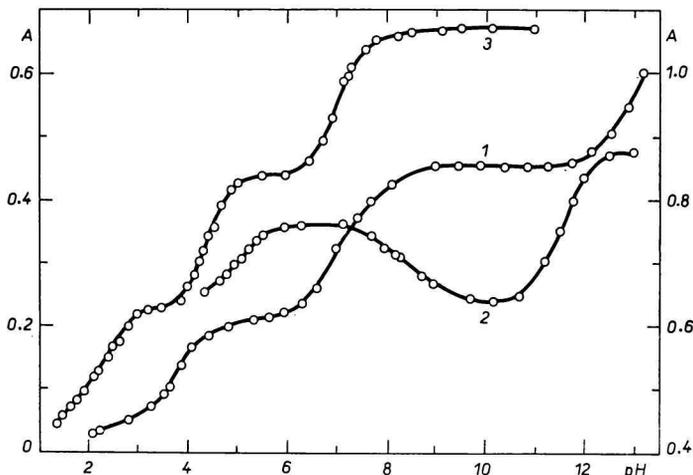

*Fig. 1. A−*pH plots for the BHAMP complexes.
1. (copper complexes) $c_M = 2.0 \times 10^{-3}$ M, $c_L = 8.0 \times 10^{-3}$ M, $l = 4$ cm, 650 nm; *2.* (nickel complexes) $c_M = 1.0 \times 10^{-2}$ M, $c_L = 4.0 \times 10^{-2}$ M, $l = 4$ cm, 390 nm; *3.* (iron complexes) $c_M = 5.0 \times 10^{-5}$ M, $c_L = 5.0 \times 10^{-4}$ M, $l = 4$ cm, 270 nm (the right-side absorbance scale).

composition $M : L = 1 : 1$ in both cases. The solutions with a greater excess of cations with respect to the agent ($x > 0.65$) adjusted to pH 9.5 grow turbid by excluding copper(II) hydroxide and thus could not be estimated (Fig. 2, curve 3).

The curves giving the variation of absorbance with ligand concentration at constant pH (Fig. 3, curves 1 and 2) confirm that the copper(II) complexes of the agent are formed in the ratio $M : L = 1 : 1$ over the pH range of 5.5—9.5. The spectrophotometric characteristics of the individual complexes are given in Table 3.
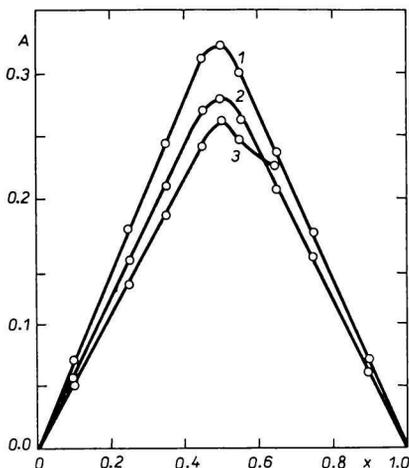

Fig. 2. Continuous variation for the Cu(II)—BHAMP system; $x = c_M/(c_M + c_L)$.
1. pH 5.5, $l = 4$ cm, 800 nm, $c_0 = 4.0 \times 10^{-3}$ M; *2.* pH 5.5, $l = 4$ cm, 725 nm or 900 nm, $c_0 = 4.0 \times 10^{-3}$ M; *3.* pH 9.5, $l = 4$ cm, 725 nm, $c_0 = 2.0 \times 10^{-3}$ M.
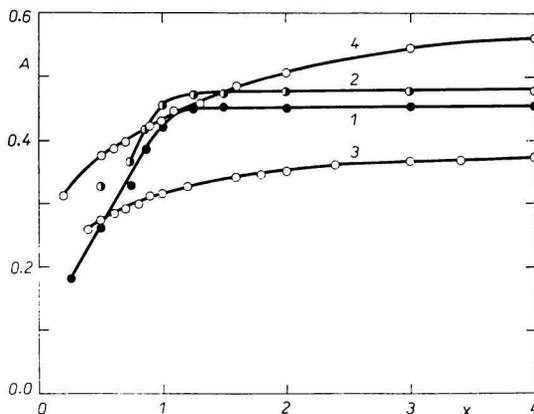

Fig. 3. Plots for the molar ratios of the BHAMP complexes; $x = c_L/c_M$.
1. (Cu), pH 5.5, $c_M = 2.0 \times 10^{-3}$ M, $l = 4$ cm, 800 nm; *2.* (Cu), pH 9.5, $c_M = 1.5 \times 10^{-3}$ M, $l = 4$ cm, 725 nm; *3.* (Ni), pH 6.0, $c_M = 1.0 \times 10^{-2}$ M, $l = 4$ cm, 390 nm; *4.* (Fe), pH 2.5, $c_M = 5.0 \times 10^{-5}$ M, $l = 4$ cm, 270 nm.

Table 3

Spectrophotometric characteristics of the BHAMP complexes

| Complex	λ_{max} [nm]	$\log \varepsilon$ [l mole^{-1} cm^{-1}]
CuL	810	1.753
Cu(OH)L$^-$	725	1.892
NiL	390; 640	0.954; 0.591
NiL$_2^{2-}$	380; 625	0.820; 0.498
Fe(OH)HL$^+$	270	3.505
Fe(OH)L	320	3.263

The graphic analysis of the first ascending branch of the $A-$pH logarithmic plots for the solutions with an excess of agent and for a reaction of non-dissociated ligand H_2L, based on the relationship

$$\log \frac{A - A_0}{A_{01} - A} = \log k_1 + \log c_L - \log\left(1 + \frac{K_{a1}}{[H]}\right) + x \, \text{pH}, \tag{2}$$

gives straight lines having the slopes $x = 0.96-1.06$ and $x = 1.70-1.85$ for the pH ranging from 2.13 to 3.48 and from 3.48 to 5.29, respectively (Fig. 4). The analysis of the $A-$pH plots for equimolar solutions by using the relationship

$$\log \frac{A - A_0}{(A_{01} - A)^2} = \log k_1 - \log(\varepsilon_1 - \varepsilon_0) - \log\left(1 + \frac{K_{a1}}{[H]}\right) + x \, \text{pH} \tag{3}$$

where $A_0 = \varepsilon_0 \, c_M$ and $A_{01} = \varepsilon_1 \, c_M$ gives straight lines with the slope $x = 1.85$, too. On the basis of these values as well as the results concerning the composition of arising complexes, it is to be assumed that the reaction (A) takes place in the solutions containing an excess of agent provided pH is less than 3.5 what involves a simultaneous creation of a proton

$$Cu^{2+} + H_2L \rightleftharpoons CuHL^+ + H^+. \tag{A}$$
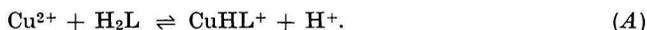
Hence in the solutions with an excess of agent at pH > 3.5 and in the equimolar solutions analysed in the pH range from 3.33 to 5.69, the reaction runs under formation of a neutral complex and loss of two protons

$$Cu^{2+} + H_2L \rightleftharpoons CuL + 2H^+. \tag{B}$$
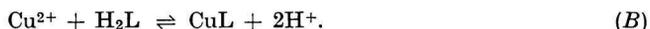
The calculation of equilibrium constants was made under the condition $\log Y = 0$ according to the relationships (2) and (3). The following expressions are valid for the calculation of the stability constants of these complexes

$$\beta_{1H} = \frac{k_{1H}}{K_{a1}}, \tag{4}$$

$$\beta_1 = \frac{k_{12}}{K_{a1} \cdot K_{a2}}. \tag{5}$$

The graphic analysis of the second ascending branch of the $A-\mathrm{pH}$ logarithmic plots for the solutions with an excess of agent (Fig. 4) affords straight lines with the slope $x = 0.98-1.02$. Since the complex arising in this field has also composition
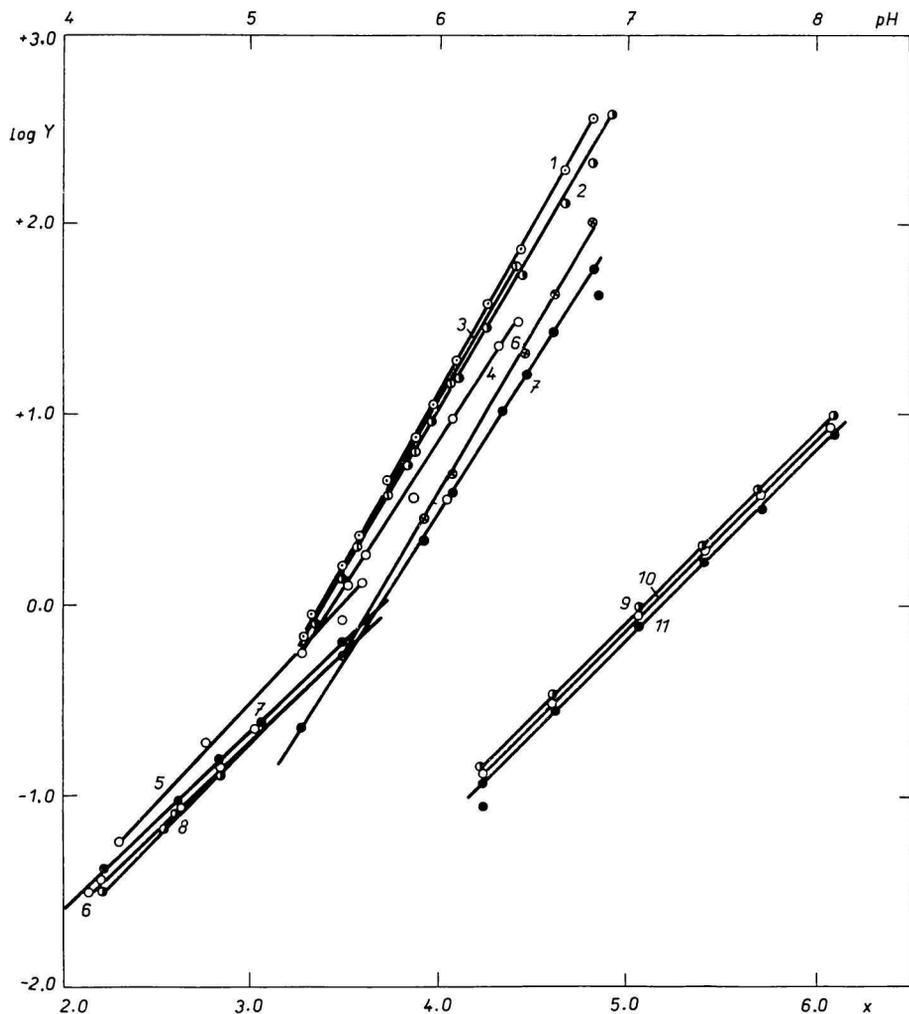

Fig. 4. Graphic analysis of the first and second branch of the $A-\mathrm{pH}$ logarithmic plots for the copper complexes; $x = \mathrm{pH} - \log(1 + K_{a1}/[\mathrm{H}])$.

1. $c_{\mathrm{M}} = c_{\mathrm{L}} = 4.0 \times 10^{-3}$ M, 900 nm; *2.* $c_{\mathrm{M}} = c_{\mathrm{L}} = 4.0 \times 10^{-3}$ M, 850 nm; *3.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 2.0 \times 10^{-2}$ M, 900 nm; *4.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 2.0 \times 10^{-2}$ M, 850 nm; *5.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 2.0 \times 10^{-2}$ M, 725 nm; *6.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 900 nm; *7.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 800 nm; *8.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 735 nm; *9.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 700 nm; *10.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 725 nm; *11.* $c_{\mathrm{M}} = 2.0 \times 10^{-3}$ M, $c_{\mathrm{L}} = 8.0 \times 10^{-3}$ M, 650 nm (for *9, 10, 11* the upper-side pH scale).

$M : L = 1 : 1$, the equilibrium (C) giving rise to the formation of a hydroxo-complex must be taken into consideration

$$CuL + H_2O \rightleftharpoons Cu(OH)L^- + H^+. \tag{C}$$
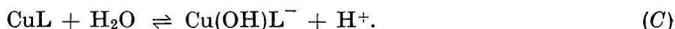
The equilibrium constant of the reaction (C) under condition $\log Y = 0$ is given by the expression

$$\log k_{1\ OH} = pK_w - (pH)_0. \tag{6}$$

For the reaction (C), it cannot, however, be excluded that the hydroxyethyl group of the agent is subjected to coordination under loosing a proton. The constants are summarized in Table 1.

Equilibria in the solutions of Ni(II) BHAMP complexes

The $A - pH$ plot obtained by evaluating the absorption spectra at 390 nm indicates the formation of three green reaction products (Fig. 1, curve 2).

As the plot of molar ratios for Ni(II) complex (Fig. 3, curve 3) points out, this complex is dissociated considerably even at pH 6 and it is not possible to determine unambiguously its composition from the course of the corresponding curve. Thus the Asmus's method of evaluation has been used [13]. The relationship $v^{-n} = f(A^{-1})$ for the solutions of the Ni(II) complex with a varying excess of agent is linear only for $n = 1$ what confirms that the composition of complex corresponds to $M : L = = 1 : 1$ (Fig. 5). Analogously at pH 10, the relationship is linear for $n = 2$ and the complex has the composition $M : L = 1 : 2$ (Fig. 5).
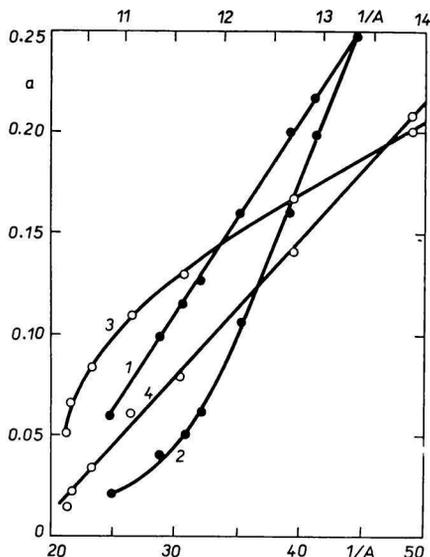

Fig. 5. Graphic analysis of the $A = f(c_L)$ plots according to Asmus for the Ni—BHAMP system.
1. $n = 1$, $a = 1/v$; 2. $n = 2$, $a/4 = 1/v^2$, $c_M = 1.0 \times 10^{-2}$ M, $l = 4$ cm, 390 nm, pH 6.0 (the upper-side scale of $1/A$); 3. $n = 1$, $a = 1/v$; 4. $n = 2$, $a/5 = 1/v^2$, $c_M = 7.5 \times 10^{-3}$ M, $l = 4$ cm, 400 nm, pH 10.0.

The graphic analysis of the first ascending branch of the $A-$pH logarithmic plot for the reaction of H_2L by means of the expression (2) gives straight lines with the slope $x = 2.00-2.25$ provided the correction for the dissociation of agent has been made. Assuming that a reaction of the dissociated HL^- molecule takes place, the graphic analysis of the $A-$pH plots by the use of the expression

$$\log \frac{A - A_0}{A_{01} - A} = \log k_{11} + \log c_L - \log\left(1 + \frac{[H]}{K_{a1}}\right) + x\,\text{pH} \tag{7}$$

furnishes straight lines, the corrected values of their slopes being $x = 0.96-1.02$. On the basis of this fact as well as the found composition of the complex, the subsequent reactions must be considered

$$Ni^{2+} + H_2L \rightleftharpoons NiL + 2H^+, \tag{D}$$

$$Ni^{2+} + HL^- \rightleftharpoons NiL + H^+. \tag{E}$$
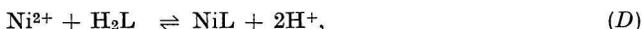
Since it holds $k_{12} = k_{11} \cdot K_{a1}$, the stability constant of the NiL complex may be calculated from both equilibrium constants

$$\beta_1 = \frac{k_{11}}{K_{a2}}; \qquad \beta_1 = \frac{k_{12}}{K_{a1} \cdot K_{a2}}.$$

The values obtained are presented in Table 1.

The values of the slopes corresponding to the logarithmic transformation performed for the second branch of the $A-$pH plot for the solutions with an excess of agent by using the expression

$$\log \frac{A - A_{01}}{A_{02} - A} = \log k_2 + \log\left(c_L - \frac{A}{\varepsilon_2}\right) + x\,\text{pH}, \tag{8}$$

approach to one ($x = 1.02-1.10$) over the pH range from 7.68 to 8.95. Thus in this region another ligand is bonded according to the reaction (F) whilst one proton is yielded

$$NiL + HL^- \rightleftharpoons NiL_2^{2-} + H^+. \tag{F}$$
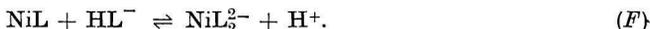
Provided that pH > 11, the hydrolysis of the NiL_2^{2-} complexes involving a successive formation of hydroxo-complexes takes place.

Equilibria in the solutions of Fe(III) BHAMP complexes

The $A-$pH plot (Fig. 1, curve 3) obtained at 270 nm indicates the formation of three reaction products. The regions of existence of the second and third complex (pH 5.2—6.3 and pH 8.0—11.0) agree with the regions of maximum formation of the Fe(III) BHG complexes. The composition of the Fe(III) complexes was followed again by the method of molar ratios (Fig. 3, curve 4). Since the Fe(III) complexes are like Ni(II) complexes considerably dissociated at the pH values used, these plots were evaluated as the relationship $v^{-n} = \mathrm{f}(A^{-1})$. Regardless of the pH value which was either 2.5 or 9.0 (Fig. 6), this relationship was linear only for $n = 1$ what confirms the composition $M : L = 1 : 1$. *Ramsey* [14], too, describes isolation of a complex having the composition Fe(OH)L from neutral medium. Opposite to us,

he also describes the isolation of a water soluble complex at pH 9.2 and on the basis of analysis, he assumes that its composition is $Fe(OH)L_3Na_4$. We have not proved the existence of such a complex having the composition $M : L = 1 : 3$ in aqueous solution as yet (Fig. 6). It would mean that the hydroxyethyl groups of agent did
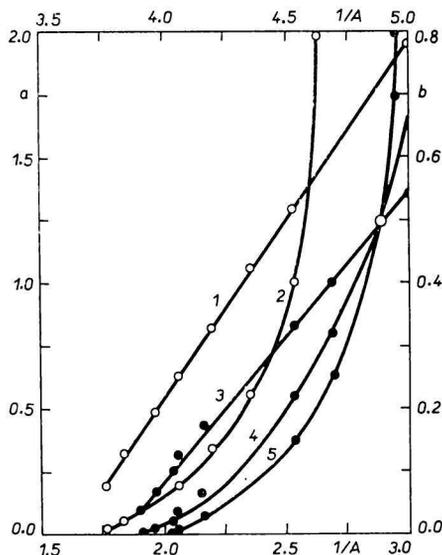

Fig. 6. Graphic analysis of the $A = f(c_L)$ plot according to Asmus for the Fe — BHAMP system.

$$c_M = 5.0 \times 10^{-5} \text{ M}, \ l = 4 \text{ cm}, \ 270 \text{ nm}.$$

1. $n = 1, \ a = 1/v$; *2.* $n = 2, \ 2a = 1/v^2$, pH 2.50; *3.* $n = 1, \ b = 1/v$; *4.* $n = 2, \ b/2 = 1/v^2$; *5.* $n = 3, \ b/4 = 1/v^3$, pH 9.0 (for *3, 4, 5* the upper-side scale of $1/A$).

not take part in chelating what would be less probable in case of iron. The original substance BHG also creates according to other authors [15, 16] as well as according to our comparative measurement complexes with Fe(III) having the composition $M : L = 1 : 1$.

The graphic analysis of the first ascending branch of the A—pH logarithmic plots for the reaction of H_2L furnishes at pH from 1.36 to 2.48 a straight line with the slope $x = 1.03$. Since the complex existing in this pH range has according to electrophoretic measurement one positive charge its formation may be expressed by the equilibrium

$$Fe(OH)^{2+} + H_2L \ \rightleftharpoons \ Fe(OH)HL^+ + H^+. \tag{G}$$

The equilibrium constant of this reaction has been calculated for log $Y = 0$

$$\log k_{1H} = -\log c_L + pK_w - 2(\text{pH})_0. \tag{9}$$

Only when the pH value reaches 4 or 5, the second proton is split off and the Fe(OH)L complex is formed. The graphic analysis of the second ascending branch of the A—pH logarithmic plots confirms that the only one proton is released ($x = 0.98-1.02$) in this pH region

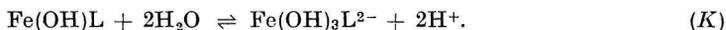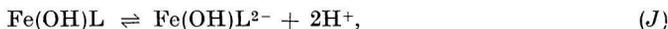$$Fe(OH)HL^+ \ \rightleftharpoons \ Fe(OH)L + H^+. \tag{H}$$

To confirm the composition of the electroneutral complex the patent specification [14] is to be mentioned according to which a complex of the same composition was isolated at pH 6. However, no data are given about its stability and structure. As the reaction (H) expresses dissociation of the complex, the dissociation constant of which is given by the formula

$$\log K_{Ka1} = - (\text{pH})_0, \tag{10}$$

the stability constant of the Fe(OH)L complex has been computed according to the equation

$$\log \beta_{1\,\text{OH}} = \log K_{Ka1} + \log \beta_{1H} + pK_{a2}. \tag{11}$$

The analysis of the third ascending branch of the $A-\text{pH}$ plots for the Fe(III) complexes points out that the formation of another complex at about pH 7 is accompained by a simultaneous loss of two protons ($x = 2.04-2.08$). Since we have found the composition $M : L = 1 : 1$ for this complex, the following equilibria must be considered

$$\text{Fe(OH)L} \rightleftharpoons \text{Fe(OH)L}^{2-} + 2\text{H}^+, \tag{J}$$

$$\text{Fe(OH)L} + 2\text{H}_2\text{O} \rightleftharpoons \text{Fe(OH)}_3\text{L}^{2-} + 2\text{H}^+. \tag{K}$$

In the reaction (J) the coordination of both hydroxyethyl groups of agent under simultaneous loss of two protons must be assumed [16].

In Table 2, the values of stability constant of the BHAMP complexes are compared with those of some comparable BHG complexes. In contrast to BHG, the agent studied also forms hydrogen-complexes, namely with Cu(II) and Fe(III). The formation of a complex having the composition $Cu : L = 1 : 2$ has not been found for BHAMP. Provided that pH rises, the CuL complex transforms gradually into Cu(OH)L$^-$ and Cu(OH)$_2$L^{2-} complexes. A hydroxo-complex of the same composition arises in strong alkaline medium from Cu(II) and BHG. On the other hand, BHAMP as well as BHG form with Ni(II) a complex having the composition NiL$_2$ which in both cases is gradually transformed in alkaline medium into hydroxo-complexes. As follows from Table 2, the comparable complexes containing BHAMP and BHG have practically equal values of stability constants (with respect to the different pK_a values of acids). The substitution of the phosphonic group for the carboxylic group of investigated ions did not produce a more marked change in the stability and colour shade of particular complexes. On the basis of these facts, it may be assumed that the BHAMP and BHG complexes which have equal composition possess a similar structure, too.

References

1. Schwarzenbach G., Ackermann H., Ruckstuhl P., *Helv. Chim. Acta 32*, 1175 (1949).
2. Westerback S., Rajan K. S., Martell A. E., *J. Amer. Chem. Soc. 87*, 2567 (1965).
3. Hendrickson H. S., *Anal. Chem. 39*. 998 (1967).
4. Carter R. P., Carrol R. L., Irani R. R., *Inorg. Chem. 6*, 939 (1967).
5. Westerback S., Martell A. E., *Nature 178*, 321 (1956).
6. Djatlova N. M., Kabačnik M. I., Medved T. J., Rudomino M. W., Belugin I. F., *Dokl. Akad. Nauk SSSR 161*, 607 (1965).

7. Kabačnik M. I., Djatlova N. M., Medved T. J., Belugin I. F., Sidorenko V. V., *Dokl. Akad. Nauk SSSR* **175**, 351 (1967).
8. Rajan K. S., Murase I., Martell A. E., *J. Amer. Chem. Soc.* **91**, 4408 (1969).
9. Sommer L., Jin Tsin-Jao, *Chem. Listy* **55**, 576 (1961).
10. Job P., *Ann. Chim.* (Paris) **9**, 113 (1928).
11. Hildebrand G. P., Reilley C. N., *Anal. Chem.* **29**, 258 (1957).
12. Sommer L., *Folia of the Faculty of Natural Sciences, Purkyně University* (Brno), No **1**, 1 (1964).
13. Asmus E., Hinz U., Ohls K., Richly W., *Z. Anal. Chem.* **178**, 104 (1960).
14. Ramsey W. M., *U. S. Patent* No. 2 964 549 (1960).
15. Toren P. E., Kolthoff J. M., *J. Amer. Chem. Soc.* **77**, 2061 (1955).
16. Nightingale E. R., Benck R. F., *Talanta* **11**, 241 (1964).
17. Špringer V., Karlíček R., Majer J., *Collect. Czech. Chem. Commun.* **32**, 774 (1967).
18. Chabereck S., Courtney R. C., Martell A. E., *J. Amer. Chem. Soc.* **75**, 2185 (1953).

Translated by R. Domanský