STUDY OF PROPERTIES OF COMPLEXES OF SNAZOXS AND NAPHTHYLAZOXINE 6S WITH COPPER(II), ZINC(II) AND LEAD(II) IONS IN SOLUTION BY NON-LINEAR REGRESSION OF SPECTROPHOTOMETRIC DATA*

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Complexation equilibria of two metallochromic indicators *viz.* 7-(4-sulpho-1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid (SNAZOXS) and 7-(6-sulpho-2-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid (Naphthylazoxine 6S) with copper(II), zinc(II), and lead(II) ions have been studied by various spectrophotometric methods in 0·1M-$NaClO_4$ medium at 25°C. Number of the coloured complexes in solution, their stoichiometry, and their overall and conditional stability constants have been determined by computer-assisted non-linear regression of the curves of continuous variations, the curves of molar ratios, the absorbance-pH curves, the curves of corresponding solutions, and by regression matrix analysis of the spectra. Besides the yellow complexes ML and ML_2 the orange protonated forms MLH and $M(LH)_2$ have also been determined.

The previous communications of this series dealt with protonation equilibria of two 7-arylazo derivatives of 8-hydroxyquinoline-5-sulphonic acid SNAZOXS and Naphthylazoxine 6S and with the complex formation equilibria of SNAZOXS with copper(II), nickel(II), and cobalt(II) ions. The both derivatives are used in analytical chemistry as metallochromic indicators and are position isomers differing in structure of the 7-arylazo group: SNAZOXS is 7-(4-sulpho-1-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid (*I*), Naphthylazoxine 6S is 7-(6-sulpho-2-naphthylazo)-8-hydroxyquinoline-5-sulphonic acid (*II*).

The present communication deals with the complex formation equilibria, *i.e.* determination of number of complexes, their stoichiometry, and stability constants of the both indicators with copper(II), zinc(II), and lead(II) ions by computer-assisted non-linear regression of some absorbance dependences.

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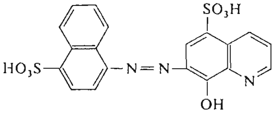

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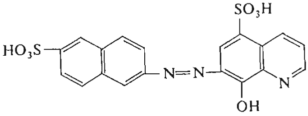

II

EXPERIMENTAL

Chemicals and Solutions

Zinc(II) and lead(II) nitrates were prepared from *p.a.* chemicals (Lachema), and their solutions were standardized by chelatometric titration. The other reagents are described in the previous communication[1-3].

Spectrophotometric Measurements

The spectrophotometric measurements involving spectral records for investigation and evaluation of the equilibrium, records of curves of continuous variations, curves of molar ratios, and absorbance-pH curves were described in the previous communication[3].

For measurements of the curves of corresponding solutions 10 ml solution containing the metal in buffer was pipetted in one titration flask, and 10 ml pure buffer was pipetted into another titration flask. Mixture of the coloured ligand, metal and buffer and mixture of pure ligand and buffer of the same volume were added in the former and the latter flask, respectively, by means of piston microburettes. The solutions were transported from the respective titration flasks into the sample and the reference cells by means of a plunger device, whereupon absorbance was measured, and the whole cycle was repeated. The cells of 50·02, 10·01 and 5·02 mm pathlengths were used.

Methods of Evaluation of Experimental Data

Methods of the regression matrix analysis of spectra, of continuous variation curves, curves of molar ratios, and absorbance-pH curves are given in ref.[3].

Method of corresponding solutions

The spectrophotometric determination of the stability constants β_n of gradual formation of the mononuclear complexes ML_n ($n = 1, \ldots, N$) in solution[4,5] is based on the formation function $\boldsymbol{n}$ which is defined by the average ligand number bound in the complexes with respect to overall concentration of the cation

$$\bar{n} = \frac{c_L - [L]}{c_M} = \frac{\sum_{n=1}^{N} n\,\beta_n[L]^n}{1 + \sum_{n=1}^{N} \beta_n[L]^n} . \qquad (1)$$

The absorbance measurement of the corresponding solutions consists in the following procedure: using constant wavelength, the functional dependences $A' = f(c'_L)$ and $A'' = f(c''_L)$ are measured in cells of d' and d'' pathlengths, respectively, at constant concentrations c'_M and c''_M, respectively, the latter being chosen to fulfil the relation $c'_M d' = c''_M d''$. Values c'_L and c''_L are read from the curves $A = f(c_L)$ at the same absorbance value to give pairs of corresponding solutions, wherefrom $\bar{n}$ and [L] are calculated.

Out of a number of procedures[4,5] for calculation of the stability constants from the functional relation $\bar{n} = f([L])$ the methods of linear extrapolation, elimination method, and numerical method using a computer were chosen.

The formation function (Eq. (*1*)) was linearized by Rossotti and Rossotti[6] for $N = 2$; modification of (*1*) gave Eq. (*2*)

$$\bar{n}/\{(1 - \bar{n})\,[L]\} = \beta_1 + \beta_2[L]\,(2 - \bar{n})/(1 - \bar{n}) , \qquad (2)$$

describing a straight line whose slope and intercept determine the stability constants β_1 and β_2.

Scatchard[7] modified Eq. (*1*) to the form

$$Q(L) = \bar{n}/((N - \bar{n})\,[L]) . \qquad (3)$$

Extrapolation of the curve $Q(L) = f([L])$ for $[L] \rightarrow 0$ gives the ratio K_1/N and hence also the stability constant $K_1 = \beta_1$, whereas extrapolation for $[L] \rightarrow \infty$ gives the value $N \cdot K_N$. For $N = 2$ it is then

$$\beta_2 = \beta_1 \cdot K_2 . \qquad (4)$$

The elimination methods are applied for $N = 2$ in the case of two consecutive equilibria. The formation function can be written in the form

$$x \cdot p_1 + y \cdot p_2 = 1 , \qquad (5)$$

TABLE I

Transformation Relations of Equation (*5*)

Relation	Parameter		Functional relation $\bar{n} = f([L])$	
	p_1	p_2	x	y
I	β_1	β_2	$(1 - \bar{n})\,[L]/\bar{n}$	$(2 - \bar{n})\,[L]^2/\bar{n}$
II	$1/\beta_1$	β_2/β_1	$\bar{n}/((1 - \bar{n})\,[L])$	$(\bar{n} - 2)\,[L]/(1 - \bar{n})$
III	$1/\beta_2$	β_1/β_2	$\bar{n}/((2 - \bar{n})\,[L]^2)$	$(\bar{n} - 1)/((2 - \bar{n})\,[L])$

where the variables x and y are the functional relations $\boldsymbol{n}$ and [L], and the parameters p_1 and p_2 relate to the constants β_1 and β_2, respectively. Possible transformations are given in Table I. From a pair of the experimental data $\boldsymbol{n}$ and [L] the pair of the values x and y in Eq. (5) is calculated. Linear dependence $p_1(p_2)_{x,y}$ between p_1 and p_2 is constructed by drawing straight line through the points $(1/x; 0)$ and $(0; 1/y)$. If p_1 and p_2 are constants, then all the straight lines intersect in one point (p_1, p_2).

Romary, Donelly and Andrews[8] published a program for calculation of consecutive stability constants of the complexes ML_n from the formation function $\boldsymbol{n} = f(—\log L)$ which was used in the present work. The program solves a system of independent simultaneous equations

$$\boldsymbol{n} + \sum_{n=1}^{N} (\boldsymbol{n} — n)\,[L]^n \,.\, \beta_n = 0\,, \tag{6}$$

where $\beta_n = K_1 \,.\, K_2 \ldots K_n$. The consecutive stability constants K_n are then determined by solution of N equations with n unknowns ($n \leqq N$) by the matrix method of gradual elimination.

Computations

The computations were carried out on computers ODRA 1013 (8 kwords), Hewlett Packard 2116 (16 k) and EC 1040, Robotron (500 k). The programs were in autocode Most F 13 and in Fortran for the former and the two later computers, respectively.

RESULTS AND DISCUSSION

Description of Absorption Spectra of the Equilibria Studied

Character of absorbance curves of the yellow products formed from SNAZOXS and Naphthylazoxine 6S with copper(II), zinc(II), and lead(II) ions in aqueous media was studied within the wavelength interval 400 to 650 nm. The absorbance curves are very similar in character, and, therefore, the equilibria of the both indicators with the mentioned ions will be discussed together. For individual combinations of the metal with the ligand it is possible to outline three cases of different experimental conditions giving spectral curves of different character.

Table II gives description of the absorption spectra of the coloured species present in solutions with various concentration ratios $q_M = c_M/c_L$ and various pH values exhibiting distinct isosbestic points for the mentioned equilibria of SNAZOXS and Naphthylazoxine 6S.

a) *The value* q_M *varied*, c_L *and* pH *constant*. In the equilibrium of copper(II) ions with SNAZOXS and Naphthylazoxine 6S increasing q_M value causes the absorption band of the protonated form of the ligand to disappear and a new band to appear in the range of shorter wavelengths with the absorption maximum at 443 nm (SNAZOXS–Cu^{2+}) and 420 nm (Naphthylazoxine 6S–Cu^{2+}). Set of the absorption spectra for the equilibrium of Naphthylazoxine 6S with Cu^{2+} ions, the ratio q_M being

TABLE II

Description of Absorption Spectra of Complexes of SNAZOXS and Naphthylazoxine 6S with Copper(II), Zinc(II), and Lead(II) Ions

I 0·1 ($NaClO_4$); SNAZOXS: c_L 8·0 . 10^{-5}M; Naphthylazoxine 6S: c_L 6·0 . 10^{-5}M. The symbol ↕ denotes shift of maximum of absorption band by corresponding change of experimental conditions. The system SNAZOXS–Cu^{2+} is given in the previous communication[3] of this series.

Type of dependence	Ratio of c_M/c_L	Studied pH range	Maxima of absorption bands				Isosbestic points	
			reaction product		free form of ligand			
			λ_{max} nm	pH region or c_M	λ_{max} nm	pH region or c_M	λ_{iso} nm	pH region or c_M
			Naphthylazoxine 6S and Cu^{2+}					
a	0—100	2·02	420	$c_M > 2 . 10^{-4}$M	520	$c_M < 8 . 10^{-5}$M	483	$c_M > 5 . 10^{-6}$M
b	250	1·2—3·9	420	pH > 1·5	520	pH < 1·3	470	pH > 1·7
							475	pH < 1·7
	50	1·2—3·3	420	pH > 1·5	520	pH < 1·3	475	pH > 1·75
							480	pH < 1·75
	10	1·1—3·4	420	pH > 1·9	520	pH < 1·6	482	pH < 2·3
c	0·5	1·3—3·8	430	pH > 3·0	520	pH < 2·0	487	pH < 4·4
			420	pH ≈ 2·3				
			SNAZOXS and Zn^{2+}					
a	0—100	4·45	460	$c_M > 2 . 10^{-4}$M	511	$c_M < 2 . 10^{-5}$M	487	$c_M \geqq 0$
b	100	1·7—6·2	↑ 456	pH = 6·2 ↑	540	pH < 1·7	493	pH > 2·9
			↓ >456	pH < 6·2 ↓				
	10	1·6—5·8	↑ 456	pH = 5·8 ↑	540	pH < 2·0	493	pH > 3·1
			↓ >456	pH < 5·8 ↓				

c	0·5	2·0—6·7	↑ 460 ↓ >460	pH = 6·7 ↑ pH < 6·7 ↓	512 ↑ 535 ↓	pH = 3·7 ↑ pH < 2·0 ↓	492	5·7 > pH > 4·0
				Naphthylazoxine 6S and Zn^{2+}				
a	0—100	4·51	↑ 467 ↓ 440	$c_M = 6 . 10^{-3}$M ↑ $c_M = 1·5 . 10^{-4}$M ↓	500	$c_M < 1·5 . 10^{-5}$M	464 495	$c_M < 6 . 10^{-5}$M $c_M > 10^{-4}$M
	250	1·3—6·5	↑ 436 ↓ 470	pH = 6·5 ↑ pH = 3·9 ↓	518	pH < 3·0	480	4·5 > pH > 2·8
b	100	1·4—5·2	↑ 436 ↓ 470	pH = 5·2 ↑ pH = 3·7 ↓	518	pH < 3·2	480	5·2 > pH > 3·4
	10	1·7—6·2	↑ 436 ↓ 470	pH = 6·2 ↑ pH = 4·2 ↓	500 ↑ 518 ↓	pH = 3·5 ↑ pH < 2·5 ↓	—	—
c	0·5	2·5—6·6	430	pH > 5·7	500 ↑ 518 ↓	pH = 3·7 ↑ pH < 2·5 ↓	450	5·7 > pH > 4·0
				SNAZOXS and Pb^{2+}				
a	0—10	4·68	↑ 450 ↓ >450	$c_M < 4 . 10^{-4}$M ↑ $c_M < 4 . 10^{-4}$M ↓	510	$c_M < 10^{-5}$M	480 (considerably unsharp)	
c	0·5	2·3—6·2	↑ 460 ↓ >460	pH = 6·2 ↑ pH < 6·2 ↓	510 ↑ 530 ↓	pH = 3·6 ↑ pH < 2·3 ↓	472	pH > 4·10
				Naphthylazoxine and Pb^{2+}				
a	0—5	5·12	430	$c_M > 6 . 10^{-5}$M	500	$c_M < 10^{-5}$M	458 471	$c_M < 1·5 . 10^{-6}$M $c_M > 6·0 . 10^{-5}$M
c	0·5	2·7—6·5	430	pH > 6·0	500 ↑ 500< ↓	pH > 3·0 ↑ pH < 3·0 ↓	—	—

varied (Fig. 1), exhibits a sharp isosbestic point at 483 nm; in the case of the equilibrium of SNAZOXS with Cu^{2+} ions the isosbestic point is less sharp at 497 nm. For each of the both indicators only one equilibrium of complex formation is possible.

In the equilibrium of zinc(II) ions with the both indicators the increasing q_M value causes an absorption band to be formed in region of shorter wavelengths; in the equilibrium of Naphthylazoxine 6S this band is distinctly split into two bands with λ_{max} at 440 and 467 nm, their intensity depending on the ratio q_M. In the equilibrium SNAZOXS–Zn^{2+} the splitting of absorption band is not observed and the respective set of absorption spectra shows a sharp isosbestic point at 487 nm indicating formation of a single complex, whereas the equilibrium Naphthylazoxine 6S–Zn^{2+} shows two isosbestic points.

In the equilibrium of lead(II) ions with the both indicators precipitate was formed with larger excess of Pb^{2+} ions, so that the absorption spectra could be measured for q_M 0 to 10 (SNAZOXS–Pb^{2+}) and 0 to 5 (Naphthylazoxine 6S–Pb^{2+}). Increasing q_M causes the absorption band of the ligand to disappear and a new absorption band to appear in the range of shorter wavelengths. For both SNAZOXS and Naphthylazoxine 6S the isosbestic points are not sharp with Pb^{2+}, which indicates formation of more than one complex.

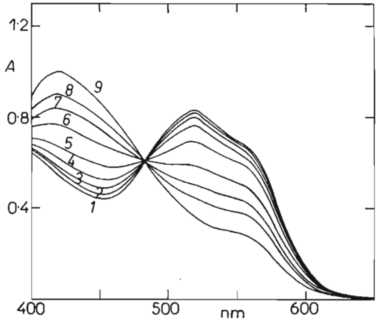

FIG. 1

Absorption Spectra of Solutions of Naphthylazoxine 6S and Copper(II) Ions for Various Ratios $q_M = c_M/c_L$

1 0; *2* 0·1; *3* 0·25; *4* 0·5; *5* 1·0; *6* 2·5; *7* 5·0; *8* 10; *9* 100. (c_L 6·0 . 10^{-5}M; pH 2·02; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

b) *The* pH *value varied*, $q_M > 1, c_L$ *and* c_M *constant.* In equilibrium of Naphthylazoxine 6S with copper(II) ions at $q_M = 50$ the wavelengths of absorption maxima of the coloured species correspond to those obtained for varrying q_M ratio at constant pH (Fig. 2). In equilibria of the both indicators it is possible to observe two close isosbestic points at some q_M ratios. At higher pH values the isosbestic point always has a lower wavelength than that at lower pH. If Cu^{2+} ion is present in excess ($q_M \gg 1$), then the isosbestic points are shifted to shorter wavelengths as compared with the cases of excess ligand ($q_M = 0{\cdot}5$).

With decreasing pH value of the solution absorption maxima of the reaction products of Zn^2 ions with the both indicators are shifted from lower to higher wavelengths, and the absorption band of the equilibrium Naphthylazoxine 6S–Zn^{2+} is split into further two bands (Fig. 3). However, position of both the absorption maxima and isosbestic points does not change with changing excess of Zn^{2+} ions. For both the indicators within pH 1 to 3 the intensity of absorption band of the ligand H_2L^- exceeds considerably that of H_2L^- in solutions of the pure ligand of the same concentration and that of the solutions containing excess of the ligand. Position of this absorption band which reaches its maximum intensity at pH 2·5 and 2·2

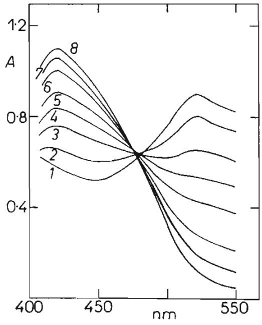

FIG. 2

Absorption Spectra of Naphthylazoxine 6S and Copper(II) Ions for Various pH Values

1 1·19; *2* 1·38; *3* 1·58; *4* 1·75; *5* 1·93; *6* 2·26; *7* 2·55; *8* 3·29. (c_L 6·0 . 10^{-5}M; c_M 3·07 . . 10^{-3}M; $q_M = 50$; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

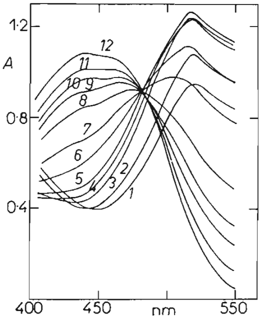

FIG. 3

Absorption Spectra of Naphthylazoxine 6S and Zinc(II) Ions for Various pH Values

1 1·14; *2* 1·35; *3* 1·95; *4* 2·41; *5* 2·78; *6* 3·05; *7* 3·30; *8* 3·63; *9* 3·89; *10* 4·10; *11* 4·44; *12* 6·51. (c_L6·0 . 10^{-5}M; c_M 1·5 . 10^{-2}M; $q_M = 250$; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

for the equilibria of Naphthylazoxine 6S and SNAZOXS, respectively, almost does not change. At pH < 2·5 and 2·2, respectively, intensity of this band again decreases. In the wavelength region below 450 nm at pH 1 to 3 it is possible to follow the absorbance decrease of the studied solutions in comparison with absorbance of solution of pure ligand of the same concentration.

In equilibria with Pb^{2+} ions the absorption spectra could not be followed with any greater excess of Pb^{2+} ions, because at pH below 4·5 solutions of the both indicators become turbid with excess lead(II) ions, and a precipitate is formed.

c) *The* pH *value varied*, $q_M < 1$, c_L *and* c_M *constant*. The absorption curves (Fig. 4) show (in the region of absorption of the complexes) different values of wavelengths of absorption maxima than in the cases of the presence of excess Cu^{2+} ion in the solution. However, wavelengths of these maxima are (with decreasing pH) shifted to the values approaching those of absorption maxima of the reaction products in solutions containing excess of Cu^{2+} ions ($q_M \gg 1$). Similar dependences can be observed when comparing the isosbestic points, too.

In the equilibria of the both indicators with Zn^{2+} ions at pH 2·5 to 3·5 and acid–base transition of the free ligand form H_2L^- to the form HL^{2-} can be observed. Further increase of pH causes the absorption band of the ligand HL^{2-} to disappear and a new absorption band of the complex being formed to appear in the spectral

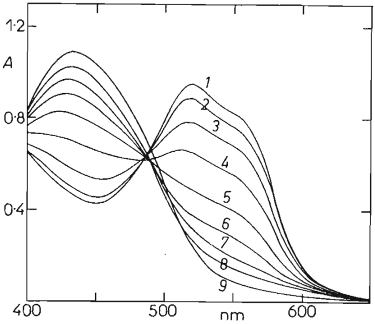

FIG. 4

Absorption Spectra of Naphthylazoxine 6S and Copper(II) Ions for Various pH Values *1* 1·35; *2* 1·70; *3* 2·02; *4* 2·29; *5* 2·56; *6* 2·79; *7* 3·05; *8* 3·34; *9* 3·81. (c_L 6·0 . 10^{-5}M; c_M 3·07 . 10^{-5}M; $q_M = 0·5$; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

region of shorter wavelengths (Fig. 5). In accordance therewith are the isosbestic points exhibited by the equilibria of the both indicators in the pH region 4 to 5·7.

In the equilibria with lead(II) ions at pH below 4 deprotonation of the form H_2L^- to the form HL^{2-} makes itself felt with increaing pH, and at pH 4 the absorption band of the formed ligand form HL^{2-} disappears, a new absorption band of the complex appearing in the region of shorter wavelengths. In reaction of SNAZOXS with Pb^{2+} ions a single complex is probably formed, because the spectrum shows sharp isosbestic point at 472 nm. No such point exists with Naphthylazoxine 6S, which indicates a more complicated equilibrium than that with SNAZOXS.

From the given results of study of absorption spectra it can be concluded that the both indicators form, with copper(II) ions, two complexes. In acid medium($pH < 2$) containing excess Cu^{2+} ions complexes with absorption maxima at 420 nm (Naphthylazoxine 6S–Cu^{2+}) and 443 nm (SNAZOXS–Cu^{2+}) are formed. In solutions with excess ligand ($q_M < 1$) at $pH > 3$ formation of a further complex with absorption maximum at 430 nm (Naphthylazoxine 6S–Cu^{2+}) and 460 nm (SNAZOXS–Cu^{2+}) can be observed.

For equilibria of Zn^{2+} ions with the both indicators it follows that at $pH > 5$ the complex with absorption maximum within the wavelengths 456 to 460 nm and 430 to 440 nm predominates for SNAZOXS–Zn^{2+} and Naphthylazoxine 6S–Zn^{2+},

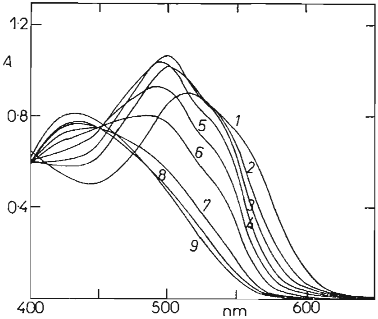

FIG. 5

Absorption Spectra of Naphthylazoxine 6S and Zinc(II) Ions for Various pH Values *1* 2·50; *2* 3·27; *3* 3·67; *4* 4·04; *5* 4·29; *6* 4·56; *7* 5·09; *8* 5·72; *9* 6·57. (c_L 6·0 . 10^{-5}M; c_M 3·0 . 10^{-5}M; q_M = 0·5; I 0·1 ($NaClO_4$); d 10·01 mm; 25°C).

respectively. With decreasing pH value it is possible to observe a shift of wavelength of the absorption maximum of reaction product of SNAZOXS with Zn^{2+} ions to higher values and intensity increase of the absorption band with the absorbance maximum within 467 to 470 nm for Naphthylazoxine 6S–Zn^{2+}, due obviously to formation of another complex with different composition. This conclusion is also supported by two isosbestic points at pH 4·68 in the absorption spectra of Naphthylazoxine 6S with zinc(II) ions at 495 and 464 nm for $q_M > 2·5$ and $q_M < 1$, respectively. At pH < 3·5 the both indicators show similar behaviour, *viz.* with excess ligand ($q_M < 1$) acid–base transition of the free ligand form H_2L^- to the form HL^{2-} is observed, wheres in solutions containing excess Zn^{2+} ions ($q_M > 10$) intensity of the absorption bands of the form H_2L^- is considerably greater than that of pure indicator of the same concentration. This fact indicates that in solutions containing excess Zn^{2+} ions a reaction product is formed which is transformed into another species at higher pH values. Complexity of the equilibria of Zn^{2+} ions with SNAZOXS and Naphthylazoxine 6S is also suggested by different wavelengths of isosbestic points of the spectra measured under different conditions.

For the equilibria of SNAZOXS with lead(II) ions it can be concluded that in solutions containing small excess of ligand the complex formed has the absorption maximum at 460 nm. This maximum is shifted to shorter wavelengths with increasing ratio q_M. Since isosbestic point of the spectra measured under the conditions type (*a*) is unsharp, too, formation of a further complex species can be presumed at $q_M > 1$. In reactions of Naphthylazoxine 6S with Pb^{2+} ions the presence of more than one complex species can be anticipated even in solutions containing small excess of the ligand.

Analysis of Curves of Continuous Variations

The evaluated curves of continuous variations are the corrected Job's curves. The ligand concentration was the same in the sample and reference cells, buffer with the metal and pure buffer being added in the former and the latter, respectively. The most probable stoichiometry of the formed complex species was assessed both from graphs of curves of continuous variations directly and by non-linear regression with the program JOBCON (ref.[9]) with the aim of determination of the stoichiometry and stability constant of the formed complex.

Reproducibility check of the measured curves and their evaluation by the program JOBCON are given in Table III. From the values given excellent agreement of the determined parameters can be seen (*i.e.* absorbance A_{max}, conditioned stability constants β'_{mn}, and relative standard deviations of repeated measurements).

From position and shape of the Job's curves of the equilibrium of Naphthylazoxine 6S with copper(II) ions at different pH values it follows that the stoichiometry M : L =

= 1 : 1 predominates at low pH values, being transformed into 1 : 2 stoichiometry at pH above 4·0.

Curves of continuous variations of equilibria of the both indicators with zinc(II) ions indicate formation of the complex M : L = 1 : 1 at pH about 4. At pH 5·35 a shift of the maximum to lower x_M values can be observed, which is probably due to formation of the complex M : L = 1 : 2.

TABLE III

Search for Stoichiometric Coefficients *m*, *n* and Value of the Conditioned Stability Constant β'_{mn} of the Most Probable Complex M_mL_n by Non-Linear Regression of Curves of Continuous Variations for Equilibrium Naphthylazoxine 6S–Cu^{2+} Ions Using the Hewlett–Packard Computer 2116 and the Program JOBCON. (*A*) Reproducibility of the Measurement, (*B*) pH Dependence

Experimental conditions: *c* 2·5 . 10^{-5}M; pH 5·35; 555 nm; *d* 50·02 mm; acetate buffer, *I* 0·1 (KNO_3), 25°C.

Curve	Tested ratio *m* : *n*	A_{max}	$x_{M,max}$	y_{max}	log β'_{mn}	Rel. standard deviation %
			A			
1	1 : 1	0·809	0·500	0·502	5·21	39·09
	1 : 2	0·529	0·333	0·841	11·87	16·28
2	1 : 1	0·809	0·500	0·496	5·19	39·20
	1 : 2	0·528	0·333	0·833	11·81	16·51
3	1 : 1	0·808	0·500	0·495	5·19	39·40
	1 : 2	0·529	0·333	0·826	11·75	17·11
The most probable complex 1 : 2, log β'_{12} = 11·81						
			B			
pH						
3·12	1 : 1	1·499	0·500	0·378	4·89	40·81
	1 : 2	0·955	0·333	0·646	10·72	13·31
3·94	1 : 1	0·911	0·500	0·495	5·19	36·87
	1 : 2	0·583	0·333	0·872	12·18	10·64
5·35	1 : 1	0·809	0·500	0·496	5·19	39·20
	1 : 2	0·528	0·333	0·833	11·81	16·51
6·75	1 : 1	0·681	0·500	0·532	5·29	40·55
	1 : 2	0·447	0·333	0·882	12·29	13·76
9·70	1 : 1	0·427	0·500	0·431	5·03	32·64
	1 : 2	0·276	0·333	0·748	11·23	15·23

The most probable complex 1 : 2, log β'_{12} = 11·81 at 5·35.

The presence of two complexes ML and ML_2 in solutions of the both indicators with Zn^{2+} ions is shown in the Job's curves in Fig. 6. At the wavelength 496 nm the maximum of the curve approaches the value $x_M \approx 0.33$, which indicates the complex ML_2. At other wavelengths the maxima of the curves of continuous variations are shifted to higher values $x_M \approx 0.5$. The same conclusions about the complexes ML and ML_2, as those made for the equilibrium SNAZOXS–Zn^{2+}, can be made from the Job's curves measured at various wavelengths at pH 5·35 for the equilibrium Naphthylazoxine 6S–Zn^{2+} (Table IV).

For the equilibria of lead(II) ions it was impossible to follow the pH dependence of position of the maximum and shape of the Job's curves, because at pH 4·5 the whole curves could not be measured. At pH below 4·5 the solutions become gradually turbid with increasing molar fraction x_M, and at $x_M > 0.5$ precipitate is formed. From the shape of the Job's curves for various wavelengths at pH 5·35 or from their evaluation (Table V) it can be concluded that the complexes ML and ML_2 are present simultaneously. In solutions of SNAZOXS–Pb^{2+} at pH > 5 the complex ML_2 predominates, whereas in the solutions of Naphthylazoxine 6S–Pb^{2+} the complex ML is predominant under the same experimental conditions. If the overall concentration c is increased by about two orders of magnitude, the maxima of the curves are shifted from the value $x_M = 0.5$ (ML complex) to lower values $x_M = 0.33$ (ML_2 complex).

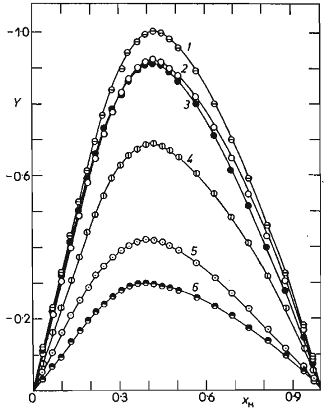

FIG. 6

Curves of Continuous Variations for Equilibrium of SNAZOXS with Zinc(II) Ions Measured for Various Wavelengths (nm)

1 540; *2* 524; *3* 560; *4* 510; *5* 580; *6* 496. (c 5·0 . 10^{-4}M; pH 5·35; acetate buffer; I 0·1 (KNO_3); d 5·02 mm; 25°C).

TABLE IV

Search for Stoichiometric Coefficients m, n and Value of the Conditioned Stability Constant β'_{mn} of the Most Probable Complex M_mL_n by Non-Linear Regression of Curves of Continuous Variations for Equilibria of SNAZOXS and Naphthylazoxine 6S with Zinc(II) Ions Depending on Wavelength (Hewlett–Packard 2116; Program JOBCON)

Experimental conditions: pH 5·35; acetate buffer, I 0·1 (KNO_3), 25°C; SNAZOXS + Zn^{2+}: c 5·0 . 10^{-4}M, d 5·02 mm; Naphthylazoxine 6S + Zn^{2+}: c 1·0 . 10^{-4}M, d 19·95 mm.

Wavelength nm	Tested ratio $m:n$	A_{max}	$x_{M,max}$	y_{max}	log β'_{mn}	Rel. standard deviation %
SNAZOXS + Zn^{2+}						
496	1 : 1	0·563	0·500	0·550	4·04	16·23
	1 : 2	0·603	0·333	0·522	7·63	36·12
510	1 : 1	1·319	0·500	0·539	4·00	13·97
	1 : 2	1·275	0·333	0·575	7·83	35·95
524	1 : 1	2·099	0·500	0·441	3·75	14·03
	1 : 2	1·895	0·333	0·521	7·63	38·08
540	1 : 1	1·889	0·500	0·544	4·02	11·47
	1 : 2	2·031	0·333	0·521	7·63	83·30
560	1 : 1	1·780	0·500	0·527	3·97	16·91
	1 : 2	1·608	0·333	0·594	7·90	31·94
580	1 : 1	0·869	0·500	0·499	3·90	23·08
	1 : 2	0·726	0·333	0·596	7·91	26·43
The most probable complex 1 : 1, log β'_{11} = 3·95						
Naphthylazoxine 6S + Zn^{2+}						
490	1 : 1	1·675	0·500	0·570	4·79	36·52
	1 : 2	1·106	0·333	0·775	10·19	12·63
500	1 : 1	1·899	0·500	0·578	4·81	28·92
	1 : 2	1·292	0·333	0·794	10·31	17·85
530	1 : 1	1·783	0·500	0·591	4·85	19·88
	1 : 2	1·440	0·333	0·677	9·66	26·76
540	1 : 1	1·775	0·500	0·595	4·86	23·88
	1 : 2	1·398	0·333	0·710	9·82	25·78
560	1 : 1	0·897	0·500	0·567	4·78	29·54
	1 : 2	0·602	0·333	0·798	10·34	19·46

The most probable complex 1 : 2, log β'_{12} = 10·06.

TABLE V

Search for Stoichiometric Coefficients m, n and Value of the Conditioned Stability Constant β'_{mn} of the Most Probable Complex M_mL_n by Non-Linear Regression of Curves of Continuous Variations for Equilibria of SNAZOXS and Naphthylazoxine 6S with Lead(II) Ions Depending on Wavelength (Hewlett–Packard 2116; Program JOBCON)

Experimental conditions: pH 5·35; acetate buffer, I 0·1 (KNO_3), 25°C; SNAZOXS + Pb^{2+}: c 5·0 . 10^{-4}M, d 5·02 mm; Naphthylazoxine 6S + Pb^{2+}: c 2·0 . 10^{-4}M, d 0·07 mm.

Wavelength nm	Tested ratio $m:n$	A_{max}	$x_{M,max}$	y_{max}	log β'_{mn}	Rel. standard deviation %
			SNAZOXS + Pb^{2+}			
480	1 : 1	0·706	0·500	0·372	3·58	54·26
	1 : 2	0·490	0·333	0·487	7·51	16·48
496	1 : 1	1·560	0·500	0·432	3·73	37·10
	1 : 2	1·018	0·333	0·643	8·10	11·19
510	1 : 1	2·079	0·500	0·465	3·81	31·74
	1 : 2	1·339	0·333	0·724	8·49	13·20
540	1 : 1	2·220	0·500	0·469	3·82	25·34
	1 : 2	1·560	0·333	0·676	8·25	21·81
560	1 : 1	1·752	0·500	0·517	3·95	29·82
	1 : 2	1·199	0·333	0·764	8·72	20·81
The most probable complex 1 : 2, log β'_{12} = 8·21						
			Naphthylazoxine 6S + Pb^{2+}			
470	1 : 1	0·640	0·500	0·637	4·68	26·17
	1 : 2	0·518	0·333	0·717	9·25	24·68
480	1 : 1	0·872	0·500	0·628	4·66	22·21
	1 : 2	0·707	0·333	0·726	9·30	26·95
490	1 : 1	1·050	0·500	0·656	4·74	17·74
	1 : 2	0·941	0·333	0·694	9·13	31·73
500	1 : 1	1·145	0·500	0·649	4·72	14·20
	1 : 2	1·116	0·333	0·637	8·88	34·64
530	1 : 1	0·973	0·500	0·700	4·89	4·19
	1 : 2	1·248	0·333	0·520	8·42	43·19
560	1 : 1	0·598	0·500	0·169	4·63	19·32
	1 : 2	0·512	0·333	0·681	9·07	28·70

The most probable complex 1 : 1, log β'_{11} = 4·72.

Analysis of Curves of Molar Ratios

Preliminary graphical analysis of the curves of molar ratios measured for the reactions of copper(II) ions with the both indicators showed that within pH 4·5 to 5·5 the ML_2 complex is formed predominantly (Fig. 7). In the wavelength regions about 600 nm and below 540 nm the upper parts of oblique sections of the curves show bendings. At pH < 4·5 greater deformations of the curves are observed due probably to gradual formation of the complexes ML and ML_2.

In the equilibria of the both indicators with Zn^{2+} and Pb^{2+} ions the stoichiometry could not be determined by graphical analysis due to considerable rounding-off of the curves of molar ratios. These curves were evaluated by non-linear regression using the program MRMCH-LETAG (ref.[10]). Besides the tested stoichiometric ratio $m : n = 1 : 2$ we also determined the conditioned stability constant β'_{mn} of the considered complex, negative decadic logarithm of the ligand concentration factor ($-\log f_L$), and extrapolated absorbance of the formed complex (A_{ext}). Close agreement of the experimental points with the calculated regression curve (following from alternation of signs of the residuals and from their low values which were mostly of the same magnitude as the standard deviation of absorbance for the used spectrophotometer) supports reliability of the determined parameters.

The described method was used for evaluation of only a limited number of the curves, as it is seen in Table VI. From the not very close agreement of the experimental points with the calculated curves in some cases it can be concluded that the

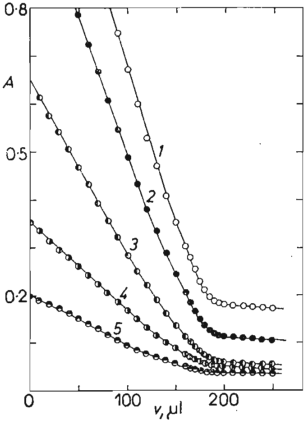

FIG. 7

Curves of Molar Ratios for Equilibrium of SNAZOXS with Copper(II) Ions Measured for Various Wavelengths (nm)

1 560; *2* 570; *3* 580; *4* 590; *5* 600. (c_L 2·0 . 10^{-4}M; $c_{M,0}$ 2·078 . 10^{-3}M; V_0 4·00 ml; pH 5·18; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

TABLE VI

Determination of Indicator Content and Values of the Conditioned Stability Constant of Complex ML_2 from SNAZOXS or Naphthylazoxine 6S and Cu^{2+}, Zn^{2+} or Pb^{2+} Ions by Non-Linear Regression of Curves of Molar Ratios Measured at Various Wavelengths (ODRA 1013 Computer; Program MRMCH-LETAG) (Experimental conditions: acetate buffer, I 0·1 (KNO_3); d 10·01 mm; 25°C).

Wavelength nm	pH	$c_L \cdot 10^4$ mol l^{-1}	$\log \beta'_{12} \pm \sigma$	Average
		SNAZOXS + Cu^{2+}		
Various[b]	5·40			11·77
		Naphthylazoxine 6S + Cu^{2+}		
565	4·62	1·0	12·50 ± 0·46	
565	4·62	1·5	13·04 ± 0·01	12·09
550	4·62	2·0	11·32 ± 0·06	
560	4·62	2·0	11·49 ± 0·01	
		SNAZOXS + Zn^{2+}		
555	5·18	1·5	9·79 ± 0·01	
570	5·18	2·0	9·89[a]	9·83
575	5·18	2·0	9·79 ± 0·01	
590	5·18	2·0	9·86[a]	
		Naphthylazoxine 6S + Zn^{2+}		
560	5·18	1·5	11·03 ± 0·03	
565	5·00	2·0	11·31[a]	11·02
565	5·18	2·0	10·64 ± 0·01	
565	5·18	2·0	11·10 ± 0·00	
		SNAZOXS + Pb^{2+}		
575	5·18	0·5	10·02[a]	
575	5·18	5·0	8·58 ± 0·04	9·37
560	5·18	2·0	9·78 ± 0·00	
580	5·18	2·0	9·11[a]	
		Naphthylazoxine 6S + Pb^{2+}		
550	5·18	1·5	8·89[a]	
550	5·18	1·7	9·02 ± 0·06	9·18
550	5·18	1·7	9·18 ± 0·08	
550	5·18	1·7	9·61 ± 0·11	

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[a] The standard deviation was not determined by the used program; [b] the results taken from the previous communication of this series.

TABLE VII

Evaluation of Stability Constants β'_1 and β'_2 of Complexes of SNAZOXS and Napthylazoxine 6S with Copper(II) Ions for Various Wavelengths from the Formation Functions $n = f(\mathrm{pL})$; pH 5·35; I 0·1 (KNO$_3$); Acetate Buffer; t 25°C

A. SNAZOXS + Cu^{2+}: c'_M 5·0 . 10^{-5}M; c''_M 1·0 . 10^{-5}M; d' 10·00 mm; d'' 50·00 mm; *B*. SNAZOXS + Cu^{2+}: c'_M 1·0 . 10^{-4}M; c''_M 1·0 . 10^{-5}M; d' 5·00 mm; d'' 50·00 mm; *C*. Naphthylazoxine 6S + Cu^{2+}: c'_M 5·0 . 10^{-5}M; c''_M 1·0 . 10^{-5}M; d' 10·00 mm; d'' 50·00 mm.

Wavelength nm	Graphical methods												Numerical method	
	linear extrapolation				elimination methods						mean			
	Eq. (2)		Eq. (3)		transform. I		transform. II		transform. III					
	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2
							A							
500	5·11	11·03	5·13	10·59	5·15	10·97	5·13	11·00	5·10	11·00	5·12	10·92	5·13	11·02
505	5·11	11·00	5·48	10·95	5·34	11·02	5·28	10·98	5·16	11·01	5·27	10·99	5·16	11·01
520	5·40	11·33	5·71	11·32	5·52	11·33	5·45	11·30	5·47	11·33	5·51	11·32	5·48	11·33
540	5·56	11·38	5·72	11·31	5·63	11·35	5·55	11·34	5·60	11·38	5·61	11·35	5·57	11·39
565	5·28	11·27	5·63	11·35	5·43	11·29	5·35	11·25	5·30	11·28	5·40	11·29	5·32	11·29
580	5·53	11·26	5·67	11·21	5·52	11·26	5·55	11·25	5·53	11·24	5·56	11·24	5·52	11·26
							B							
500	5·41	11·21	5·56	11·09	5·53	11·21	5·46	11·20	5·45	11·24	5·48	11·19	5·43	11·21
505	5·34	11·11	5·46	10·95	5·41	11·10	5·39	11·10	5·38	11·12	5·40	11·08	5·35	11·11
520	5·58	11·45	5·75	11·38	5·63	11·44	5·64	11·41	5·68	11·43	5·66	11·42	5·63	11·44
540	5·65	11·52	5·76	11·49	5·72	11·52	5·71	11·51	5·69	11·53	5·71	11·52	5·67	11·52
565	5·57	11·34	5·64	11·22	5·60	11·33	5·60	11·34	5·59	11·33	5·60	11·31	5·60	11·35
580	5·46	11·26	5·62	11·19	5·65	11·31	5·49	11·24	5·59	11·29	5·56	11·26	5·49	11·27
							C							
480	5·69	11·70	5·51	11·26	5·81	11·69	5·72	11·66	5·72	11·67	5·69	11·60	5·77	11·68
490	5·84	11·79	5·82	11·62	5·83	11·83	5·86	11·81	5·83	11·82	5·84	11·77	5·91	11·81
506	5·83	11·89	5·64	11·51	5·86	11·97	5·88	11·96	5·85	11·98	5·81	11·86	5·96	11·92
530	5·59	11·56	5·63	11·25	5·70	11·53	5·65	11·48	5·68	11·53	5·65	11·47	5·74	11·51
550	5·46	11·44	5·45	11·11	5·45	11·47	5·49	11·41	5·44	11·43	5·46	11·37	5·53	11·43
556	5·36	11·34	5·48	11·07	5·54	11·30	5·43	11·27	5·44	11·30	5·45	11·26	5·43	11·28

presumption concerning the chemical model was not fulfilled, *i.e.* that the equilibrium has a stepwise character, and besides the complex ML_2, also the complex ML (which has similar colour) is present. Therefore, the assessments of the conditional stability constants must be accepted with reserve.

Analysis of Curves of the Corresponding Solutions

The formation function $\boldsymbol{n} = f(\text{pL})$ for the equilibrium of SNAZOXS and Naphthylazoxine 6S with copper(II), zinc(II), and lead(II) ions was calculated from curves of the dependence of absorbance on the varying ligand concentration added to the solution of the metal ion the concentration of which was constant throughout the measurement of the whole curve. The curves were measured at pH 5·35 when only one form of the ligand (LH^{2-}) is present in the solution.

Course of the curve $\boldsymbol{n} = f(\text{pL})$ for all the studied equilibria corresponds to consecutive formation of the mononuclear complex ML_2 *via* the complex ML. Graphical and numerical methods (using computer) were used for treatment of the formation functions $\boldsymbol{n} = f(\text{pL})$ to obtain the conditional stability constants of the mononuclear complexes (β'_1 and β'_2) for the equilibria of SNAZOXS and Naphthylazoxine 6S with copper(II), zinc(II), and lead(II) ions at various wavelengths (Tables VII to IX).

From the values $\log \beta'_1$ and $\log \beta'_2$ a very good agreement is obvious between the results of the numerical method and the values found graphically for the equilibrium of SNAZOXS with Cu^{2+} ions and that of Naphthylazoxine 6S with Cu^{2+} and Zn^{2+} ions. For the equilibria of SNAZOXS with Zn^{2+} ions and those of Naphthylazoxine 6S with Pb^{2+} ions the mutual agreement between the results of individual graphical procedures is worse. Some graphical procedures did not allow at all to evaluate the formation curve $\boldsymbol{n} = f(\text{pL})$ of these equilibria, even though numerical method gave reliable results of $\log \beta'_1$ and $\log \beta'_2$.

Agreement between the conditional stability constants determined by various techniques of evaluation of the formation function is influenced by stability of the formed complexes and, consequently, by choice of applicable regions of the overall concentrations c_L and c_M and ratio c'_M/c''_M with respect to high absorption of the free form of ligand. The complexes of SNAZOXS and Naphthylazoxine 6S with copper(II) ions are sufficiently stable and dissociate little at low metal concentrations $c_M \approx \approx 10^{-5}\text{M}$. Hence, it is possible to choose the ratios $c'_M/c''_M > 2$, which increases the differences $c'_L - c''_L$ and $c'_M - c''_M$ and enables a more precise determination of $\boldsymbol{n}$ and [L].

For the equilibria of the both indicators with zinc(II) and lead(II) ions it is only possible to choose the ratio $c'_M/c''_M = 2$ in the concentration range $1{\cdot}2 \,.\, 10^{-4}\text{M} < c_M < < 2{\cdot}5 \,.\, 10^{-4}\text{M}$. For the stronger complexes of zinc(II) ions with the both indicators these experimental conditions are sufficient, but in the case of weaker complexes

TABLE VIII

Evaluation of Stability Constants β'_1 and β'_1 of Complexes of SNAZOXS and Naphthylazoxine 6S with Zinc(II) Ions for Various Wavelentghs from the Formation Functions $\bar{n} = f(pL)$; pH 5·35; I 0·1 (KNO_3); Acetate Buffer; t 25°C

A. SNAZOXS + Zn^{2+}: c'_M 2·5 . 10^{-4}M; c''_M 1·25 . 10^{-4}M; d' 5·00 mm; d'' 10·00 mm; *B*. Naphthylazoxine 6S + Zn^{2+}: c'_M 2·5 . 10^{-4}M; c''_M 1·25 . 10^{-4}M; d' 5·00 mm; d'' 10·00 mm.

Wavelength nm	Graphical methods												Numerical method	
	linear extrapolation				elimination methods						mean			
	Eq. (2)		Eq. (3)		transform. I		transform. II		transform. III					
	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2
							A							
496	4·40	9·94			4·40	8·95	4·48	8·95	4·33	9·00	4·40	8·96	4·37	8·92
510	5·29	9·81			5·28	9·81	5·29	9·24	5·32	9·82	5·30	9·67	5·26	9·79
524	5·42	9·95			5·38	9·92			5·38	9·87	5·39	9·91	5·37	9·93
540	5·28	9·80			5·23	9·78	5·21	9·43	5·23	9·80	5·24	9·70	5·25	9·80
560	5·01	9·46			4·62	9·23			5·93	9·42	4·85	9·37	5·92	9·43
580	4·68	9·19			4·44	9·03			4·72	9·12	4·61	9·11	4·65	9·15
							B							
480	5·42	10·31	5·34	10·44	5·41	10·34	5·42	10·34	5·41	10·32	5·40	10·35	5·38	10·33
490	5·18	10·07	5·03	9·98	5·14	10·08	5·15	10·09	5·13	10·05	5·13	10·05	5·11	10·05
500	4·81	9·85	4·76	9·60	4·89	9·82	4·79	9·84	4·82	9·83	4·81	9·79	4·84	9·83
514	4·60	9·67	4·34	9·16	4·56	9·67	4·55	9·67	4·54	9·66	4·52	9·57	4·63	9·64
530	4·38	9·46	4·32	9·03	4·53	9·45	4·50	9·43	4·43	9·46	4·43	9·37	3·47	9·44
540	4·54	9·57	4·13	8·88	4·58	9·56	4·54	9·57	4·57	9·55	4·47	9·43	4·56	9·54
560	4·86	9·82	4·75	9·60	4·86	9·85	4·86	9·82	4·87	9·83	4·84	9·78	4·85	9·83

TABLE IX

Evaluation of Stability Constants β'_1 and β'_2 of Complexes of SNAZOXS and Naphthylazoxine 6S with Lead(II) Ions for Various Wavelengths from the Formation Functions $\bar{n} = f(pL)$; pH 5·35; I 0·1 (KNO$_3$); Acetate Buffer; t 25°C

A. SNAZOXS + Pb^{2+}: c'_M 2·4 . 10^{-4}M; c''_M 1·2 . 10^{-4}M; d' 5·00 mm; d'' 10·00 mm; *B*. Naphthylazoxine 6S + Pb^{2+}: c'_M 2·4 . 10^{-4}M; c''_M 1·2 . 10^{-4}M; d' 5·00 mm; d'' 10·00 mm.

Wave-length nm	Graphical methods										Numerical method	
	linear extrapolation				elimination methods				mean			
	Eq. (2)		Eq. (3)		transform. II		transform. III					
	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2	log β'_1	log β'_2
						A						
490			3·88	8·86					3·88	8·86	3·68	8·76
500	4·76	8·70	4·58	9·50					4·67	9·10	4·28	9·12
510	4·63	9·25	4·71	9·74					4·67	9·50	4·46	9·33
524	4·87	9·67							4·87	9·67	4·75	9·63
540	5·07	9·82							5·07	9·82	4·92	9·82
560	4·70	9·53							4·70	9·53	4·65	9·59
580	4·54	8·72							4·54	8·72	3·79	8·91
						B						
470	4·15	9·83	4·73	10·01	4·70	9·75	4·65	9·63	4·56	9·81	4·10	9·90
480	4·23	9·73	4·61	9·81	4·60	9·59			4·48	9·71	4·15	9·83
490	4·64	9·54	4·56	9·82	4·56	9·48	4·65	9·51	4·60	9·59	4·27	9·75
500	4·41	9·36	4·46	9·58	4·44	9·32	4·48	9·30	4·48	9·39	4·14	9·52
530	4·36	9·21	4·33	9·43	4·37	9·18	4·59	9·14	4·43	9·24	3·72	9·37
560	4·61	9·51	4·67	9·86	4·66	9·44	4·65	9·47	4·65	9·57	3·94	9·77

of lead(II) ions they are at the limit of applicability of this experimental technique. From analysis of the formation function $n = f(\text{pL})$ obtained by the method of the corresponding solutions for the equilibria of SNAZOXS and Naphthylazoxine 6S

TABLE X

Evaluation of Absorbance-pH Curves for Equilibrium of SNAZOXS with Copper(II) Ions by Linear Regression (part *B*) and by Non-Linear Regression for $q_M = 100$ by the Program APHM-LETAG using ODRA 1013 Computer (part *A*)

c_L 1·2 . 10^{-5}M; 528 nm; *I* 0·1 (KNO_3); *d* 50·01 mm, 25°C.

Part *A*

Tested complex	Form of ligand	Coeff. mnr	q	$\varepsilon_{\text{compl.}}$	$\log \varkappa_{\text{mnr}}$	σ, A	$m_{R,1}$	$m_{R,2}$	$m_{R,3}$	$m_{R,4}$
ML	H_2L	110	2	13 900 ± 152	—0·61 ± 0·06	0·076	0·000	0·069	—1·94	3·38
MHL	H_2L	111	1	43 900 ± 18 000	—0·36 ± 0·32	0·202	0·015	0·184	—1·46	1·33
ML_2	H_2L	120	4	4 090 ± 3 850	0·83 ± 0·86	0·440	0·000	0·401	—0·43	—1·16
$M(HL)_2$	H_2L	122	2	4 140 ± 2 990	3·58 ± 0·60	0·516	0·000	0·471	—0·51	—1·09

Part *B*[a]

Tested complex	Form of ligand	Coeff. mnr	No of points	r_{xy}	ε_2 (of the complex)	$\log \varkappa_{\text{mnr}}$	Det. q
			q_M 100				
ML	H_2L	110	12	0·81814	1·36 . 10^4	—0·54	
				0·98600		—0·70	2
ML_2	H_2L	120	12	0·58670	2·07 . 10^4	2·86	
				—0·55324		7·98	2
ML_3	H_2L	130	12	0·85088	3·33 . 10^4	3·11	
				—0·99032		9·71	1
ML_4	H_2L	140	12	0·78591	4·34 . 10^4	5·29	
				—0·98481		13·58	1
MHL	H_2L	111	12	0·24010	1·18 . 10^4	0·96	
				0·98586		—0·70	2
$M(HL)_2$	H_2L	122	12	0·59578	2·08 . 10^4	4·68	
				—0·55324		7·98	2

TABLE X
(*Continued*)

Tested complex	Form of ligand	Coeff. mnr	No of points	r_{xy}	ε_2 (of the complex)	$\log \varkappa_{mnr}$	Det. q
			q_M 10				
ML	H_2L	110	10	0·99443	1·37 . 10^4	0·00	
				0·99953		—0·03	2
ML_2	H_2L	120	10	0·65140	1·99 . 10^4	2·57	
				—0·78290		8·97	1
ML_3	H_2L	130	10	0·69660	3·01 . 10^4	3·46	
				—0·98770		11·10	1
ML_4	H_2L	140	10	0·64544	3·97 . 10^4	5·37	
				—0·98376		14·93	1
MHL	H_2L	111	10	0·48152	1·88 . 10^4	4·16	
				0·99953		3·04	2
$M(HL)_2$	H_2L	122	10	0·71700	2·03 . 10^4	4·63	
				0·78297		8·97	1

[a] The first row of each model is evaluated according to Eq. (*16*), the second row according to Eq. (*17*). The equations are given in the previous communication[3] of this series.

with copper(II), zinc(II), and lead(II) ions it follows that, in the region of the existence of the ligand in the form LH^{2-}, the complex ML_2 is formed gradually *via* the complex ML with increasing concentration of the ligand.

Analysis of Absorbance-pH *Curves*

For the measurements of absorbance-pH curves we selected the wavelengths of the free ligand form, that of absorption maximum of the formed yellow reaction products, and those of the distinct isosbestic points. The curves were measured for various q_M values in the interval 0 to 250. In the case of excess concentration of the metal ion ($q_M \gg 1$) formation of only one particle in the solution was presumed, and the *A*–pH curves were evaluated with the use of linear regressions of the transformation relations given elsewhere, too[11]. In equimolar solutions ($q_M \approx 1$) and in those containing small excess of the ligand ($q_M < 1$) consecutive formation of the complexes ML and ML_2 can be presumed, and, therefore, the transformation relations were not used.

In Table X(*B*), giving results of linear regression of *A*–pH curves for $q_M = 100$ and 10, various stoichiometric ratios $m : n$ and various protonation degrees of the formed complex particle were tested. The correlation coefficient r_{xy} chosen as reliability criterion is here badly conditioned for the tested stoichiometric coefficients m, n, z, and its use does not seem very reliable. Tables X(*A*) and XI give results of evaluation of *A*–pH curves of SNAZOXS and Naphthylazoxine 6S with copper(II) ions by non-linear regression using the program APHM-LETAG, where the reliability criterion of the determined parameters is given by agrrement between the experimental points and the calculated regression curve, by standard deviation of the absorbance (σ(A)), and by magnitude of the residuals. For the equilibrium of SNAZOXS and Naphthylazoxine 6S with copper(II) ions under the given conditions the most probable complex seems to be the complex 1 : 1.

TABLE XI

Evaluation of Absorbance-pH Curves for Equilibrium of Naphthylazoxine 6S with Copper(II) Ions in High Excess (ODRA 1013 Computer; Program APHM-LETAG)

c_L 6·0 . 10^{-5}M; 414 nm; I 0·1 (NaClO$_4$); d 10·01 mm, 25°C.

Tested complex	Form of ligand	Coeff. mnr	q	$\varepsilon_{compl.}$	$\log \varkappa_{mnr}$	σ(A)	$m_{R,1}$	$m_{R,2}$	$m_{R,3}$	$m_{R,4}$
					q_M 250					
ML	H_2L	110	2	17 690 ± 10	−1·63 ± 0·06	0·096	0·000	0·089	−0·62	−0·61
MHL	H_2L	111	1	18 990 ± 1 070	0·14 ± 0·14	0·242	0·000	0·222	−1·44	1·01
ML_2	H_2L	120	4	12 760 ± 4 520	−0·57 ± 0·93	0·701	0·000	0·545	−1·01	0·43
$M(HL)_2$	H_2L	122	2	12 830 ± 3 520	3·00 ± 0·61	0·848	0·000	0·780	−1·10	0·61
					q_M 50					
ML	H_2L	110	2	16 500 ± 20	−0·77 ± 0·20	0·029	0·000	0·026	−1·61	1·89
MHL	H_2L	111	1	28 820 ± 7 230	0·13 ± 0·20	0·141	0·003	0·128	−1·32	0·66
ML_2	H_2L	120	4	7 720 ± 5 220	0·27 ± 0·78	0·430	0·000	0·392	−0·80	−0·14
$M(HL)_2$	H_2L	122	2	7 820 ± 4 440	3·60 ± 0·60	0·506	0·000	0·462	−0·93	0·03
					q_M 10					
ML	H_2L	110	2	17 190 ± 70	−0·56 ± 0·06	0·059	0·004	0·055	−0·04	−1·48
MHL	H_2L	111	1	22 530 ± 2 140	0·94 ± 0·11	0·072	0·000	0·065	−0·84	−0·64
ML_2	H_2L	120	4	1 240 ± 3 060	−1·63 ± 0·56	0·458	−0·012	0·334	0·47	−1·08
$M(HL)_2$	H_2L	122	2	8 460 ± 4 740	3·63 ± 0·66	0·593	0·000	0·482	−0·28	−0·97

The wavelengths of the isosbestic points of acid–base transition of the ligand H_2L^- to the form HL^{2-} were chosen to eliminate influence of dissociation of the ligand itself on shape of the *A*–pH curve at various ratios of the metal and the ligand.

For the equilibrium of Naphthylazoxine 6S and SNAZOXS with Zn^{2+} ions there appears formation of a further complex for $q_M \gg 1$, because course of the *A*–pH curve in the region of the ligand itself is somewhat anomalous (Fig. 8). The results are given in Table XII, *i.e.* the most likely are the complexes ML and MLH.

Analogous conclusions were also made for the equilibrium of the both indicators with lead(II) ions. In these cases higher concentrations of Pb^{2+} ions could not be used, because at pH < 4·5 precipitate is formed. The results are given in Table XIII showing also the most likely complexes ML and MLH.

TABLE XII

Evaluation of Absorbance-pH Curve for Equilibrium of SNAZOXS with Zinc(II) Ions in High Excess by Graphical (direct and logarithmical) Analysis and Non-Linear Regression Using APHM-LETAG Program

c_L 8·0 . 10^{-5}M; $q_M = 100$; 430 nm; *I* 0·1 ($NaClO_4$), *d* 10·01 mm; 25°C.

Graphical analysis			Direct, Eq. (*16*)[a]			Logarithmical Eq. (*17*)[a]	
Tested complex	form of ligand	coeff. mnr	ε_{H_xL}	$\varepsilon_{compl.}$	$\log \varkappa_{mnr}$	$\log \varkappa_{mnr}$	det. *q*
ML MHL	HL H_2L	110 111	3 410	12 960	—0·75	—0·73	0·99

Non-linear regression — program APHM-LETAG

Tested complex	form of ligand	coeff. mnr	*q*	$\varepsilon_{compl.}$	$\log \varkappa_{mnr}$	σ(A)	$m_{R,1}$	$m_{R,2}$	$m_{R,3}$	$m_{R,4}$
ML	H_2L	110	2	12 070 ± 50	—3·66 ± 0·07	0·107	0·000	0·095	0·53	—0·76
ML	HL	110	1	12 960 ± 20	—0·74 ± 0·01	0·010	0·000	0·009	1·42	1·40
MHL	H_2L	111								
ML_2	H_2L	120	4	15 140 ± 530	—5·34 ± 0·90	0·663	0·000	0·585	—0·06	—0·97
ML_2	HL	120	2	8 880 ± 2 720	—0·47 ± 0·67	0·639	0·000	0·564	—0·31	—0·83
$M(HL)_2$	H_2L	122								

[a] The equations are given in the previous communication[3] of this series.

Analysis of Spectra

Analysis of the spectral curve of SNAZOXS and Naphthylazoxine 6S with copper(II), zinc(II), and lead(II) ions was carried out by regression matrix analysis using the program FA608 + EY608. Number of the coloured particles (n_c) in solution is equal to the rank of the absorbance matrix for that value of resulting residual error which is numerically closest to the absorbance error s_k of the used spectrophotometer. Within determination of the chemical model, *i.e* number of the complex species, their stoichiometric coefficients and reaction scheme, the equilibrium constants $\varkappa_{mn}$ of the reaction and curves of molar absorption coefficients of all coloured species in the solution are determined, too. The measure of agreement between the calculated spectra and the experimental points which is assessed from the value of stan-

TABLE XIII

Evaluation of Absorbance-pH Curve for Equilibrium of Naphthylazoxine 6S with Zinc(II) Ions in High Excess by Graphical (direct and logarithmical) Analysis and Non-Linear Regression Using APHM-LETAG Program

c_L 6·0 . 10^{-5}M; q_M = 100; 414 nm; I 0·1 ($NaClO_4$); d 10·01 mm; 25°C.

Graphical analysis			Direct, Eq. (*16*)[a]			Logarithmical Eq. (*17*)[a]	
Tested complex	form of ligand	coeff. mnr	ε_{H_xL}	$\varepsilon_{compl.}$	$\log \varkappa_{mnr}$	$\log \varkappa_{mnr}$	det. q
ML	HL	110	6 000	15 500	—0·99	—1·22	1·01
MHL	H_2L	111					

Non-linear regression — program APHM-LETAG

Tested complex	form of ligand	coeff. mnr	q	$\varepsilon_{compl.}$	$\log \varkappa_{mnr}$	$\sigma(A)$	$m_{R,1}$	$m_{R,2}$	$m_{R,3}$	$m_{R,4}$
ML	H_2L	110	2	14 620 ± 10	—4·59 ± 0·12	0·196	0·005	0·123	0·03	—1·39
ML	HL	110	1	15 510 ± 50	—0·19 ± 0·01	0·009	0·000	0·008	1·29	1·02
MHL	H_2L	111								
ML_2	H_2L	120	4	13 570 ± 2 850	—8·22 ± 0·82	0·485	0·000	0·429	—0·13	—1·30
ML_2	HL	120	2	13 540 ± 2 210	—0·10 ± 0·62	0·602	0·000	0·531	—0·08	—1·32
$M(HL)_2$	H_2L	122								

[a] The equations are given in the previous communication[3] of this series.

dard deviation of absorbance ($\sigma(A)$) is a criterion as to whether the tested chemical model complies with the experimental data. Determination of the chemical model is the more reliable the closer is the standard deviation of absorbance ($\sigma(A)$) after carrying out the regression analysis to the resulting residual error s_k determined by factor analysis.

From the results of regression matrix analysis of the spectra of SNAZOXS and Naphthylazoxine 6S with copper(II) ions (Table XIV) it follows that at high excess of Cu^{2+} ions ($q_M > 100$) and at low pH values (pH region below 2) the protonated complexes of the most probable composition CuLH are formed predominantly and are transformed into the complex CuL with decreasing ratio q_M and with increasing pH. The complex CuL is then converted to the complex CuL_2 on further decreasing of the ratio q_M and increasing of pH.

Tables XV and XVI give the results of analysis of spectra of SNAZOXS and Naphthylazoxine 6S with zinc(II) and lead(II) ions. With high excess of the metal ions formation of the non-protonated complex ML by reaction of the metal ion with the ligand form H_2L^- is impossible. Probably reaction of this form lead to the complexes MHL and $M(HL_2)$ whereas the complexes ML and ML_2 are formed by reaction of the ligand form HL^{2-}. With excess of the ligand ($q_M < 1$) the complexes with the ratio M : L = 1 : 2 are formed predominantly.

The absorbance standard deviation is decreased during testing of the chemical model, if protonation equilibrium of the ligand is considered besides the complex

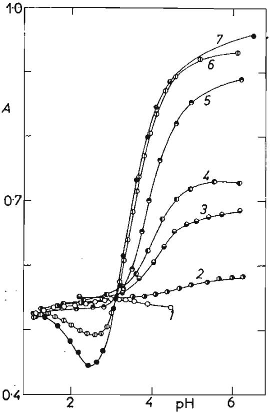

FIG. 8

Absorbance-pH Curves for Equilibrium Naphthylazoxine 6S–Zn^{2+} Measured at Various Ratios $q_M = c_M/c_L$

1 0; *2* 0·125; *3* 0·5; *4* 1·0; *5* 10·0; *6* 100·0; *7* 250·0. (c_L 6·0 . 10^{-5}M; 414 nm; *I* 0·1 ($NaClO_4$); *d* 10·01 mm; 25°C).

TABLE XIV

Search for the Most Probable Chemical Model, *i.e.* Number and Stoichiometry of the Complex Species Existing in Solution, by Regression Matrix Analysis of Spectral Curves for Equilibria of Naphthylazoxine 6S with Copper(II) Ions Using EC 1040 Computer and FA608 + EY608 Program

c_L 6·0 . 10^{-5}M; I 1·0 ($NaClO_4$); 25°C.

q_M	pH	s_k (n_c)	n_k	Tested complex	Coloured species	$\bar{\sigma}(A)$	log $\varkappa_{mnr}$	n_v
250	1·16—3·06	0·004 (2)	1	CuL	CuL; H_2L	0·022	—1·53 ± 0·06	99
				CuHL	CuHL; H_2L	0·004	0·39 ± 0·01	
				CuL_2	CuL_2; H_2L	0·031	—0·72 ± 0·06	
				CuL(HL)	CuL(HL); H_2L	0·019	1·00 ± 0·04	
				$Cu(HL)_2$	$Cu(HL)_2$; H_2L	0·005	2·80 ± 0·01	
50	1·19—2·36	0·006 (2)	1	CuL	CuL; H_2L	0·013	—0·83 ± 0·02	99
				CuHL	CuHL; H_2L	0·006	0·95 ± 0·00	
				$Cu(HL)_2$	$Cu(HL)_2$; H_2L	0·006	3·32 ± 0·02	
10	1·45—2·48	0·005 (2)	1	CuL	CuL; H_2L	0·008	—0.52 ± 0·02	81
				CuHL	CuHL; H_2L	0·005	1·54 ± 0·00	
				CuL(HL)	CuL(HL); H_2L	0·008	1·71 ± 0·02	
				$Cu(HL)_2$	$Cu(HL)_2$; H_2L	0·004	3·63 ± 0·01	
0·0 0·05 0·1 0·25 0·5; 1 2·5; 5 10; 100	2·02	0·005 (2)	1	CuL	CuL; H_2L	0·004	—0·16 ± 0·01	250
				CuHL	CuHL; H_2L	0·004	1·86 ± 0·01	
				CuL_2	CuL_2; H_2L	0·008	—0·20 ± 0·01	
				$Cu(HL)_2$	$Cu(HL)_2$; H_2L	0·008	3·84 ± 0·01	
0·0 0·05 0·1 0·25 0·5 1·0 2·5 5·0 10·0 100·0	1·84—3·81	0·008 (3)	2	CuL	CuL; HL H_2L	0·071	—0·64 ± 0·01	500
				CuHL	CuHL; HL H_2L	0·122	1·15 ± 0·05	
				CuL_2	CuL_2; HL H_2L	0·027	—0·16 ± 0·03	
				$Cu(HL)_2$	$Cu(HL)_2$; HL H_2L	0·039	3·85 ± 0·01	

TABLE XV

Survey of the Determined Conditioned (β'_{mn}) and Overall (β_{mnr}) Stability Constants of Complexes of SNAZOXS with Copper(II), Zinc(II) and Lead(II) Ions (t 25°C)

Constant	Medium	pH	log β			Method[a]
			Cu^{2+}	Zn^{2+}	Pb^{2+}	
β'_{11}	I 0·1	2·30	4·31			*A*
	(KNO_3, acetate buffer)			3·95		*A*
		5·35	5·49	4·97	4·63	*B*
			5·45	4·97	4·36	*C*
β'_{12}	I 0·1		11·09		8·21	*A*
	(KNO_3, acetate buffer)	5·35	11·25	9·45	9·31	*B*
			11·27	9·54	9·31	*C*
		5·18	11·65	9·83	9·37	*D*
	I 0·01					
	(KNO_3, urotropine buffer)	5·19		10·55	10·31	*D*
						ref.[12]
β_{110}	I 0·1			6·21		*E*
			9·86			*F*
	($NaClO_4$, $HClO_4$)		9·81	6·21		*G*
			9·90	6·14	7·24	*H*
			10·0	6·95		ref.[13]
β_{111}	I 0·1			2·17		*E*, G
	($NaClO_4$, $HClO_4$)		5·05	2·10	3·20	*H*
β_{120}	I 0·1		19·99	13·91	14·63	*H*
	($NaClO_4$, $HClO_4$)		18·8			ref.[13]
β_{122}	I 0·1		9·75	5·83	6·55	*H*
	($NaClO_4$, $HClO_4$)					

[a] *A* the non-linear regression of curves of continuous variations (JOBCON program); *B* the corresponding solutions, the formation functions $\bar{n} = f(pL)$ were evaluated by graphical methods; *C* the corresponding solutions, the formation functions $\bar{n} = f(pL)$ were evaluated by numerical method; *D* non-linear regression of curves of molar ratios (MRMCH-LETAG program); *E* graphical evaluation of the absorbance-pH curves; *F* linear regression of the absorbance-pH curve s; *G* non-linear regression of the absorbance-pH curves (APHM-LETAG program); *H* analysis of the absorption spectra (regression matrix analysis, FA608 and EY608 program).

formation equilibrium in the calculation or if a greater number of complex compounds are tested side by side.

TABLE XVI

Survey of the Determined Conditioned (β'_{mn}) and Overall (β_{mnr}) Stability Constants of Complexes of Naphthylazoxine 6S with Copper(II), Zinc (II) and Lead(II) Ions

Constant	Medium	pH	log β			Method[a]
			Cu^{2+}	Zn^{2+}	Pb^{2+}	
β'_{11}	I 0·1			4·86	4·72	*A*
	(KNO_3, acetate buffer)	5·35	5·65	4·80	4·53	*B*
			5·72	4·83	4·05	*C*
β'_{12}	(I 0·1		11·59	10·28	9·21	*A*
	KNO_3, acetate buffer)	5·35	11·56	9·76	9·55	*B*
			11·61	9·81	9·69	*C*
	I 0·01	4·62	12·09			
	(KNO_3, urotropine buffer)	5·0—5·8		11·02		*D*
		5·18			9·18	
		5·19		10·69	9·83	*D* ref.[12]
β_{110}	I 0·1			6·28		*E*
	($NaClO_4$, $HClO_4$)		9·77	6·19		G
			10·38	5·87		H
			10·4	7·2		ref.[13]
β_{111}	I 0·1			2·06		*E*
	($NaClO_4$, $HClO_4$)			1·97		*G*
			5·03	1·65		H
β_{120}	I 0·1		20·91	13·85		H
	($NaClO_4$, $HClO_4$)					
			19·4			ref.[13]
β_{122}	I 0·1		9·95	5·42		H
	($NaClO_4$, $HClO_4$)					

[a] See Table XV.

CONCLUSIONS

The metallochromic indicators SNAZOXS and Naphthylazoxine 6S form yellow complexes with copper(II), zinc(II) and lead(II) ions, their stoichiometry being $M : L = 1 : 1$ and $1 : 2$.

The reaction with Cu^{2+} ion at $pH < 2$ gives the complex CuL as the dominant product. Great excess of Cu^{2+} ions ($q_M > 10$) also leads to the protonated complexes in this pH region, the formation of CuHL complex being admittable.

Red colouration becomes more intensive and deeper in solutions of SNAZOXS and Naphthylazoxine 6S at $pH < 3$ in the presence of a larger excess of zinc(II) ions, whereas the presence of lead(II) ions causes red precipitate to be formed. These phenomena can be explained by formation of the reaction products in which central metal ion is bound to nitrogen atom of azo group, in contrast to the yellow complex particles in which the metal ion is bound to the nitrogen heteroatom of quinoline ring.

In the solutions containing excess of the metal ions ($q_M > 5$) formation of the complexes ML or possibly also that of the protonated complexes MLH can be followed. With excess of the ligand the complexes of stoichiometric ratio $M : L = 1 : 2$ are formed besides those of ratio $1 : 1$. For copper(II) ions at $pH > 5$ the complex CuL_2 completely predominates. In this pH region zinc(II) and lead(II) ions were proved to form the complexes ML and ML_2 side by side, the protonated forms of these complexes MLH and $M(LH)_2$ being not excluded either.

Structure of the discussed complexes can be described by the formulas given in the previous communication[3].

Tables XV and XVI give average values of the conditional stability constants β'_{mn} along with the overall concentration stability constants $\beta_{mnr} = [M_mL_nH_r] : ([M]^m[L]^n[H]^r)$ calculated from the values of the respective dissociation constants of the ligand and from equilibrium constants $\varkappa_{mnr} = [M_mL_nH_r][H]^q/([M]^m . [H_jL]^n)$, q being equal to $(nj - r)$, which were determined by regression matrix analysis of the absorption spectra and evaluation of the absorbance-pH curves. For comparison the Tables also give values of the stability constants taken from literature[12,13].

The methods of continuous variations, molar ratios, and absorbance-pH curves used for evaluation of correct values of formation constants are limited by the presumption of sufficiently separated complex-formation equilibria when only one complex particle exists in the analyzed solution. This presumption was not sufficiently fulfilled specially for the reactions with zinc(II) and lead(II) ions, and quantitative evaluation of the data by these methods gives the stability constants having only limited values.

The values of the conditioned stability constants obtained by the method of the corresponding solutions can be affected by inaccessibility of the $\bar{n}$ values above 1·7 at the wavelengths studied due to high absorption of light radiation by the free ligand form HL^{2-}.

The most reliable values of the stability constants are obtained by the method of analysis of absorption spectra, where the regression matrix analysis determines the species existing in the solution side by side and evaluates their formation constants serving for calculation of the overall concentration stability constants.

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