COMPLEXES OF GALLOCYANINE METHYL ESTER WITH BISMUTH(III) IONS*

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Reaction of Bi^{3+} ions with gallocyanine methyl ester (so called "prune") has been studied in perchloric acid medium. The two complex give a blue complex 1 : 1. Its stability constants have been calculated by analysis of the dependence of absorbance *vs* concentration of the metal ion $A = f(c_{Bi})_{cL, pH = const}$ using a digital computer and by analysis of the curves of continual variations by the Klausen method. In 0.02M-$HClO_4$ medium the complex shows the highest stability. This medium has been used for chelatometric determination of bismuth on prune as the metallochromic indicator with a colour change from blue to purple. As low as 0.2 mg Bi content per 50 ml solution can be determined.

Phenoxazine dyestuffs with phenolic group including gallocyanine and its derivatives form coloured solutions with many ions, which can be utilized for analytical purposes. So far only the parent substance — gallocyanine — has been used in complexometry. It was used for photometric determination of indium, gallium[1] and scandium[2,3]. As a chelatometric indicator it was used for determination of gallium, thorium[4,5] and for qualitative tests for some other ions. Extensive use of gallocyanine is prevented by its slight solubility in water and usual organic solvents.

Methyl ester of gallocyanine (called "prune") exhibits better properties. Its solubility, although again limited, is greater than that of gallocyanine itself, especially in organic solvents, and its reactions with metal ions are accompanied by more marked colour changes. The dyestuff exhibits two dissociation steps in the pH region $0-14$: $H_2L^+ \rightleftarrows HL \rightleftarrows L^-$, the respective equilibrium constants being[6] $pK_1 = 3.40$ and $pK_2 = 8.53$. In the medium of $HClO_4$ prune forms blue complexes with Bi^{3+} ions the composition of which was studied photometrically. The colour of the solutions appears immediately after mixing the components and does not change within 90 minutes.

EXPERIMENTAL

Reagents and Apparatus

Gallocyanine methyl ester was prepared by condensation of methyl ester of gallic acid with *p*-nitrosodimethylaniline hydrochloride in methanolic medium[7]. After recrystallization the purity

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Part I in the series Complexes of Gallocyanine Methyl Ester with Inorganic Ions.

of the substance was checked by chromatography (Whatman paper No 1 with butanol–acetic acid–water 5 : 1 : 4, or butanol–pyridine–water 5 : 3 : 3, and silica gel thin layer with acetone–ammonia 9 : 1 or benzene–ammonia 3 : 1) and by elemental analysis (C, H, N). $2 \cdot 10^{-4}$M solution of the substance was prepared in 96% (by wt.) ethanol.

Bismuth(III) salt stock solution was prepared by dissolution of $Bi(NO_3)_3 . 5 H_2O$ in 1M-$HClO_4$. The bismuth content was determined by direct chelatometric titration on xylenol orange[8]. Solutions of lower concentrations were prepared by the appropriate dilution of the stock solution with water or perchloric acid. 0·01M solution of Chelaton 3 was standardized by 0·01M--$Pb(NO_3)_2$ on xylenol orange[9].

The solutions used were not buffered, pH values were adjusted by perchloric acid of various concentrations. The optimum ethanol concentration in the samples measured ($\approx 35\%$ by wt.) was determined from dependence of absorbance of the complex vs ethanol concentration. Effect of ionic strength on the absorbance was followed similarly. The absorption curves of the complex in the range $I = 0.02$ to 0.2 were almost identical, therefore a constant value I 0·1 was chosen for all the measurements.

All the photometric measurements were carried out with a recording spectrophotometer Specord UV VIS (Zeiss, Jena). The pH measurements were carried out with a Beckman Model G pH meter calibrated with the use of aqueous potassium hydrogen phthalate. The calculations of the conditional stability constants of the complexes from curves of molar ratios were realized by means of a digital computer Minsk 22.

Procedure of chelatometric determination of bismuth: The sample containing 0·2 to 50 mg Bi is mixed with $HClO_4$ to make the resulting pH 1·5 to 2 (after dilution with water to about 50 ml) ($c_{HClO_4} \approx 0.02$M). After addition of 0·1 ml 5% (by wt.) prune solution in 96% (by wt.) ethanol the solution is titrated with 0·01 Chelaton 3 from blue to purple colour.

RESULTS AND DISCUSSION

The reaction between Bi^{3+} ions and prune dyestuff proceeds in perchloric acid medium in the pH range 0·5 to 2·5. The absorption curves of solutions with variable Bi^{3+} ion concentration (0 to $2 . 10^{-3}$M) and constant ligand concentration ($4 . 10^{-5}$M) show a bathochromic shift of the maximum. The absorption maximum at λ 534 nm belongs to the ligand, whereas the complex has two maxima at λ 563 and 610 nm (Fig. 1). The curves intersect in one isosbestic point at λ 550 nm.

The curves of continual variations and those of molar ratios agree in giving unambiguously the complex formation with the components ratio 1 : 1. The coordination reaction can thus be written as follows. In the studied pH region ≈ 1 to 2 the predominant ligand form present is H_2L, reacting with Bi^{3+} according to Eq. (*1*).

$$Bi + H_2L \rightleftarrows BiH_{(2-n)}L + nH . \qquad (1)$$
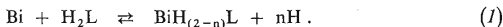
The stability constant *$\beta_{1,n}$ and the conditional constant β'_{11} are given by relations (*2*) and (*3*).

$$*\beta_{1,n} = [BiH_{(2-n)}L][H]^n/[Bi][H_2L] \qquad (2)$$

$$\beta'_{11} = [BiL']/[Bi][L'] . \qquad (3)$$

In the region pH < 2 the reaction fits a simple formalism where $[L'] \equiv [H_2L]$, and

$$*\beta_{1,n} = \beta'_{11}[H]^n . \qquad (4)$$

In the method of molar ratios the conditional stability constants and also molar absorption coefficients of the complex for various pH values were determined from relations

$$A = f(c_{Bi})_{c_L, pH=const} , \qquad (5)$$

$$A = \varepsilon_{H_2L}[H_2L] + \varepsilon[BiH_{(2-n)}L] . \qquad (6)$$

Using the digital computer Minsk 22 the experimental points of the functions (5) were interlaced by an ideal curve for β'_{11} and ε obtained by the least squares method and fulfilling best the hypothesis of formation of the complex $BiH_{(2-n)}L$.

The method of Klausen[10] was used for calculation of conditional stability constants β'_{11} from the curves of continual variations. If c represents the total concentration in solution ($c = c_{Bi} + c_{H_2L}$), and x stands for molar fraction ($x = c_{H_2L}/c$), then Eq. (7) holds for $x = 0.5$.

$$[Bi] = [L'] = cx - [BiL'] . \qquad (7)$$

From Eqs (3) and (7) it follows

$$(cx - [BiL'])^2 = [BiL']/\beta'_{11} . \qquad (8)$$

Introducing $y = [BiL']/c$ for $x = 0.5$ we get after modification
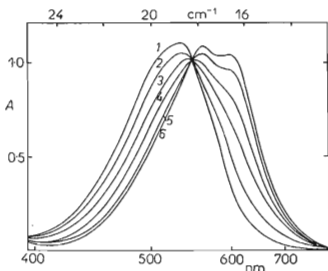
$$(0.5 - y)^2 - (1/\beta'_{11}c) = 0 . \qquad (9)$$

Fig. 1

Curves of Dependence $A = f(c_{Bi})$
$c_L = 4 . 10^{-5}$M, pH = 1.72, 35% (by wt.) ethanol, I 0.1; c_{Bi}: Curve 1 0M, 2 1 . 10^{-5}M, 3 2 . 10^{-5}M, 4 3 . 10^{-5}M, 5 4 . 10^{-5}M, 6 2 . 10^{-4}M.

From the published[10] values of the dependence $y = f(\log(\beta'_{11}c))$ obtained from the computer it is possible to construct a graph the use of which along with experimental value of $y = (A_{max}/A_{0,max}) \cdot 0.5$ (calculated from the maxima of the real and the quantitative Job curves) allows to determine the conditional stability constant β'_{11}.

The real curves of continual variations show a very mild concave bending near the extreme points $x = 0$ and $x = 1$. To verify the absence of dimer complexes[11] M_2L_2, analogous calculations to the abovementioned ones were carried out for various total concentrations $c_q = c/q$ (where $q = 2, 3, ..., etc.$) with the cell width $l_q = lq$. A series of $y_{c/q}$ values is thus obtained representing the same β' value, but for various fractions of the total concentration c. Then

$$\frac{y_{c/q}}{y_c} = \frac{A_{c/q}}{A_c} = f(c/q, c),\tag{10}$$

where A are the absorbances of maxima of the real Job curves. The theoretical values of this ratio of the functions $\log(\beta'_{11}c)$ and $\log(\beta'_{22}c^3)$ for the complexes ML and M_2L_2, respectively, obtained from the computer and from the Tables[10], give (in graphical representation) a curve serving for calculation of the constants and for differentiation of monomer and dimer complexes. The ratios $f(c/q, c)$ obtained from real curves of continual variations gave identical values only for the function $\log(\beta'_{11}c)$ in our case. Thereby it was proved that there is only one complex in the solution, its component ratio being 1 : 1. The concave bending of the curves is due to some other side reaction, probably hydrolysis of Bi^{3+} ions.

The complex is formed already in $0.4M$-$HClO_4$, which is, however, very slightly seen in the absorption curves. With increasing pH of the solution the amount of the complex increases, its stability increases up to pH ≈ 2. At pH > 2 where the influence of the further ligand form HL must be expected the stability of the complex is decreased. This fact is supported by the conditional stability constants β'_{11} determined by two independent methods. From the graphical representation of the pH dependence of the conditional constants it follows that the reaction is accompanied by splitting off of one proton. Thus Eq. (1) can be made more precise for the quantitatively studied pH region 0.9 to 2.0 in the form

$$Bi + H_2L \ \rightleftarrows \ BiHL + H.\tag{11}$$

The found stability constants are given in Table I.

The medium of $0.02M$-$HClO_4$ (pH 1.72), in which the complex stability constants reach their maximum, appears to be optimum for using prune dyestuff as metallochromic indicator for bismuth determination. The colour change is from blue to purple. The maximum relative error of individual determination was $+1.4\%$ for titration of 0.211 mg Bi^{3+} in 50 ml volume. Results of the determinations are given in Table II.

However, the ions giving blue colour with the indicator in acid medium (Zr^{4+}, Th^{4+}, In^{3+}, Fe^{3+}, Ge^{4+}, Pd^{2+}) interfere with the determination of bismuth, the titration error being positive in all the cases.

TABLE I

Molar Absorption Coefficients and Stability Constants of the Complex Bi^{3+} Ions–Prune

Non-buffered medium, I 0·1. Constants β'_{11} are mean values of the constants for various wavelengths.

		Method of molar ratios					Method of continual variations		
pH	number of determinations	$\varepsilon_{563} \cdot 10^{-3}$	β'_{11} (log β'_{11})	$*\beta_{11}$ (log $*\beta_{11}$)	pH	number of determinations	β'_{11} (log β'_{11})	$*\beta_{11}$ (log $*\beta_{11}$)
0·95	6	19·54	$3·41 \cdot 10^5$ (5·53)		1·05	3	$4·79 \cdot 10^5$ (5·68)	
1·45	6	21·04	$1·23 \cdot 10^6$ (6·09)	$4·27 \cdot 10^4$ (4·56)	1·43	5	$1·05 \cdot 10^6$ (6·02)	$4·08 \cdot 10^4$ (4·61)
1·72	5	24·91	$2·34 \cdot 10^6$ (6·38)		1·68	5	$1·91 \cdot 10^6$ (6·28)	
2·02	5	22·36	$1·94 \cdot 10^6$ (6·29)	--	2·01	3	$1·47 \cdot 10^6$ (6·17)	--

TABLE II

Chelatometric Determination of Bismuth on Prune Indicator

Number of parallel determinations was five for each concentration. Standard deviation was calculated according to relation $s = k_n R$ (recommended for small number of determinations[12]). Chelatometric titration on xylenol orange was chosen as the standard method.

Given mg Bi	Average of results $\overline{x}$ (mg Bi)	Relative error of the average e, %	Standard deviation s, mg
0·211	0·213	0·95	0·0021
1·055	1·061	0·57	0·0052
2·113	2·108	0·24	0·0043
12·678	12·685	0·06	0·0047
21·128	21·131	0·01	0·0052
42·236	42·239	0·01	0·0086

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