

REACTIONS OF GALLOCYANINE METHYL ESTER WITH FERRIC IONS*

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The consecutive formation of complexes of Fe(III) with gallocyanine methyl ester (prune), 1 : 1 to 1 : 3, was studied spectrophotometrically in acidic aqueous-alcoholic (1 : 1) solutions. At pH values lower than 2.6 the 1 : 1 complex is formed, in less acidic media the 1 : 2 and 1 : 3 complexes were found to occur. At pH greater than 5 only the highest complex, 1 : 3, is present in the solution. The equilibrium constants of the complexes were evaluated from the curves of concentration ratios and continual variations by using a computer.

Colour reactions of ferric ions with a phenolic hydroxy group rank among the most widely used reactions for their detection and spectrophotometric determination. To reagents with such an OH group belong also gallocyanine and its derivatives; they form coloured solutions with many ions, which can be employed for photometric determinations¹⁻⁶. Since gallocyanine methyl ester (so-called prune) is better soluble than gallocyanine itself and, in addition, displays a smaller number of acid-base equilibria⁷ (pK_1 3.40, pK_2 8.54), this substance appears to be a suitable complexing agent for a series of ions. At $pH < 3.4$, solutions of prune are violet-red, in the slightly acidic region (pH 3.4–8.5) azure blue. In the presence of ferric ions, the solutions are blue-violet in perchloric acid and violet in slightly acidic media. The compositions of all the solutions were studied photometrically.

EXPERIMENTAL

Solutions and Apparatus

Solutions of ferric ions were prepared in two ways:

a) Pulverous iron pentacarbonyl was dissolved in 50 ml of 6M-HCl and the solution was brought to the volume of 1000 ml in a volumetric flask to give $2 \cdot 10^{-2} M$ standard solution.

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The total content of iron in the solution was determined indirectly complexometrically in an aliquot after oxidation with hydrogen peroxide. Chelaton 3 was retitrated with lead nitrate using xylenol orange as the indicator⁸. Solutions of the ferric salt with lower concentrations were obtained by diluting a volume of the stock solution after its oxidation with hydrogen peroxide or nitric acid and boiling.

b) For measurements at low pH values, a stock solution of $2 \cdot 10^{-2} \text{ M}$ ferric salt was prepared by dissolving FeCl_3 , reagent grade purity, in 0.1 M-HClO_4 ; solutions of lower concentrations were prepared by dilution. The titre of the solution was determined again indirectly complexometrically, with xylenol orange as the indicator.

The $2 \cdot 10^{-4} \text{ M}$ stock solution of galloycyanine methyl ester was prepared by dissolving weighed amount of the substance in 96%wt ethanol. The procedure of the reagent preparation and purity testing has been described^{6,7}.

The colour reaction between the Fe^{3+} ions and the ligand proceeds virtually instantly, the absorbance, however, is constant only in a certain interval. With a high excess of the ferric ions and with decreasing concentration of ethanol, and also with decreasing acidity, the absorbance lowers and a precipitate is slowly formed. In the whole pH range the solutions were therefore measured in the medium of 50% wt ethanol and in periods up to 20 minutes, when the compound was stable.

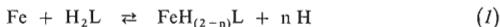
The solutions were not buffered. The low pH value of the samples was adjusted with solutions of perchloric acid of various concentrations; in the slightly acidic range the pH was adjusted with dilute hydrochloric acid or sodium hydroxide employing an automatic burette ABU 12 with a coupled titrator TTT 11 and a pH-meter PHM 26 (all Radiometer, Copenhagen). The constant ionic strength I 0.1 was adjusted with 1M solution of sodium perchlorate in the case of solutions containing perchloric acid, and with 1M-KCl in the other solutions. The pH-meter was set by means of an aqueous solution of potassium hydrogen phthalate. The spectrophotometric measurements were performed on recording instruments Cary 14 and Specord UV VIS (Zeiss, Jena) and on a hand-operated spectrophotometer Spektromom 201 (Magyar Optikai Művek, Budapest). The conditional stability constants were calculated from concentration curves on a digital computer Minsk 22 and applying the Klejner method⁹, as well as from curves of continual variations¹⁰.

RESULTS AND DISCUSSION

Ferric ions react with prune in the pH range of 2–7.5. The absorption curves of the solutions in dependence on decreasing acidity in the pH range of 1.8–3.0 exhibit a bathochromic shift of the maximum (38 nm), whereas in the slightly acidic region the maximum formed displays a hypsochromic shift (68 nm). The former shift is more pronounced in the presence of an excess of the Fe^{3+} , whereas the latter appreciable shift appears if the ligand is present in an excess. The dependence $A = f(\text{pH})$ indicates at least two coordination equilibria (Fig. 1).

In the medium of perchloric acid (pH ~2.4) the absorption curves of the solutions with a constant ligand concentration and variable Fe^{3+} concentrations intersect in a single isosbestic point, λ_{iso} 559 nm, and exhibit one absorption maximum of the complex, λ_{max} 568 nm (Fig. 2). A single equilibrium can be assumed to occur in the solution under the conditions used. Both the curves of molar ratios and the curves of continual variations indicate the 1 : 1 component ratio in the complex.

In the pH range near ~ 2 the ligand is present predominantly in the H_2L^+ form, which reacts with the Fe^{3+} ions according to the equation



(the ion charges are omitted to make the schemes clearer). The stability constants are then defined by the relations

$$*\beta_{1,n} = [FeH_{(2-n)}L][H]^n/[Fe][H_2L], \quad (2)$$

$$\beta'_{11} = [FeL']/[Fe][L']. \quad (3)$$

In this pH range the reaction can be assumed to obey simply the equality $[L'] \equiv [H_2L]$ and

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

During the application of the molar ratio method, the conditional stability constants were found for different pH values from the dependences

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

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

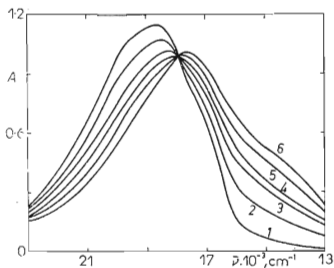


FIG. 1

Dependences of Absorbance on the pH Value of Solutions of Prune and Fe^{3+} Ions

$c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$, $d = 1 \text{ cm}$, $c_{Fe} (\lambda)$
 1 $4 \cdot 10^{-5}$ (570), 2 $2 \cdot 10^{-5}$ (640), 3 0.67 $\cdot 10^{-5}$ (640), 4 0.67 $\cdot 10^{-5} \text{ mol l}^{-1}$ (506 nm).

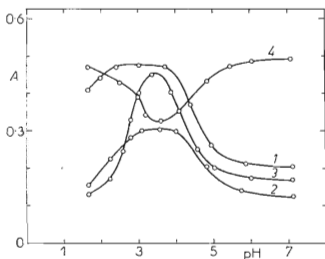


FIG. 2

Absorption Curves of Solutions of Prune and Fe^{3+} Ions

$c_L = 4 \cdot 10^{-5} \text{ mol l}^{-1}$, pH 2.16, $d = 1 \text{ cm}$,
 c_{Fe} 1 0, 2 $1 \cdot 10^{-5}$, 3 $2 \cdot 10^{-5}$, 4 $4 \cdot 10^{-5}$,
 5 $6 \cdot 10^{-5}$, 6 $12 \cdot 10^{-5} \text{ mol l}^{-1}$.

By employing the computer Minsk 22, the nonlinear least squares method was applied to calculate an ideal curve for β'_{11} and ε fitting the experimental points of the function (5) such that the assumption of the formation of the $[\text{FeH}_{(2-n)}\text{L}]$ complex is best satisfied.

In order to verify the results obtained, the analysis of the curves of continual variations was applied. For the $[\text{FeH}_{(2-n)}\text{L}]$ complex it holds that

$$[\text{Fe}] = [\text{L}'] = cx - [\text{FeL}'], \quad (7)$$

where $c = c_{\text{Fe}} + c_{\text{L}}$ and $x = c_{\text{L}}/c$.

A combination of Eqs (3) and (7) yields the expression

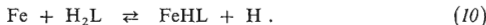
$$(cx - [\text{FeL}'])^2 = [\text{FeL}']/\beta'_{11}. \quad (8)$$

Substituting y for $[\text{FeL}']/c$ and rearranging we obtain

$$(0.5 - y)^2 - (1/\beta'_{11}c) = 0. \quad (9)$$

From the tabulated values¹⁰ of the dependence $y = f(\log(\beta'_{11}c))$ obtained from a computer a plot can be set up, from which, in conjunction with the experimental value of $y = 0.5(A_{\text{max}}/A_{0,\text{max}})$, the β'_{11} constant can be determined (A_{max} and $A_{0,\text{max}}$ are the maxima of the actual and quantitative Job curves).

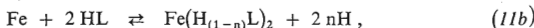
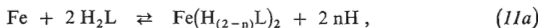
The two methods displayed a good agreement of the conditional constants β'_{11} . From the dependence of $\log \beta'_{11}$ on pH it follows that one proton is detached during the reaction. Thus for the pH region of 2.0–2.6, Eq. (1) can be specified to the form



The calculated constants are given in Table I.

At $\text{pH} > 2.6$, the complex with the Fe : L ratio 1 : 2 manifests itself on the curves of molar ratios and of continual variations in addition to the 1 : 1 complex. At $\text{pH} 3.25$ the two complexes are distinctly separated on the molar ratio curves at $\lambda > 600$ nm, and the stability constant β'_{12} could be calculated.

For the first section of the dependence $A = f(c_{\text{Fe}})_{c_{\text{L}}, \text{pH} = \text{const}}$, the relations



hold true. As $[\text{H}_2\text{L}] + [\text{HL}] = [\text{L}']$, the conditional constant β'_{12} can be expressed as

$$\beta'_{12} = [\text{FeL}'_2]/([\text{Fe}][\text{L}'^2]) \quad (12)$$

According to Klejner⁹ the concentration of the FeL_2 complex and the corresponding absorbances are interrelated through

$$[\text{FeL}'_2]/[\text{FeL}'_2]_{\text{max}} = A_{\text{FeL}_2}/A_{\text{max}}, \quad (13)$$

where A_{max} is the absorbance for the maximum possible concentration of the FeL_2 complex. Assuming a constant concentration of the ligand, c_{L} , we have for the equilibrium concentration $[\text{FeL}'_2]$

$$[\text{FeL}'_2] = (c_{\text{L}}/2)(A_{\text{FeL}_2}/A_{\text{max}}) \quad (14)$$

TABLE I

Stability Constants of Complexes of Prune with Iron

I 0.1, n Number of determinations at the various wavelengths.

pH	Equilibrium	$\log * \beta_{1,n}$	$\log \beta'_{1,n}$	n	λ	ϵ
			$\log \beta'_{11}$			
2.16			6.14	7 ^a		
2.21			6.25	8 ^a	571	$2.53 \cdot 10^4$
2.28	$[\text{FeL}'_2]/[\text{Fe}][\text{L}'^2]$		6.31	6 ^b		
2.47			6.42	7 ^b		
2.68			6.65	6 ^a		
	$[\text{FeHL}][\text{H}]/[\text{Fe}][\text{H}_2\text{L}]$	$\log * \beta_{11}$ 4.01				
			$\log \beta'_{12}$			
3.25	$[\text{FeL}'_2]/[\text{Fe}][\text{L}'^2]$ $[\text{FeL}_2][\text{H}]^2/[\text{Fe}][\text{HL}]^2$ or $[\text{Fe}(\text{HL})_2][\text{H}]^2/[\text{Fe}][\text{H}_2\text{L}]^2$	$\log * \beta_{12}$ 5.58	12.08	3 ^c	600	$3.25 \cdot 10^3$
			$\log \beta'_{13}$			
4.57			16.06	3 ^b		
5.49	$[\text{FeL}'_3]/[\text{Fe}][\text{L}'^3]$		16.41	4 ^b		
6.56			18.01	5 ^b	505	$6.12 \cdot 10^4$
7.58			17.88	4 ^b		

^a Molar ratio method using the computer Minsk 22; ^b Klausen method¹⁰; ^c Klejner method⁹.

If $\varepsilon_{\text{Fe}} = 0$, then

$$A_{\text{FeL}_2} = A - A_L = A - (c_L - 2[\text{FeL}'_2]) \varepsilon_L d. \quad (15)$$

Substituting (with d 1 cm) in Eq. (14) and rearranging we obtain

$$\begin{aligned} [\text{FeL}'_2] &= (c_L/2) \{(A - c_L \varepsilon_L)/(A_{\text{max}} - c_L \varepsilon_L)\} = \\ &= (c_L/2) \{(A - A_L)/(A_{\text{max}} - A_L)\}. \end{aligned} \quad (16)$$

The other equilibrium concentrations are

$$[\text{Fe}] = c_{\text{Fe}} - [\text{FeL}'_2], \quad (17)$$

$$[\text{L}'] = c_L - 2[\text{FeL}'_2]. \quad (18)$$

The conditional stability constant β'_{12} of the FeL'_2 complex could be calculated from Eqs (12) and (16)–(18). The value corresponding to pH 3.25 and the calculated value $^*\beta_{12}$ are given in Table I.

An additional coordination equilibrium appears at higher pH, particularly at $\text{pH} > 4$, where the reagent occurs in the nonionized form. According to the pH curves (Fig. 1) the new complex is completed at $\text{pH} > 5.5$. The maximum of the absorption curve of the violet complex (λ_{max} 505 nm) shows a considerable hypsochromic shift with respect to that of the blue ligand itself (λ_{max} 635 nm). The curves intersect in the isosbestic point λ_{iso} 535 nm, which indicates a single equilibrium in this pH range. The curves of $A = f(c_L)_{c_{\text{Fe}}, \text{pH} = \text{const}}$ and curves of continual variations plotted for this range evidence unambiguously the presence of the complex with the component ratio $\text{Fe} : \text{L} = 1 : 3$. The conditional stability constant β'_{13} of the system



is

$$\beta'_{13} = [\text{FeL}'_3]/([\text{Fe}'][\text{L}']^3). \quad (20)$$

If c represents the total concentration, $c = c_{\text{Fe}} + c_L$, and x the molar fraction, $x = c_L/c$, then

$$[\text{Fe}'] = c(1 - x) - [\text{FeL}'_3], \quad (21)$$

$$[\text{L}'] = cx - 3[\text{FeL}'_3]. \quad (22)$$

From Eqs (20)–(22) it follows that

$$(1/\beta'_{13}) [\text{FeL}'_3] = \{c(1 - x) - [\text{FeL}'_3]\} \{cx - 3[\text{FeL}'_3]\}^3. \quad (23)$$

Denoting $[\text{FeL}'_3]/c = y$ we have

$$(1/\beta'_{13}) yc = \{c(1 - x - y)\} \{c(x - 3y)\}^3; \quad (24)$$

a rearrangement leads to the general Job curve for the 1 : 3 complex:

$$(1 - x - y)(x - 3y)^3 - (1/\beta'_{13}c^3)y = 0. \quad (25)$$

The parameter $1/\beta'_{13}c^3$ determines the departure of the real Job curve of the FeL'_3 complex from that of the quantitatively formed complex. From Eq. (25), the theoretical function $y = f\{\log(\beta'_{13}c^3)\}$ for $x = 0.75$ can be then obtained, which serves for the calculation of the constant β'_{13} (see¹⁰).

The absorbance is proportional to the concentration of the complex in the solution and consequently also to the function y :

$$A = \varepsilon d[\text{FeL}'_3] = \varepsilon dcy. \quad (26)$$

If the complex is formed quantitatively, then y equals the limit value 0.25; thus

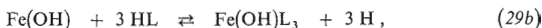
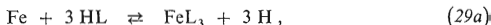
$$A_0 = \varepsilon d[\text{eL}'_3]_0 = 0.25\varepsilon dc. \quad (27)$$

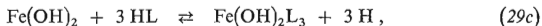
From the absorbance ratio in the maximum of the Job curve follows then

$$y_{\max} = 0.25(A_{\max}/A_{0,\max}). \quad (28)$$

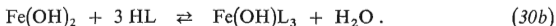
This y_{\max} value, found from the experimental curves of continual variations and from plots of the dependence $y = f(\log(\beta'_{13}c^3))$ obtained by employing a computer and the tabulated data¹⁰, served for the calculation of the constants β'_{13} .

In the pH range applied during the study of the FeL'_3 complex, the hydrolysis of ferric ions — Fe^{3+} , FeOH^{2+} , $\text{Fe}(\text{OH})_2^+$, and $\text{Fe}_2(\text{OH})_4^{4+}$ — must be taken into account. The coefficient of the side reaction, $\alpha_{\text{Fe}(\text{OH})} = 1 + \beta_{11}^{\text{OH}}[\text{OH}^-] + \beta_{12}^{\text{OH}}[\text{OH}^-]^2 + [\text{Fe}] \beta_{22}^{\text{OH}}[\text{OH}^-]^2$ (β^{OH} are the stability constants of the hydroxo complexes¹¹ for $l = 1 : \log \beta_{11}^{\text{OH}} = 11.2$, $\log \beta_{12}^{\text{OH}} = 22.0$, $\log \beta_{22}^{\text{OH}} = 25.3$) indicates that the solution — with regard to the negligible concentration of Fe^{3+} and consequently a low content of the $[\text{Fe}_2(\text{OH})_4^{4+}]$ complex — contains predominantly the $\text{Fe}(\text{OH})_2^+$ ions and a lower amount of the FeOH^{2+} ions. The ferric ion as well as the two hydroxo complexes can take part in the complex formation with the organic ligand, either by a direct reaction,





or, which is more probable, by substitution of the hydroxyl by the ligand:



The conditional complex concentration can be then written as

$$[\text{FeL}'_3] = [\text{FeL}_3] + [\text{Fe(OH)L}_3] + [\text{Fe(OH)}_2\text{L}_3]. \quad (31)$$

The manifestation of the hydrolysis should be seen in the fact that the concave deflection of the left branch of the Job curve with respect to the theoretical curve is according to Eq. (25) slightly deeper and that the slope of the plot of $\log \beta'_{13}$ vs. pH does not correspond to three protons ($n = 0.8$ for pH 4–5.5; $n = 1.7$ for pH 5.5–6.7). For these reasons the value of the constant $^*\beta_{13}$ could not be found.

In order to verify the correctness of the applied method of calculation of the conditional stability constant β'_{13} , we plotted curves as functions $y = f(x)$ calculated from Eq. (26). The tangent line constructed from the right end point ($x = 1$) must attain the value of $y = 0.25$ for $x = 0.75$. In this case it is then also parallel with the tangent line¹² calculated and plotted according to the general equation (for an A_mB_n complex),

$$y = -(1/m)x + (n-1)/\{m(m+n-1)\}, \quad \text{for } n \geq 2 \quad (32)$$

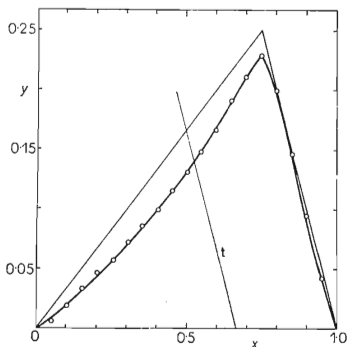


FIG. 3

Curve of Continual Variations of the FeL_3 Complex According to Equation (26)

$c = c_{\text{Fe}} + c_{\text{L}} = 4 \cdot 10^{-5} \text{ mol l}^{-1}$, pH 6.56,
 λ 600 nm, $y = [\text{FeL}'_3]/c$, $x = c_{\text{L}}/c$, t tangent line.

which in the particular case of the FeL_3 complex is

$$y = -x + 0.667. \quad (33)$$

So it has been proved that in slightly acidic medium, FeL'_3 is the only complex present (Fig. 3) and the applied technique of calculation of the conditional stability constants β'_{13} from the curves of continual variations is an appropriate method. The values of β'_{13} are given in Table I.

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