

REACTIONS OF GALLOCYANINE METHYL ESTER WITH VANADATES AND MOLYBDATES*

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Reactions of gallocyanine methyl ester with vanadates and molybdates were examined spectrophotometrically in weakly acidic solutions in 10% (m/m) ethanol. Vanadates form the VO_2L_2 , $\text{VO}_2(\text{OH})\text{L}$, and VO_3L complexes at pH 3–6.5, molybdates form the MoO_2L_2 and MoO_3L complexes at pH 1.5–4.4 and pH 3–5.3, respectively. The equilibrium constants of the systems concerned were calculated from the data of the concentration curves. Use has been made of the formation of the MoO_2L_2 complex for photometric determination of molybdenum.

The affinity of V(V) and Mo(VI) to oxygen as a strong electron donor plays a significant part, and so vanadates and molybdates or their iso- and heteropolyanions are most frequently encountered in aqueous solutions. The monomeric species only predominate at low vanadium or molybdenum concentrations ($c_M < 10^{-4} \text{ mol l}^{-1}$) (ref.¹). Vanadium in acidic solutions exhibits a pronounced tendency to form the VO_2^+ ion, which hydrolyses with increasing pH (refs¹⁻⁴). Simpler equilibria have been found in the case of molybdate^{1,5}, where the H_2MoO_4 acid formed in acidic solutions only dissociates to HMoO_4 or as far as MoO_4^{2-} .

As a consequence of the affinity of the two elements to donor atoms, they react readily with organic substances involving an O,O-, O,N-, O,S-, or S,N- or S,S-chelating grouping. Thus polyphenols, hydroquinones, hydroxy acids and ketocarboxylic acids, triphenylmethane dyes, flavones, hydroxyazo dyes, dithiols, etc., are significant ligands. Among O,O-donor ligands is also gallocyanine methyl ester, which — like other hydroxyphenoxazones⁶⁻⁸ — in weakly acidic systems forms coloured solutions with vanadates and molybdates.

The aim of the present work was therefore to study the coordination properties of gallocyanine methyl ester (so-called prune) with these ions in aqueous-ethanolic solutions, and to find conditions for analytical application of the reagent to photometric determination of vanadates and molybdates.

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EXPERIMENTAL

Solutions and Apparatus

0.01M vanadate stock solution was prepared by dissolving NH_4VO_3 *p.a.* (Lachema, Brno) in 0.01M-NaOH. The vanadate content was determined indirectly ferrometrically⁹.

0.1M molybdate stock solution was obtained by dissolving $\text{Na}_2\text{MoO}_4 \cdot 2\text{H}_2\text{O}$ *p.a.* (Lachema, Brno) in water. Molybdenum was determined in the solution gravimetrically as the oxinate¹⁰.

$2 \cdot 10^{-4}\text{M}$ stock solution of galloycyanine methyl ester was prepared by dissolving a weighed amount of the substance in 96% (m/m) ethanol. For the photometric determination of molybdenum, a $4 \cdot 10^{-4}\text{M}$ solution was used. The preparation of the reagent and checking of its purity have been reported¹¹.

The pH of the solutions was adjusted by using acetate or chloroacetate buffers. The ionic strength was adjusted to 0.1 (for VO_3^- and MoO_4^{2-}) or 0.02 (for Mo_4^{2-}) with 1M-KCl.

The pH values were measured on a PHM 4d pH-meter using a G 200B glass electrode — K 100 calomel electrode system (all Radiometer, Copenhagen); NBS aqueous buffers were used for calibration. The absorbances were measured on Specord UV VIS (Zeiss, Jena) and Unicam SP 1800 (Pye Unicam, Cambridge) instruments in 1 cm cells.

Photometric Determination of Molybdenum

The sample containing 7–80 μg Mo is placed in a 50 ml volumetric flask containing 9 ml of $4 \cdot 10^{-4}\text{M}$ ethanolic solution of the dye, 10 ml of a buffer pH 2.5, and 4 ml of 1M-KCl, the mixture is diluted to volume with water, and its absorbance is measured at 630–640 nm against a blank.

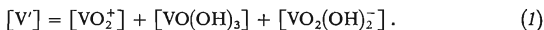
RESULTS AND DISCUSSION

Reaction of Vanadates

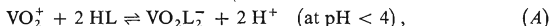
Vanadates form with galloycyanine methyl ester (prune) violet solutions in weakly acidic medium. At $\text{pH} < 3$, the colour intensity drops and ultimately vanishes. The analogous effect observed with the Fe(III)-galloycyanine system has been explained in terms of the photo-activated destruction of the dye by the metal ion¹². The basis of the irreversible reaction of vanadates with prune may be a redox process, during which an unstable complex radical is formed. In fact, vanadates with organic hydroxy compounds give radicals known to act as activators in catalytic reactions¹³.

The optimum conditions for the coordination reaction of vanadates with prune are the medium of 10% (m/m) ethanol and pH 3–6.5. The dependence $A = f(\text{pH})$ (Fig. 1) points to a complex system of equilibria in this acidity range. The two isosbestic points occurring on the $A = f(c_V)_{c_L}$ curves for the pH 3.5–4.6 range, at 570 and 635, indicate two coordination equilibria at this acidity. The concentration dependences $A = f(c_V)_{c_L, \text{pH}, I}$ and $A = f(x)$, where $x = c_L/c$ and $c = c_V + c_L = \text{const}$, revealed the presence of complexes with the V : L ratios 1 : 1 and 1 : 2.

The conditional vanadium concentration is constituted mainly by three hydrolytic species¹ (at $c_V < 10^{-4} \text{ mol l}^{-1}$), viz.



The active component in the complex formation in acidic solutions (pH < 4) will be the VO_2^+ species (its fraction is 57.8% at pH 3, 15% at pH 3.7). The formation of the V : L = 1 : 2 complex can be thus represented by the equation



with the constant

$${}^*\beta_2 = [VO_2L_2^-][H]^2[VO_2^+]^{-1}[HL]^{-2} \quad (2)$$

The conditional concentrations of vanadium (I) and of the ligand can be expressed via the coefficients of the side reactions:

$$[V'] = [VO_2^+](1 + K_{h1}[H]^{-1} + K_{h2}[H]^{-2}) = [VO_2^+] \cdot \alpha_{V(OH)}, \quad (3)$$

where $K_{h1} = [VO(OH)_3][H][VO_2^+]^{-1} = 10^{-3.2}$ and $K_{h2} = [VO_2(OH)_2][H]^2 \cdot [VO_2^+]^{-1} = 10^{-7.0}$ (ref.²), and

$$[L'] = [H_2L^+] + [HL] = [HL](1 + [H]K_{a1}^{-1}) = [HL] \cdot \alpha_{L(H)}, \quad (4)$$

where K_{a1} is the dissociation constant of the reagent ($K_{a1} = 10^{-3.68}$).

The equilibrium constant ${}^*\beta_2$ of the reaction (A) takes then the form

$${}^*\beta_2 = \beta'_2 \cdot \alpha_{V(OH)} \cdot \alpha_{L(H)} \cdot [H]^2, \quad (5)$$

where $\beta'_2 = [VO_2L_2^-][V']^{-1}[L']^{-2}$.

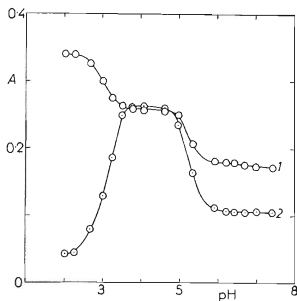


FIG. 1

Dependence of Absorbances on the pH Values for Solutions of Gallocyanine Methyl Ester with Vanadate

$c_L = c_V = 1.8 \cdot 10^{-5}$ mol l⁻¹ in 10% (m/m) ethanol; $d = 1$ cm, λ (nm): 1 530, 2 630.

With increasing pH, another equilibrium (B) takes place, following the reaction (A); at pH 3.8–4.5, both reactions operate. The function of the complexing component is taken over by the $\text{VO}_2(\text{OH})_2^-$ species, at pH > 3.8 predominating appreciably over the other hydrolysis products (51.2% at pH 3.9, and 82.6% at pH 4.5).

The complexation equilibrium



can be characterized by the constant

$$\beta_1 = [\text{VO}_2(\text{OH})\text{L}][\text{VO}_2(\text{OH})_2]^{-1}[\text{HL}]^{-1}. \quad (6)$$

Using the hydrolysis constants², Eq. (1) can be written as

$$[\text{V}'] = [\text{VO}_2(\text{OH})_2] (K_{h2}^{-1}[\text{H}]^2 + K_{h3}^{-1}[\text{H}] + 1) = [\text{VO}_2(\text{OH})_2] \cdot \alpha_{\text{VO}(\text{OH})}, \quad (7)$$

where $K_{h3} = [\text{VO}_2(\text{OH})_2][\text{H}][\text{VO}(\text{OH})_3]^{-1} = 10^{-3.8}$.

The constant (6) of the equilibrium (B) is then

$$\beta_1 = \beta'_1 \cdot \alpha_{\text{VO}(\text{OH})} \cdot \alpha_{\text{L}(\text{H})}, \quad (8)$$

where $\beta'_1 = [\text{VO}_2(\text{OH})\text{L}][\text{V}']^{-1}[\text{L}']^{-1}$.

The conditional stability constants β'_2 and β'_1 were calculated from the continual variations curves at 540–550 nm and 650–670 nm, respectively, where the differences between the absorbances of the complexes and the ligand are highest. For a VL_n complex

$$[\text{V}'] = c(1 - x) - [\text{VL}_n], \quad (9)$$

$$[\text{L}'] = cx - n[\text{VL}_n], \quad (10)$$

where $c = c_v + c_L$ and $x = c_L/c$.

From the relations for β'_n , (9) and (10), and on rearrangement, a general Job curve equation is obtained:

$$(1 - x - y)(x - ny)^n - (1/\beta'_n c^n) y = 0, \quad (11)$$

where $y = [\text{VL}_n]/c$.

Using the tabulated values of the $y = f[\log(\beta'_n c^n)]$ dependence, obtained from a computer¹⁴, a plot can be constructed for $x = 0.67$ or 0.50 , by means of which the β'_2 and β'_1 values can be calculated knowing the maxima of the quantitative and actual curves of the y values ($y = (Y_{\text{max}}/Y_{0,\text{max}})(1 + n)^{-1}$).

Moreover, the value of the conditional stability constant β'_2 was verified by calculation from the data of the concentration ratios curves for $c_V \leq c_L/2$ at $c_L = \text{const}$, where the content of the VL' complex is negligible. The actual and the maximum absorbances are

$$\Delta A = \epsilon_{K2}[\text{VL}'_2] + \bar{\epsilon}_L([L'] - c_L) \quad (12)$$

$$\Delta A_{\text{max}} = (\epsilon_{K2}/2 - \bar{\epsilon}_L) c_L, \quad (13)$$

where ϵ_{K2} is the molar absorptivity of the VL'₂ complex and $\bar{\epsilon}_L$ is the mean molar absorptivity of the ligand. Since

$$[\text{VL}'_2] = (\Delta A/\Delta A_{\text{max}}) c_V \quad \text{for} \quad c_V \leq c_L/2, \quad (14)$$

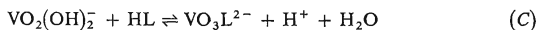
the stability constant is

$$\beta'_2 = (\Delta A/\Delta A_{\text{max}})(1 - \Delta A/\Delta A_{\text{max}})^{-1} (c_L - 2c_V \Delta A/\Delta A_{\text{max}})^{-2}. \quad (15)$$

The β'_2 values calculated by the two methods are in a good mutual agreement. The dependence $\log(\beta'_2 \cdot \alpha_V \cdot \alpha_L) = f(\text{pH})$ is linear and corresponds to two protons for the reaction (A). The equilibrium constants β_2 and β_1 of the reactions (A) and (B), respectively, calculated from Eqs (5) and (8), respectively, are given in Table I.

In the second reaction region, $\text{pH} > 6$, only one complexing equilibrium occurs, viz. for the V : L = 1 : 1 complex. The $A = f(c_V)_{c_L, \text{pH}}$ curves exhibit a single maximum of the complex at 570 nm and a single isosbestic point at 576 nm, even in a wide vanadium concentration region, $c_V = (0-10) c_L$, $c_L = 2 \cdot 10^{-5} \text{ mol l}^{-1}$. The equilibrium was confirmed by the Ketelaar transformation¹⁵ of the concentration curves; at the same time, the transformation was employed to determine the ϵ_{K1} value. The conditional constant $\beta'_1(C)$ was calculated by the procedure applied to β'_2 from the equations (12)–(15).

The dependence $\log \beta'_1 = f(\text{pH})$ in the region $\text{pH} 6-6.5$ is linear with a slope of unity. This fact in conjunction with the assumption of a simple formalism for $[V'] \equiv [\text{VO}_2(\text{OH})_2^-]$ and $[L'] \equiv [\text{HL}]$ ($K_{a2} = 10^{-7.99}$) allows the coordination equilibrium to be formulated as



with the constant

$$*\beta_1 = [\text{VO}_3\text{L}][\text{H}][\text{VO}_2(\text{OH})_2^-]^{-1}[\text{HL}]^{-1}. \quad (16)$$

This equilibrium constant is then in a simple relationship with the conditional stability constant β'_1 :

$$*\beta_1 = \beta'_1 \cdot [H], \quad (17)$$

and is given in Table I.

The applicability of the reactions to photometric determination of vanadium is not satisfactory in any pH range. In a more acidic region (pH \approx 4), the VO_2L_2 complex is moderately stable; the difference $\epsilon_{K2} - \bar{\epsilon}_L$, however, is low in the region of the complex and ligand maxima and is unsuitable for analytical use. In the other acidity range, pH 6–6.5, the VO_3L complex is not sufficiently stable and thus is not suited to photometric determination either.

Reactions of Molybdates

Galloyanine methyl ester reacts with molybdates in the pH 1.5–5.5 region with the formation of violet solutions, steady only for a short period: at low pH and with excess ligand, the absorbance is constant for 15 min; with excess molybdate, for approximately 30 min. The content of ethanol does not affect the absorbance up to the concentration of 20% (m/m). Increasing ionic strength affects adversely the complex formation too – at $I \geq 0.5$ the violet colour does not appear. As the optimum conditions emerged 10% (m/m) ethanol and I 0.1; the measurements should be accomplished within 5–10 min after mixing the constituents.

TABLE I

Equilibrium Constants of the System Vanadium–Galloyanine Methyl Ester and Molar Absorptivities of the Complexes (10^4 l mol $^{-1}$ cm $^{-1}$)

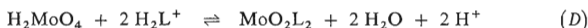
10% (m/m) ethanol, I 0.10; the constants were calculated from the conditional stability constants β' , averages of 8–10 values for different wavelengths.

pH	$\log \beta_1$	$\log * \beta_1$	$\log * \beta_2$	$\epsilon_{K1(max)}$ (564 nm)	$\epsilon_{K2(max)}$ (620 nm)	Equilibrium
3.81	—	—	4.46	—	—	A
4.14	6.95	—	4.83	1.98	3.25	B, A
4.34	7.04	—	5.00	1.97	3.66	B, A
4.41	—	—	4.96	—	3.64	A
4.43	7.07	—	5.03	—	—	B, A
5.99	—	-1.27	—	—	—	C
6.30	—	-1.25	—	1.67	—	C
6.39	—	-1.29	—	—	—	C

The region of complex formation divides into three parts, *viz.* pH 1.5–2.8, pH 2.9–4.4, and pH 4.5–5.5.

In the pH 1.5–2.8 range, the $A = f(c_{\text{Mo}})_{c_{\text{L}}, \text{pH}, 1}$ curves characterize a single equilibrium, λ_{iso} 553 nm, λ_{max} 630 nm (hence with a 100 nm bathochromic shift with respect to the ligand maximum). The curves were transformed according to Ketelaar¹⁵ to establish the occurrence of the complex with the Mo : L ratio 1 : 2 (Fig. 2) and to calculate the $\epsilon_{\text{K}2}$ value. The conditional constant was calculated by using Eqs (12)–(15).

Practically the only reagents in the solution are H_2MoO_4 and H_2L^+ , only negligibly affected by dissociation (87% H_2MoO_4 and 89% H_2L^+ at pH 2.8). We can thus assume the occurrence of the equilibrium



characterized by the constant

$$*\beta_2 = [\text{MoO}_2\text{L}_2][\text{H}]^2[\text{H}_2\text{MoO}_4]^{-1}[\text{H}_2\text{L}]^{-2}. \quad (18)$$

This constant is interrelated with the stability constant β'_2 through

$$*\beta_2 = \beta'_2 \cdot \alpha_{\text{Mo}(\text{H})} \cdot \alpha_{\text{L}(\text{H})}^2 \cdot [\text{H}]^2, \quad (19)$$

where the α 's are the coefficients of the side reactions induced by the dissociation of the components. Thus their conditional concentrations are

$$[\text{Mo}'] = [\text{H}_2\text{MoO}_4] + [\text{HMoO}_4^-] + [\text{MoO}_4^{2-}] \quad (20)$$

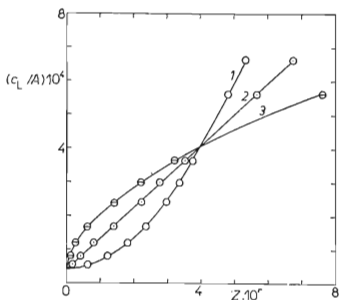


FIG. 2

Ketelaar Transformation of the $A = f(c_{\text{Mo}})$ Curves

$c_{\text{L}} = 1.8 \cdot 10^{-5} \text{ mol l}^{-1}$, pH 2.32, λ 630 nm, 10:1: $Z = [(c_{\text{Mo}} - \Delta A / \Delta \epsilon) \Delta A^{n-1}]^{-1/n}$; 1 $n = 1$, $r = -4$; 2 $n = 2$, $r = -3$; 3 $n = 3$, $r = -2$.

at $c_{\text{Mo}} < 10^{-4} \text{ mol l}^{-1}$ (ref.¹), and

$$[\text{L}'] = [\text{H}_2\text{L}^+] + [\text{HL}]. \quad (21)$$

The $\log \beta_2' = f[-\log([\text{H}] \cdot \alpha_{\text{Mo(H)}} \cdot \alpha_{\text{L(H)}}^2)]$ dependence is linear, with a slope corresponding to two protons in the reaction (D). The equilibrium constant ${}^*\beta_2$ was also calculated from the $A = f(\text{pH})_{c_{\text{Mo}}, c_{\text{L}}}$ curves according to the relation

$$\begin{aligned} \log \frac{(A - A_L) A_{\text{max}} - A_L^2}{[2pA_{\text{max}} - A - (2p - 1)A_L](A_{\text{max}} - A)^2} = \\ = \log {}^*\beta_2 + 2 \text{pH} - 2 \log(1 + K_{a1}[\text{H}]^{-1}) + 2 \log c_L, \end{aligned} \quad (22)$$

where $A_L = \bar{\epsilon}_L c_L$, $A_{\text{max}} = \epsilon_{\text{K}2} c_L / 2$, $A = \epsilon_{\text{K}2} [\text{MoO}_2\text{L}_2] + \bar{\epsilon}_L [\text{L}']$, $p = c_{\text{Mo}} / c_L \geq 1/2$.

The ${}^*\beta_2$ constant values calculated by the two procedures (Table II) are in a fairly good agreement ($\Delta \log {}^*\beta_2 = 0.5$). The assumed equilibrium (D) can be thus supposed to be the probable mechanism of formation of the binary complex at higher acidities of the systems.

In the pH 2.9–4.4 region, the stability of the MoO_2L_2 complex decreases and ultimately vanishes, and the complex with the component ratio 1:1 forms. A new

TABLE II

Equilibrium Constants of the System Molybdenum-Galloyanine Methyl Ester and Molar Absorptivities of the Complexes ($10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$)

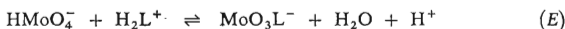
10% (m/m) ethanol, I 0.10; the constants were calculated from the conditional stability constants β' , average of 5–10 values for different wavelengths.

pH	$\log {}^*\beta_1$	$\log {}^{**}\beta_1$	$\log {}^*\beta_2$	$\epsilon_{\text{K}1(\text{max})}$ (570 nm)	$\epsilon_{\text{K}2(\text{max})}$ (630 nm)	Equilibrium
1.5–2.7 ^a	—	—	5.22	—	—	D
2.32	—	—	4.71	—	4.25	D
2.44	—	—	4.71	—	—	D
2.76	—	—	4.73	—	—	D
2.71 ^b	—	—	5.32	—	3.64	D
2.89 ^c	—	—	4.30	—	—	D
3.19 ^c	3.74	—	3.78	—	3.35	E, D
4.91	—	10.10	—	2.20	—	G
5.20	—	9.98	—	2.20	—	G

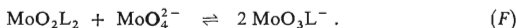
^a Calculated from the pH curve (22); ^b ionic strength 0.02; ^c 20% (m/m) ethanol.

maximum at 570 nm and another isosbestic point at 523 nm appear on the $A = f(c_{\text{Mo}})_{c_{\text{L}}}$ curves (Fig. 3).

The new complex can form either *via* the direct reaction



or *via* conversion of the higher complex, formed by the reaction (D):



The stability constant β'_1 of the reaction (E) can be calculated by using the conditional stability constant K'_1 of the reaction (F) ($K'_1 = [\text{MoO}_3\text{L}^-]^2/[\text{Mo}'][\text{MoO}_2\text{L}_2]$):

$$\beta'_1 = (K'_1 \cdot \beta'_2)^{1/2} \quad (23)$$

The right side values can be calculated from the absorbances of the isosbestic points of the concentration curves (Fig. 3). For $\lambda_{\text{iso}} 523 \text{ nm}$, the relation

$$[\text{MoO}_2\text{L}_2] = (\Delta A/\Delta A_{\text{max}}) \cdot c_{\text{Mo}} \quad (24)$$

is obeyed for $c_{\text{Mo}} \leq c_{\text{L}}/2$, and thus relations (12)–(15) can be employed for the calculation of β'_2 . At $\lambda_{\text{iso}} 553 \text{ nm}$ (for $c_{\text{Mo}} \geq c_{\text{L}}/2$), a quantitative formation of Mo_2L_2 can be assumed, and the concentration of the MoO_3L complex (E) can be written as

$$[\text{MoO}_3\text{L}] = (A/A_{\text{max}}) \cdot c_{\text{L}} \quad \text{for } c_{\text{Mo}} = c_{\text{L}}, \quad (25)$$

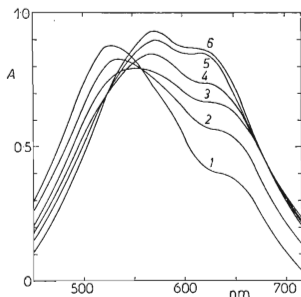


FIG. 3

Absorption Curves of Solutions of Galloyl-methyl Ester with Molybdate

$c_{\text{L}} = 4 \cdot 10^{-5} \text{ mol l}^{-1}$, pH 3.19, 10% (m/m) ethanol, $I 0.1$, $d = 1 \text{ cm}$; c_{Mo} (mol $\cdot \text{l}^{-1}$): 1 0; 2 $0.8 \cdot 10^{-5}$; 3 $1.6 \cdot 10^{-5}$; 4 $2.4 \cdot 10^{-5}$; 5 $4.0 \cdot 10^{-5}$; 6 $3.0 \cdot 10^{-4}$.

where $A = \varepsilon_{K1}[\text{MoO}_3\text{L}] + \varepsilon_{K2}[\text{MoO}_2\text{L}_2]$ and $A_{\max} = \varepsilon_{K1}c_L$.

The partial stability constant K'_1 can be then calculated as

$$\begin{aligned} K'_1 &= (A/A_{\max})^2 c_L^2 [c_L/2 - (A/A_{\max}) c_L/2]^{-2} \\ &= 4(A/A_{\max})^2 (1 - A/A_{\max})^{-2}. \end{aligned} \quad (26)$$

The equilibrium constant $^*\beta_1$ of the equilibrium (E) found from the relation

$$^*\beta_1 = \beta'_1 \cdot \alpha_{\text{Mo(H)}} \cdot \alpha_{\text{L(H)}} \cdot [\text{H}] \quad (27)$$

for pH 3.19 is given in Table II.

In the pH 4.5–5.5 region, a single complex with the component ratio 1 : 1 predominates absolutely. The equilibrium is characterized by λ_{\max} 570 nm and by two isosbestic points, at 582 and 684 nm, between which the complex absorbs less than the free ligand.

In this acidity region the HL species and the molybdate anion species MoO_4^{2-} predominate appreciably (90% and 78%, respectively, at pH 4.5). These two components react to release OH^- ions:

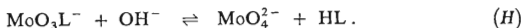


This assumption is supported by the decrease of the linear dependence $\log(\beta'_1 \cdot \alpha_{\text{Mo}}, \alpha_{\text{L}}) = f(\text{pH})$ with a slope of unity. The equilibrium (G) is characterized by the constant

$$\begin{aligned} **\beta_1 &= [\text{MoO}_3\text{L}][\text{MoO}_4]^{-1} [\text{HL}]^{-1} [\text{H}]^{-1} \\ &= \beta'_1 \cdot \alpha_{\text{Mo(H)}} \cdot \alpha_{\text{L(H)}} \cdot [\text{H}]^{-1}, \end{aligned} \quad (28)$$

whose values for different pH are in a good agreement (Table II); this, too, bears out the complex formation mechanism (G).

As the pH increases, the complex decomposes to its initial constituents:



This is corroborated by the occurrence of the maximum due to the ligand, at 642 nm on the $A = f(c_{\text{Mo}}, c_{\text{L}})$ curves; it is expressive even with a three-fold quantity of molybdate. The decreasing values of the conditional stability constant β'_1 ($\log \beta'_1 = 5.21$ and 4.79 at pH 4.91 and pH 5.20, respectively) calculated from the Ketelaar transformation¹⁵ data of the concentration curves by applying the procedure of Eqs (12)–(15) evidence the lowering stability of the complex.

Photometric Determination of Molybdenum

At pH 2.5–2.8, the stability of the MoO_2L_2 complex is high enough to allow the dye under study to be employed as a reagent for photometric determination of molybdenum. The determination was performed at 640 nm, where the $\epsilon_{\text{K}_2} - \epsilon_{\text{H}_2\text{L}}$ difference is highest. The colour develops instantaneously and the absorbance is steady for 20 min. With $c_{\text{L}} = 7.2 \cdot 10^{-5} \text{ mol l}^{-1}$ and ionic strength 0.1, the Lambert–Beer law is obeyed for concentrations $c_{\text{Mo}} < 1.6 \mu\text{g Mo/ml}$. The limit of determination was calculated¹⁶ as $c_{\text{min}} = ts \cdot dA/dc$ (c_{min} is the minimum determinable quantity, t is the Student coefficient value, and s is the standard deviation of determination in absorbance units) to be $0.0041 \mu\text{g/ml}$. The relative standard deviation for six replicates was 1.2% for $0.96 \mu\text{g Mo/ml}$. The Q-test was applied to prove that no gross error resulted during the determinations.

The determination can be accomplished with a $\pm 4\%$ error in the presence of alkali metal and alkaline earth ions, 50-fold excess of Ce^{3+} , Pb^{2+} , Ni^{2+} , Zn^{2+} , Cr^{3+} , La^{3+} , Tl^+ , 30-fold excess of Cu^{2+} , Co^{2+} , Mn^{2+} , Cd^{2+} , or equimolar quantities of UO_2^{2+} , Y^{3+} , Sc^{3+} , Al^{3+} , or Hg^{2+} ions. Ions of Ag^+ , CrO_4^{2-} , Au^{3+} , WO_4^{2-} , Sb^{3+} , In^{3+} , Ga^{3+} , Zr^{4+} , Th^{4+} , Bi^{3+} , and Fe^{3+} interfere.

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