

REACTION OF GALLOCYANINE METHYL ESTER WITH URANYL IONS*

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The reaction of gallocyanine methyl ester with uranyl ions was studied spectrophotometrically in slightly acid or neutral solutions in 40% (*m/m*) ethanol. A violet complex of UO_2L_2 is formed at $\text{pH} > 5$. The conditional stability constants of the complex in the $\text{pH} 6-7.4$ range and the equilibrium constants of the coordination reaction were derived from the concentration curves and continuous variations curves. The optimum conditions were sought for the spectrophotometric determination of uranium based on the occurrence of the UO_2L_2 complex. The relative standard deviation obtained for a uranium concentration of $106 \mu\text{g l}^{-1}$ was $s_r = 2.13\%$.

Uranium in its highest valency state exhibits a pronounced affinity for electron donors, particularly oxygen. Consequently, the oxo cation UO_2^{2+} appears even in strongly acid aqueous solutions, and hydroxo complexes of uranyl of various composition are formed at $\text{pH} > 3.5$ (refs^{1,2}). The affinity for donor atoms shows up also in the reactivity with organic reagents containing O,O-, O,N-, or S,N-chelating groupings. Hydroxy acids, polyphenols, triphenylmethane and xanthene dyes, flavones, hydroxazo dyes, *etc.*, are thus powerful ligands. Of phenoxazine dyes, which are among O,O-donor ligands, the coordination equilibria of florein³ and alizarine green-type compounds⁴ have been investigated. In solutions containing, in addition to uranyl ions, also a cationoid tenside, the alizarine green-type substances were found to form ternary complexes⁴.

Gallocyanine methyl ester (1-carbomethoxy-4-hydroxy-7-dimethylphenoxaz-3-one) reacts with uranyl ions in slightly acid solutions giving rise to violet colour. The aim of the present work was to examine the coordination equilibria of these components in aqueous-ethanolic solutions and to seek for the optimum conditions for the analytical application of the reagent to the determination of uranium.

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EXPERIMENTAL

Solutions and Apparatus

A stock solution of galloycyanine methyl ester (0.2 mmol l^{-1}) was prepared by dissolving the prepared⁵ chemical in 93% (*m/m*) ethanol. A stock solution of uranyl acetate (10 mmol l^{-1}) was obtained by dissolving the solid dihydrate (Lachema, Brno) in water, adding 1 ml of 70% (*m/m*) HClO_4 , and diluting to 1 000 ml. The uranyl concentration was measured chelometrically by indirect titration with thorium nitrate using xylenol orange as indicator^{6,7}. The titre of Chela-ton 3 was determined by titration with lead nitrate using the same indicator.

The pH was adjusted by means of urotropine- HClO_4 buffers⁸, the ionic strength was adjusted to 1.0 with 2M- NaClO_4 .

The absorbances were measured on Unicam SP 1800 (Pye Unicam, Cambridge) and Specord UV VIS (Zeiss, Jena) instruments in 1 cm and 3.5 cm cells. The concentration ratios curves were measured by the titration method, adding the uranyl salt by means of an ABU 12b automatic burette (Radiometer, Copenhagen) through the adapted lid of the spectrophotometer cell compartment directly to the sample cell (volume 100 ml, optical path length $d = 3.5 \text{ cm}$), containing the buffered ethanolic solution of the organic reagent. After each addition the solution was mixed by means of a stream of nitrogen for lamps and the absorbance was measured on the Unicam instrument where the cells were accommodated in a special holder⁹ manufactured at the workshop of the Faculty of Pharmacy in Hradec Králové. The photometric determination of uranium was performed on a Spekol spectrophotometer (Zeiss, Jena). The pH was measured on a PHM 4d pH-meter equipped with a system of a G 200B glass electrode and a K 100 calomel electrode (all Radiometer, Copenhagen), calibrated by means of standard aqueous buffers (Institute for Sera and Vaccines, Prague).

Evaluation of Experimental Data

The composition of the complexes and their stability constants were determined from the concentration curves¹⁰

$$A = f(c_{\text{UO}_2})_{c_{\text{L}}, \text{pH}, \text{I}} \quad (1)$$

and from the continuous variation curves

$$A = f(x)_{c_0, \text{pH}, \text{I}}, \quad (2)$$

where c_{UO_2} and c_{L} are the total analytical concentrations of the uranyl ions and the dye, respectively, c_0 is the sum of the two, and x is the mole fraction of reagent, $x = c_{\text{L}}/c_0$.

Procedure for the Photometric Determination of Uranium

Sample containing 0.5–60 $\mu\text{g U}$ is added to a mixture of 2.5 ml of the ethanolic dye solution ($c = 0.2 \text{ mmol l}^{-1}$), 10 ml of ethanol, 6.25 ml of urotropine buffer pH 6.5–7.0, and 1.25 ml of 2M- NaClO_4 in a 25 ml volumetric flask, 1.10 ml of 40% (*m/m*) ethanol is added (correction for volume contraction), and the volume is made up to the mark with water. The absorbance is measured in 10 min at 630 nm against an ethanolic solution of buffer (1.0) or a blank solution.

RESULTS AND DISCUSSION

The reaction of uranyl with gallocyanine methyl ester can be observed in slightly acid or neutral solutions. The intensity of the violet colour is highly dependent on the ethanol content of the solution. The absorbance is highest in solutions with the lowest concentration of the nonaqueous component, but it drops rapidly in a short time due to the separation of the complex from the solution. The precipitation can be prevented by using alcohol in higher concentrations. The solution composition then remains steady for a sufficiently long period, although it takes a longer time for the absorbance to attain a constant value (Fig. 1). Solutions composed of 93% (*m/m*) ethanol and water in the 1 : 1 ratio, which makes up approximately 40% (*m/m*) ethanol, were therefore used for all measurements. The absorbance can be measured 9–45 min after mixing up the components. The ionic strength in the 40% (*m/m*) ethanol, over the I 0.01–0.1 region, does not affect the absorbance appreciably, and so a constant value of I 0.1 was chosen for all experiments. Under such conditions the violet colour starts to be apparent at pH 5 and reaches its equilibrium at pH > 6.

The absorption curves for variable concentrations of uranium, $c_U = (0-2) c_L$ at 6–7.5, exhibit a marked decrease at the wavelength of the ligand peak (640 nm), formation of a low-intensity, rather broad band at 480 nm, and a single isosbestic point at 512 nm. These data together with the continuous variations curves revealed the presence of a complex of the U : L = 1 : 2 composition. At $c_U > 2c_L$ the absorption curves are steeper near the maximum of the complex and far off the isosbestic point. This change in the shape of the absorption curves can be attributed to the effect of hydrolysis of the UO_2^{2+} ions or to the formation of polymeric complexes.

The concentration ratios curves for various pH values were evaluated to obtain the conditional stability constants¹⁰

$$\beta'_2 = [UL_2]/\{[U][L]^2\} . \quad (3)$$

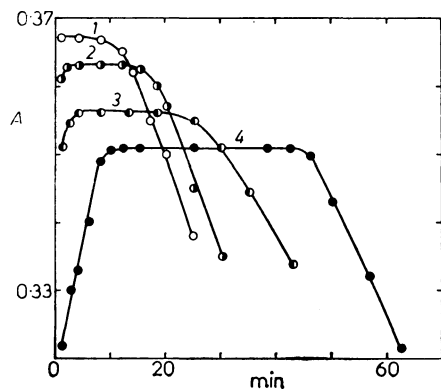


FIG. 1

Time dependence of the absorbance of complex for various ethanol contents of solvent. $c_L = c_U = 20 \mu\text{mol l}^{-1}$, $d = 1 \text{ cm}$, pH 6.58, λ 480 nm. Ethanol content, % (*m/m*): 1 1.6, 2 2.24, 3 3.32, 4 4.40

The conditional concentrations of the complex and the corresponding absorbances are interrelated through

$$[\text{UL}'_2]/[\text{UL}'_2]_{\text{max}} = A_{\text{UL}_2}/A_{\text{max}}, \quad (4)$$

where A_{max} is the absorbance for $c_U \gg c_L/2$. With $\varepsilon_U = 0$ we have

$$A_{\text{UL}_2} = A - A_L = A - (c_L - 2[\text{UL}'_2]) \varepsilon_L d. \quad (5)$$

Substituting in Eq. (4) for $[\text{UL}'_2]_{\text{max}} = c_L/2$ we obtain a relation which defines the concentration of the complex in the solution,

$$[\text{UL}'_2] = (c_L/2) \{ (A - A_L)/(A_{\text{max}} - A_L) \}. \quad (6)$$

The remaining conditional concentrations are

$$[\text{U}'] = c_U - [\text{UL}'_2] \quad (7)$$

$$[\text{L}'] = c_L - 2[\text{UL}'_2]. \quad (8)$$

The conditional stability constant of the complex then can be calculated by combining Eqs (3), (6)–(8). The values for various pH are given in Table I.

TABLE I

Conditional stability constants and equilibrium constants of the uranium(VI)–gallocyanine methyl ester system in 40% (*m/m*) ethanol at 1.0 l

pH	$\log \beta'_2$	$\log * \beta_2$	$10^4 \varepsilon_C \text{ l mol}^{-1} \text{ cm}^{-1}$	λ nm
6.06 ^a	12.21	30.60	1.82	652
6.70 ^a	12.45	30.69	—	—
7.02 ^a	12.53	30.66	1.29	650
7.43 ^a	12.64	30.70	—	—
		30.66 ^{ac}		
6.07 ^b	11.83	29.43	—	—
6.57 ^b	11.98	29.40	3.06	476
7.20 ^b	12.13	29.31	3.14	476
7.40 ^b	12.24	29.49	—	—
		29.40 ^{bc}		

^a Calculated from the absorption curves for variable uranium concentrations; ^b calculated from the continuous variations curves; ^c read off from the graphical dependence, Eq. (18). The β'_2 values are averages for 5–6 wavelengths and converted to the logarithmic scale.

The uranyl ion is the only uranium species present at $\text{pH} < 4$. As the pH is increased, the affinity for oxygen starts to manifest itself by the formation of the hydroxido complex $\text{UO}_2(\text{OH})^+$ and its dimer, $(\text{UO}_2)_2(\text{OH})_2^{2+}$, and also the trinuclear hydrolysis product $(\text{UO}_2)_3(\text{OH})_5^+$, particularly in the presence of perchlorate and nitrate¹. The conditional concentration of uranium at $\text{pH} > 4$ includes all of these hydrolytic species. In view of the increasing proportion of the polynuclear species $(\text{UO}_2)_3(\text{OH})_5^+$ with increasing pH (about 90% at pH 6), the simple formalism $[\text{U}'] \equiv [(\text{UO}_2)_3(\text{OH})_5^+]$ can be adopted for neutral solutions.

The conditional concentration of ligand in the region pH 6–7.5 involves two of the three possible equilibrium species, *viz.* HL and L^- , the former being the major component (99.2% at pH 6, 91.5% at pH 7.5); this can be expressed by the relation

$$[\text{L}'] = [\text{HL}] + [\text{L}^-] = [\text{HL}] (1 + K_{a2}/[\text{H}^+]) \quad (9)$$

($K_{a1} = 10^{-3.40}$, $K_{a2} = 10^{-8.53}$ in 41% (*m/m*) ethanol¹¹).

The dependence of $\log\{\beta'_2(1 + K_{a2}/[\text{H}^+])^2\} = f(\text{pH})$ is linear, with a slope of 0.34

The results were verified by the continuous variations method¹². The curves are smooth and also indicate the complex composition $\text{U} : \text{L} = 1 : 2$. Compared with the theoretical curve given by the equation^{13,14}

$$(1 - x - y)(x - 2y)^2 - (1/\beta'_2 c_0^2) y = 0, \quad (10)$$

where $c_0 = c_U + c_L$, $x = c_L/c_0$, $y = [\text{UL}_2]/c_0$, the left wing of the curve is more concavely deflected, presumably due to the hydrolysis of uranium.

The Job function Y is directly proportional to the concentration of complex, and thus also to the function y :

$$|Y| = \varepsilon d c_0 y, \quad (11)$$

where $\varepsilon = |\varepsilon_C - 2\varepsilon_L|$. If the complex is formed quantitatively, the mol ratio attains its limiting value of 0.333, and

$$|Y_0| = 0.333 \varepsilon d c_0. \quad (12)$$

Substituting for ε from Eq. (12) in Eq. (11), the graphical dependence $y = f(x)$ (Fig. 2) can be plotted; here the tangent from the point $x = 1$ attains the maximum y value at $x = 0.667$ and is parallel with the tangent calculated by the general equation¹⁴

$$y = -(1/m)x + (n-1)/\{m(m+n-1)\} \quad (13)$$

for $n \geq 2$. For the UL_2 complex the equation takes on the simple form

$$y = -x + 1/2. \quad (14)$$

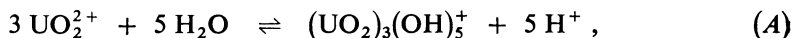
In this manner the UL_2 species was proved to be the only species manifesting itself at selected wavelengths, which makes it possible for the continuous variations method to be used for the determination of the stability constant β'_2 .

The ratio of the Job functions (11) and (12) in the maximum of the continuous variations curve gives

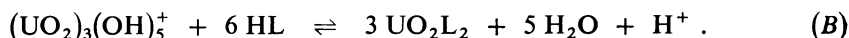
$$y_{\max} = 0.333(|Y|_{\max}/|Y_O|_{\max}), \quad (15)$$

a relation enabling the β'_2 value to be calculated from Eq. (10) for $x = 0.667$ or from the graphical dependence $y = f\{\log(\beta'_2 c_0^2)\}$, the values of which, obtained from a computer, have been tabulated¹³. Similarly as in the previous method, the dependence $\log\{\beta'_2(1 + K_{a2}/[H^+])^2\} = f(\text{pH})$ is linear and the slope is again 0.34.

The unusual value of the slope is a result of the complex mechanism involved, where the hydrolysis of the UO_2^{2+} ion,



plays a major role in the initial stage. At $\text{pH} > 6$ this equilibrium is markedly shifted to the right side¹. The polymeric hydroxido form then will take part in the coordination reaction with gallocyanine methyl ester,



The hydroxido complex being not kinetically very labile, this substitution of the OH groups by the organic ligand proceeds rather slowly. The equilibrium, establishing

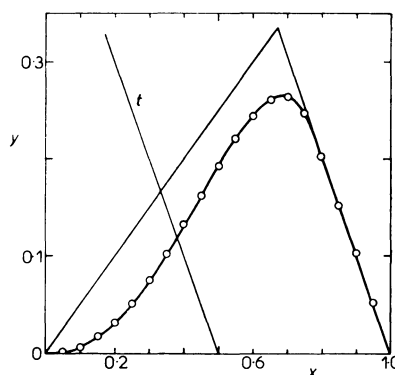


FIG. 2
Continuous variations curve for the UL_2 complex, Eq. (11). $c_O = c_U + c_L = 20 \mu\text{mol} \cdot \text{l}^{-1}$, $\text{pH} 6.57$, $\lambda 476 \text{ nm}$, $y = [UL_2]/c_O$, $x = c_L/c_O$, t tangent, Eq. (14)

only in 9 minutes, can be characterized by the constant

$$*\beta_2 = [\text{UO}_2\text{L}_2]^3[\text{H}^+]/\{[(\text{UO}_2)_3[\text{OH}]_5^+][\text{HL}]^6\}. \quad (16)$$

Since $[\text{U}'] \equiv [\text{UO}_2'] = 3[(\text{UO}_3)_2(\text{OH})_3]$, we have

$$*\beta_2 = \beta_2'(1 + K_{a2}/[\text{H}^+])^6[\text{H}^+] \quad (17)$$

and also

$$\log \{\beta_2'(1 + K_{a2}/[\text{H}^+])^2\} = (1/3) \log *\beta_2 + (1/3) \text{pH}. \quad (18)$$

Eq. (18) and the experimental data are mutually consistent and bear out the assumed equilibrium (B). The values of the equilibrium constants are given in Table I.

Photometric Determination of Uranium

The stability of the UO_2L_2 complex in nearly neutral solutions (pH 6.5–7.0) forms the basis of a photometric method of determination of uranium. The optimum wavelength, with the highest $\varepsilon_{\text{HL}} - \varepsilon_{\text{C}}$ difference, is 630 nm. At $c_{\text{L}} = 20 \mu\text{mol l}^{-1}$ and 1.0 in 40% (m/m) ethanol, Beer's law is obeyed for concentrations $c_{\text{U}} < 2.2 \text{ mg l}^{-1}$. The dependence of absorbance on the uranium concentration (in $\mu\text{g l}^{-1}$) can be described by the regression straight line equations $y = 0.2812 - 0.2423x$ for $d = 1 \text{ cm}$ and $y = 0.9854 - 0.8505x$ for $d = 3.5 \text{ cm}$. The relative standard deviation for eight replicate determinations of uranium in a concentration of $106 \mu\text{g l}^{-1}$ was $s_r = 2.13\%$. The results were treated by the t -test on the $\alpha = 0.05$ significance level with respect to the true value of $c_{\text{U}} = 212 \mu\text{g l}^{-1}$, and only random errors were found to be involved ($t_{\text{exp}} < t_{\text{crit}}$, ref.¹⁵).

Uranium can be determined with an error lower than $\pm 5\%$ in the presence of a 30-fold excess of CrO_4^{2-} or Co^{2+} ions or a 5-fold excess of La^{3+} , Zn^{2+} , or Ni^{2+} ions. Cu^{2+} , Al^{3+} , Fe^{3+} , Ga^{3+} , In^{3+} , and Th^{4+} ions interfere.

REFERENCES

1. Baes Ch. F., Mesmer R. E.: *The Hydrolysis of Cations*, p. 174. Wiley, New York 1976.
2. Ryabchikov D. I., Senyavin M. M.: *Analiticheskaya Khimiya Urana*, p. 32. Akademiya Nauk, Moscow 1962.
3. Lasovský J., Ružička E.: *This Journal* 38, 1659 (1973).
4. Nguyen Truong Son, Ružička E., Lasovský J.: *This Journal* 44, 3264 (1979).
5. Kotouček M., Bui Mai Huong: *This Journal* 42, 235 (1977).
6. Příbil R.: *Komplexometrie*, p. 151. Published by SNTL, Prague 1977.
7. Kinnunen I., Wennestrand B.: *Chemist-Analyst* 46, 92 (1957).
8. Buděšínský B.: *Fresenius' Z. Anal. Chem.* 195, 324 (1963).

9. Karliček R.: This Journal *40*, 3825 (1975).
10. Kleiner K. E.: Zh. Fiz. Khim. *34*, 416 (1960).
11. Dostál V., Kotouček M., Kalašová H., Bryndová V., Šimek J.: This Journal *47*, 1588 (1982).
12. Job P.: Ann. Chim. (Paris) *9*, 113 (1928).
13. Klausen K. S.: Anal. Chim. Acta *44*, 377 (1969).
14. Klausen K. S., Langmyhr F. J.: Anal. Chim. Acta *40*, 167 (1968).
15. Eckschlager K., Horsák I., Kodejš Z.: *Vyhodnocování analytických výsledků a metod*, p. 38, 83. Published by SNTL, Prague 1980.

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