

Physicochemical Studies On The System Uranyl-Gallic Acid in Aqueous Solutions

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Summary: Spectrophotometric, potentiometric and polarographic studies were carried out in the system uranyl-gallic acid in aqueous solution of different pH values. Composition and stability of the complex formed are determined by spectrophotometric and potentiometric method. The polarographic behaviour of the different complexes was studied and the effect of gallic acid on the reduction of U(VI) was discussed.

Introduction

Colouring organic reagents play an important role in the determination of uranium. An essential group of these reagents are the phenolic ligands used in the spectrophotometric determination of this element [1-9]. The stability of the complexes formed are determined by potentiometric methods [10-19]. Gallic acid has a considerable ability to form complexes with uranyl ion [20] where at pH 3 $[\text{UO}_2\text{RH}_3]^+$ is formed and at pH 3.5 \longleftrightarrow 5 a binuclear complex $[\text{UO}_2(\text{OH})_2\text{RH}]^-$ is formed. A complex $[\text{RH}_2\text{UO}_2(\text{OH})_2\text{UO}_2\text{RH}]^{3-}$ formed at pH 5 \longrightarrow 7 has the formula $[(\text{UO}_2(\text{RH}))]$ at pH 9. According to this report pH 8.5 is suitable for the spectrophotometric determination of uranyl ion than the others at 320 - 500 nm and in presence of 0.01 M gallic acid. Nothing has been reported on the polarographic behaviour of uranyl ion in solutions containing gallic acid. The aim of the present investiga-

tion is to determine the composition and stability of the complexes formed by spectroscopy and potentiometry, and to study the polarographic behaviour of these complexes.

Experimental

All chemicals used were of A.R. grade. Bidistilled water was used in the preparation of all solutions. Stock solution of uranyl perchlorate 10^{-2}M , its uranium content was controlled gravimetrically. The absorbance of the solutions was measured by spectrophotometer, Jean and Constant 1000, by using glass cells. pH-metric titrations were done with pH-meter model 25 China by a glass and calomel electrodes at 30°C . The polarographic measurements were carried out by a polarograph LP 60, and a capillary having $m=3.648\text{ mg./sec}$, at $t=3.3\text{ sec./drop}$, being measured in an air free solution. All solutions are air-freed by bubbling nitrogen before recording the polarogramme.

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Results and Discussion

1. Spectrophotometric Results

The absorption spectra of mixture of uranyl perchlorate and gallic acid at different pH values are shown in Fig.1a. The spectra do not show remarkable maxima, but decrease monotonically from 360 to 540 nm. By increasing the pH the absorbance increases up to pH 7.1 then it attains a limiting-value. This behaviour is due to a shift in equilibrium accompanied by liberation of hydrogen ions. Fig 1b shows the existence of different types of complexes of uranyl with gallic acid. At least three types of complexes can be deduced, the first at $pH < 3.5$, another at $pH 3.5 \rightarrow 5$ and the third at $pH > 5$, in agreement with the results obtained by Havel and Sommer [20].

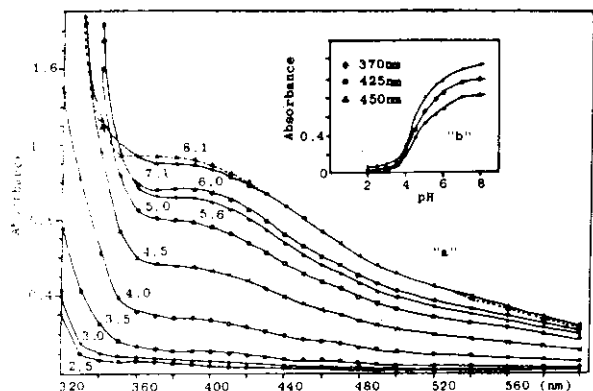


Fig.1: Spectra of $5 \times 10^{-4} M UO_2^{2+} + 1 \times 10^{-3} M$ Gallic acid at different pH's

The composition of the complexes was studied by Job's method and molar ratio method at pH 3.0, 3.5, 4.0 and 9.1 Fig 2. The complex at pH 3.0 is of the 1:1 type at pH 3.5 and 4.0 it has a composition 2:1 uranyl : gallic, whereas at pH 9.1 it is only of the 1:1 type. These results agree with those reported previously [20]. Also in our work the ratio at pH 3.5 and 4.0 reaches exact 2:1 ratio UO_2 :

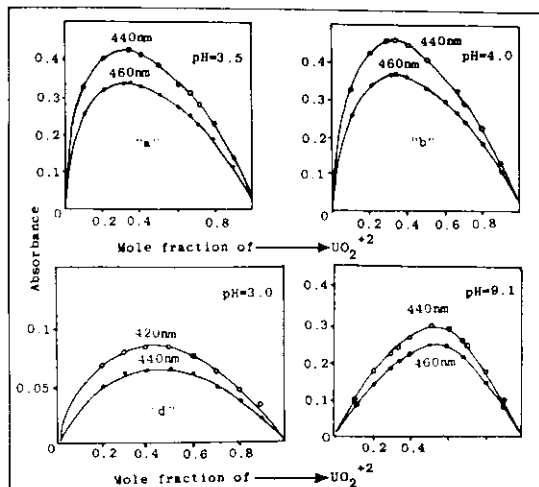


Fig.2: Composition of UO_2^{2+} - Gallic complexes at different pH's by Job's method.

gallic. This difference may be due to the presence of acetate ion in case of Sommer, which compete with gallic acid in comparison with perchlorate which is non-complexing ion.

The data obtained by the molar ratio for the 1 : 1 complex at pH 9.1 was used for the determination of the stability constant of this complex as follows:



(a-x) (b-x) x

When the absorbance reaches a constant value (A_m) in presence of excess gallic acid, Fig. 2f, at any concentration of ligand the concentration of complex is (x) and its absorbance is (A) and hence:

$$\frac{x}{a} = \frac{A}{A_m} \text{ and } x = a \cdot \frac{A}{A_m}$$

and the stability constant equals:

$$K = \frac{A/A_m}{(b-a A/A_m)(1-A/A_m)}$$

from this equation a value for log K is obtained which equals 5.51.

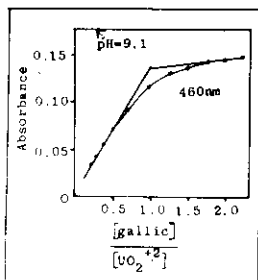


Fig.2f: Composition of UO_2^{2+} - Gallic complexes at pH 9.1 by Molar Ratio method

2. Potentiometric Studies

In these studies 40 ml. of gallic acid solution ($5 \times 10^{-3} M$), was titrated with 0.1 M KOH in absence and in presence of uranyl ion in 1:1 or 1:2 uranyl gallic ratio. The ionic strength is kept constant at 0.1 and temperature at $30^\circ C$ and inert atmosphere maintained by bubbling nitrogen during the titration. The pH reading is taken after each addition of KOH and after reaching equilibrium, and the results are plotted in Fig. 3a, for gallic and b for the mixture.

From this figure it is seen that there is a depression in pH in case of the mixture, due to complexation and liberating hydrogen ions. Calculating $[\bar{L}]$ and (\bar{n}) where $[\bar{L}]$ is the concentration of the free chelating species, and \bar{n} is the average number of molecules of ligand bound by one metal atom, the formation curve is drawn in Fig. 3c and the stability constant of the 1 : 1 complex at $\bar{n} = 0.5$ is found to equal 9.6. This value is quite different from that obtained by spectrophotometric results, which shows that this complex is different from the 1:1 complex formed at pH 9.1. Titration of a mixture of 1:2 uranyl : gallic acid was carried out in order to obtain the overall stability constant of the 1:2 complex using the equation:

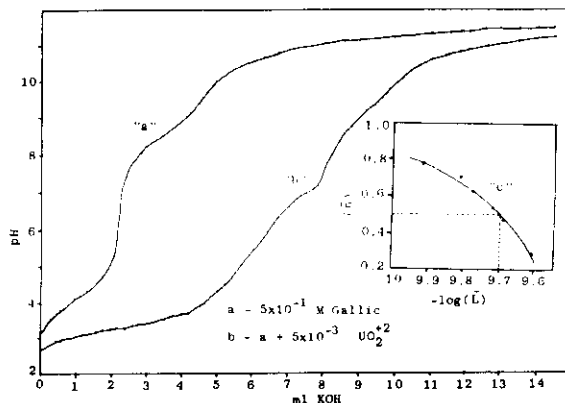


Fig.3: Potentiometric Titration of UO_2^{2+} - Gallic mixture with (0.1M) KOH in aqueous solution at $30^\circ C$

$$\frac{\bar{n}}{(\bar{n} - 1)(\bar{L})} = \frac{(2 - \bar{n})(\bar{L})}{(\bar{n} - 1)} \beta_2 - K_1$$

and subjecting the data to least square method the value of $\log \beta$ was obtained and found to be $19.17 + 0.03$, from which the value of $\log K_2$ can be obtained.

A sample of potentiometric titration of 1:1 ratio at $\mu = 0.1$, $T = 30^\circ C$, $[KOH]=0.1M$, $[UO_2]=0.005 M$, and $V_o = 40 ml$.

ml.KOH	1.000	1.100	1.200	1.300	1.400	1.500
pH	3.060	3.080	3.100	3.120	3.150	3.170
\bar{n}	0.284	0.0459	0.536	0.620	0.698	0.774
$L^- \times 10^{10}$	2.445	2.018	1.892	1.692	1.535	1.200

3. Polarographic Results

a. Uranium Waves in Various Supporting Electrolytes in Presence of Gallic Acid

The effect of increasing amounts of gallic acid on the polarograms of 1 m.mole U(VI) in 0.1 M KCl solution was investigated. The waves are shown in Fig.4. The polarograms consist of

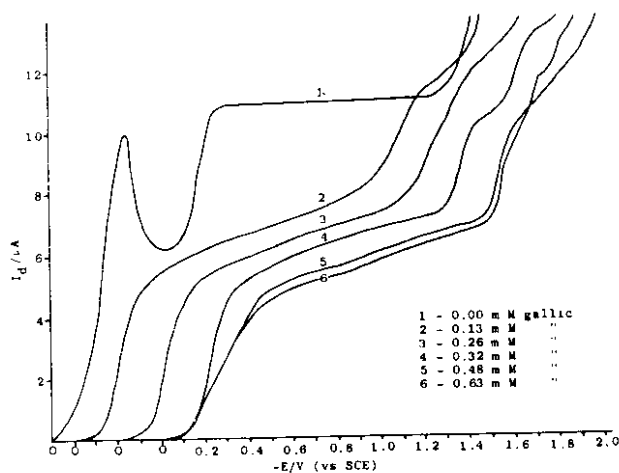


Fig.4: Effect of Gallic acid concentration on the polarogram of (1m.mole) UO_2^{2+} IN 0.1M KCl

two or three waves according to the concentration of gallic acid. Polarogram 1, in absence of gallic acid, consists of two waves, the first is accompanied by a maximum, the half wave potential is at -0.19 V vs.SCE., while that of the second is at -0.65 V. Addition of small quantity of gallic acid (0.13 m. mole) suppresses this maximum and shifts the second wave to -1.47 V. A small hump was observed on the plateau of the first wave. The height of the first wave is higher than that of the second, polarogram 2. When the concentration of gallic acid reaches 40% that of uranium a kink is noticed on the second wave, which becomes two well-defined waves at higher concentrations of gallic acid, polarogram 4. Further increase of ligand shifted the first wave to more negative and the second wave persists whereas the third wave is shifted to less negative potential.

In presence of 0.1 M perchloric acid, as a supporting electrolyte, and in presence of 2.5 m.mole gallic acid, the polarogram consists of two well-defined waves. The first wave has $E_{\frac{1}{2}} = -0.33$ V. and the second with $E_{\frac{1}{2}} = -0.89$ V. vs. SEC.

The height of the first wave is greater than half that of the second wave, which denotes that disproportionation of U(VI) is effective in this solution, due to the higher acidity of the solution. However, the disproportionation is not complete due to complexing effect of gallic acid. The total height of the polarogram in this medium is 9.7 $\mu\text{A}/\text{m. mole}$ and is due to three electrons, i.e. one electron corresponds to 3.25 μA and the first wave is due to 1.2 i.e. one electron. According to this value the reduction along the first wave, in 0.1 M KCl, in presence of gallic acid is due to the expression: $\text{U(VI)} \xrightarrow{2e} \text{U(IV)} \xrightarrow{e} \text{U(III)}$. This shows that the reduction process in presence of gallic acid is different from that in its absence, due to its effective complexing action, and its adsorption on the electrode and the charge distribution in the double layer. The appearance of the third wave may be due to the reduction of one of the U(VI)-gallic complexes investigated by the spectrophotometric results.

b. Gallic acid as a Maximum Suppressor

It is seen that gallic acid serves as a maximum suppressor for the uranyl maximum in 0.1 M KCl solution used in the present work, Fig.4 polarogram 1, where the maximum disappeared in presence of small amounts of gallic acid, and does not appear again in contrary to U(VI)-resorcinol [21]. It is known that maximum occurs less frequently with the complex rather than with the simple ions. From spectrophotometric results gallic acid gives with uranyl ion different types of complexes. A small degree of surface activity on the gallic acid would suffice to prevent maxima on the polarograms.

c. Effect of gallic acid on $E_{\frac{1}{2}}$ and I_d of uranyl waves

In both media, perchloric (0.1 M) or KCl (0.1 M), the presence of gallic

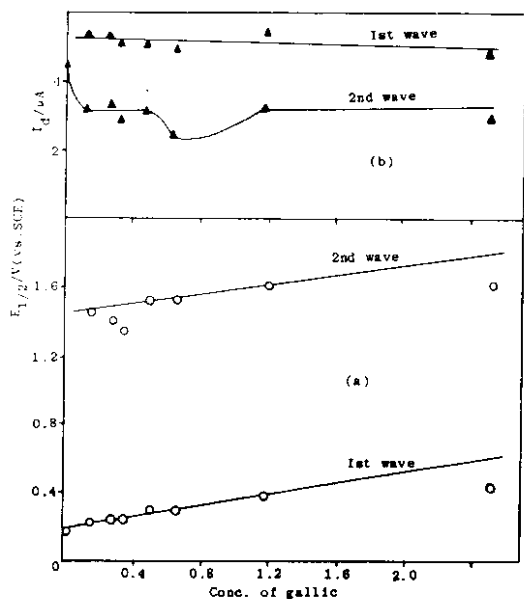


Fig.5: Effect of Gallic acid concentration on: (a) $E_{1/2}$ V (vs. SCE) (b) $I_d/\mu A$

acid affects the half-wave potential and the limiting current of uranium reduction waves. In 0.1M perchloric the half-wave potential of the first wave is shifted from -0.9 V to -0.33 V and that of the second is shifted to -0.9 V. This shift may be due to complexation or surface activity, due to specific adsorption, or due to both. In 0.1 M KCl the effect are given in Table 1, from which it is seen that $E_{1/2}$ of both waves are shifted to more negative due to complexation, and that the third to less negative, which may be due to a complex or due to the ligand itself as its height increases by the increase of gallic acid concentration. From Table 1 and Fig.5 the total height of the polarogram decreases by the increase of gallic acid which is a phenomenon usually observed on complexation.

d. Effect of pH

These studies reveal that the half-wave potential and the height of the waves depend on the pH. While at pH 3, Fig. 6. a polarogram consisting

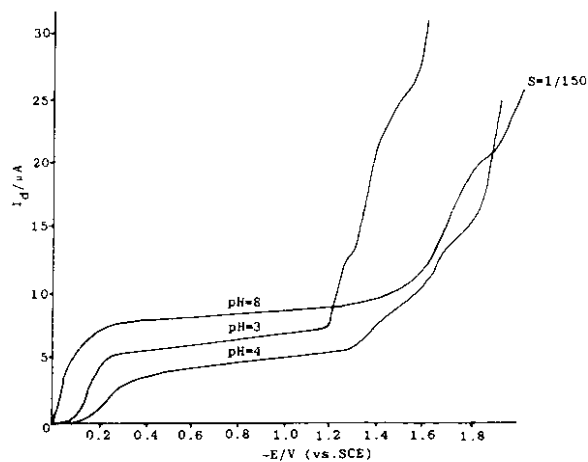


Fig.6: Effect of pH on the polarograms of $0.8 \text{ mM } \text{UO}_2^{2+} + 1 \text{ mM Gallic}$ in 0.1 M KCl

of three waves due to reduction of certain type of complex species, at pH 4 a polarogram of another complex which is difficult in reduction is obtained and its height is less than that at pH 3. At pH higher than 7 a different polarogram which consists of two waves and easier in reduction, at the first wave, which denotes that it is for a third species different from those at pH 3 and 4. The spectrophotometric results showed that there are different complexes at the different pH ranges. At pH less than 3.5 there is the 1:1 $[\text{UO}_2\text{RH}_3]^+$ complex which can be reduced at the polarogram of pH 3. Another species is formed which is binuclear complex, Fig.2 at pH 3.5 and pH 4, which is difficult to be reduced $[\text{UO}_2(\text{OH})_2\text{UO}_2\text{RH}]^-$ because of its negative charge or its bulky molecules or due to both, which explains the more negative potential and lower height. At pH 9, as revealed by the spectrophotometric results in the present work, the complex formed having the formula $[\text{RHUO}_2]$ [20] is present in the solution at pH 8, and can be easily reduced irrespective of its negative charge.

Table-1: Effect of Gallic acid concentration on I_d and $E_{1/2}$ of 1.0 m.mole UO_2^{+++} , in 0.1 M KCl.

Gallic m.mole	I_d μA			$-E_{1/2}$ V.vs.SEC		
	1st wave	2nd	3rd	1st	2nd	3rd
0.00	4.20	4.60	-	0.19	0.65	-
0.13	5.40	3.15	-	0.21	1.47	-
0.26	5.25	3.28	-	0.22	1.41	-
0.32	4.96	2.69	1.86	0.22	1.46	1.63
0.48	5.04	3.04	1.57	0.28	1.55	1.97
9.63	4.86	2.25	1.71	0.28	1.54	1.78
1.18	5.44	3.17	3.17	0.37	1.61	1.73
2.50	4.67	2.67	4.53	0.41	1.62	1.73

Table-II: Characteristics of waves of 1.0 m. mole uranyl ion in presence of Gallic acid in different supporting Electrolytes.

Supporting Electrolyte	Wave	I_d μA	$-E_{1/2}$ V.	Slope	αn_a	α	X
0.1 M KCl	<u>1st</u>	4.67	0.41	0.066	0.82	0.41	0.50
	<u>2nd</u>	2.67	1.62	0.095	0.57	0.57	0.46
	<u>3rd</u>	4.53	1.73	-	-	-	-
0.1M $HClO_4$	<u>1st</u>	3.94	0.33	0.24	0.23	0.23	0.51
	<u>2nd</u>	5.76	0.89	0.079	0.68	0.34	0.51
pH 3	<u>1st</u>	5.5	0.15	0.067	0.81	0.81	0.72
	<u>2nd</u>	5.8	1.23	0.045	0.62	0.62	0.63
	<u>3rd</u>	7.42	1.37	0.075	0.72	0.72	0.63
pH 4	<u>1st</u>	3.96	0.30	0.077	0.70	0.70	0.56
	<u>2nd</u>	3.74	1.35	0.140	0.40	0.40	0.61
	<u>3rd</u>	4.95	1.65	0.090	0.62	0.62	-
pH 8	<u>1st</u>	2.00	0.06	-	-	-	-
	<u>2nd</u>	-	1.65	-	-	-	-

e. *Effect of Mercury Height and Analysis of the Waves*

The effects of mercury height on the limiting current of the waves in presence of gallic acid is given by the slopes of $\log i_l$ vs $\log h$ plots in Table (II). The values show that the process of reduction becomes largely diffusion controlled in presence of ligand except at pH 3 where an adsorption component was observed. The waves were analyzed with the aid of $\log (i/i_d - i)$ vs. E plots which revealed that most of the waves are not reversible. The values of $E_{1/2}$ and αn_a show that the presence of the adsorbed layer of gallic acid has brought about a considerable increase in the irreversibility of the reduction process.

f. *Effect of Concentration of Uranium*

For the analytical determination of U(VI) in presence of gallic acid all the media are tested by increasing the concentration of uranium in 0.1 M KCl at pH 9, 4, 3 and 0.1 M perchloric acid. Only the 0.1 M perchloric acid is suitable for the determination of uranium, where straight lines passing through the origin for first wave, second and total current are obtained. However, the other media give straight lines not passing through the origin.

Similar results are reported by spectrophotometry where pH 4 and pH 3 complexes are not suitable for spectrophotometric determination of this ion.

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