

Spectrophotometric investigations of the reaction between gold(III) and potassium iodide*

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The equilibria of the complex formation between $\text{AuCl}_{4-n}(\text{OH})_n^-$ and I^- was studied spectrophotometrically in aqueous solutions containing $\text{KI}:\text{Au(III)} \leq 2$ in the acidity range from 1 M HCl to pH 7 at 25 °C. From the hydrogen ion and Cl^- ion dependence of the absorption spectra, it was found that $\text{AuCl}_2\text{I}_2^-$ and $\text{Au}(\text{OH})_2\text{I}_2^-$ complexes were formed. The equilibrium constants of complex formation were determined.

Keywords: Au(III), iodine, complexes, aqueous solutions.

INTRODUCTION

Due to its characteristic to be reduced to gold(I) or elementary gold, gold(III) forms a limited number of complexes, especially with inorganic ligands in aqueous solutions.^{1,2} One of the most investigated complexes of gold(III) with halogens is the tetrachloroaurate ion.³⁻⁶ The hydrolysis of this complex has been widely investigated and the equilibrium constants of successive protolytic reactions have been determined by potentiometric methods.⁵⁻⁸

Research on other gold(III)-halogen compounds revealed that gold(III) belongs to the group of typical acceptors of the Chatt-Ahrland B group,⁹ and forms very strong iodine complexes. According to studies of the electrochemical behaviour of gold in iodide solutions it was found that the iodide ion is an efficient complexing agent of gold.¹⁰ Literature data indicate that gold(III) is unstable in aqueous iodide solutions, inducing the quantitative release of iodine.¹¹ The reduction of gold(III) by iodide ions is used in the potentiometric determination of gold in ores and alloys.¹²

The reaction of tetrachloroaurate acid with potassium iodide in aqueous solution has recently found a practical application in the kinetic determination of

* Dedicated to Professor Slobodan Ribnikar on the occasion of his 70th birthday

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oxime antidotes used in the therapy of nerve toxin intoxication.^{13–15} Due to the lack of literature data on the mechanism of this reaction, the aim of this work was to investigate the reaction of Au(III) and KI, and to elucidate the equilibria reactions between I^- and $AuCl_{4-n}(OH)_n^-$ species in a wide acidity range.

EXPERIMENTAL

Reagents

All reagents were commercial products of the highest purity available. The solutions were prepared using bidistilled water. The 1.0×10^{-3} M tetrachloraurate acid ($HAuCl_4$) stock solution was prepared by dissolving the appropriate amount of $HAuCl_4 \times 3H_2O$ (Aldrich) in 1 M HCl to avoid the hydrolysis of $AuCl_4^-$. A freshly prepared solution was used; more diluted solutions were obtained by appropriate dilution with water. The concentration of the stock potassium iodide (Merck) 1.0×10^{-3} M and potassium chloride (Merck) solution was 3 M, respectively. 1 M HCl and 1 M NaOH solutions were used for the adjustment of the acidity.

Apparatus

The absorption spectra were recorded on a Beckman UV VIS 2560 spectrophotometer, in a 1 cm matched quartz cuvette, with the sample compartment thermostated at $25^\circ C \pm 0.1^\circ C$. The pH was measured using a Metrohm 713 pH-Meter with a precision of ± 0.005 pH units.

Spectrophotometric and equilibria measurements

The reaction with potassium iodide was initiated by adding the appropriate aliquot of KI into a previously prepared and equilibrated solution of $HAuCl_4$ in the medium of desired acidity and Cl^- concentration. The ionic strength was kept constant (1 M and 2.5×10^{-3} M) by addition of the appropriate amount of KCl. The acidity of the solution was adjusted by addition of the appropriate amount of 1 M HCl or NaOH. The absorption spectra and pH measuring were performed immediately after KI addition.

RESULTS AND DISCUSSION

Absorption spectra and composition of Au(III) complexes with I^-

The reaction between $HAuCl_4$ and KI was investigated spectrophotometrically in the acidity range between 1 M HCl and pH 7 in the presence of KCl from 2×10^{-3} M to 1 M. The absorption spectra of solutions containing 5×10^{-5} M $HAuCl_4$, 1×10^{-4} M KI and various concentrations of KCl at different acidities, recorded from 200 nm to 450 nm, are presented in Fig. 1.

The results show that the reaction between $HAuCl_4$ and I^- is strongly affected by the concentration ratio of the species, as well as the acidity and Cl^- concentration. The changes of the absorption spectra indicate the formation of two forms of Au(III) complexes with I^- , with different spectral characteristics.

The complex with an absorption maximum at 245 nm (Fig. 1, curve 1) was formed in the acidity range between 1 M HCl and pH 6 in the presence of 1 M Cl^- . When the Cl^- concentration was decreased the other complex, with an absorption maximum at 200 nm and a shoulder between 260–320 nm, (Fig. 1, curve 2) was formed in the acidity range between pH 2 and pH 6.

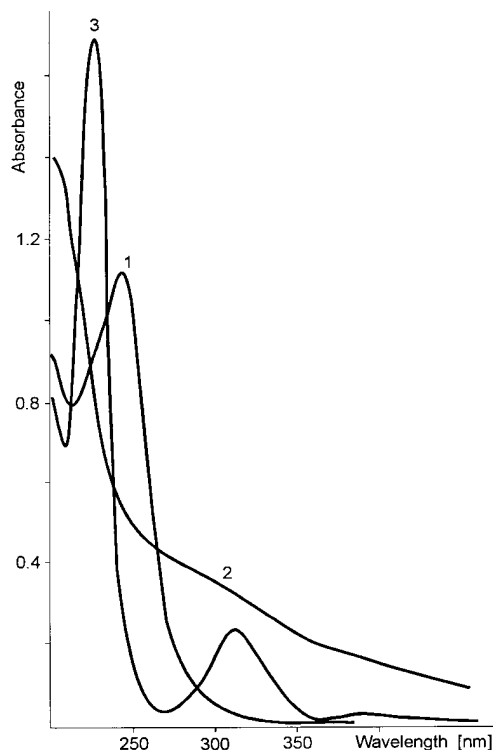


Fig. 1. Absorption spectra of the Au(III) complexes (1,2) with I^- as a function of the acidity and Cl^- concentration. $[Au(III)] = 5 \times 10^{-5}$ M, $[I^-] = 1 \times 10^{-4}$ M. 1 – pH 2.7, 1 M KCl; 2 – pH 5.7, 2.5×10^{-3} M KCl; 3 – 5×10^{-5} M $HAuCl_4$ in 1 M HCl.

The absorption spectra of 5×10^{-5} M $HAuCl_4$ in the absence of KI were also recorded as a function of acidity and Cl^- concentration, in order to compare them with the absorption spectra of Au(III) complexes with I^- . The spectra were recorded in the acidity range from 1 M HCl to pH 7, varying the concentration of Cl^- from 1 M to 2.5×10^{-3} M. As an example, the absorption spectrum of Au(III) in 1 M HCl is presented in Fig 1 (curve 3). Absorption maxima at 225 nm and 315 nm were visible, the intensities and positions of which showed no significant changes in the investigated Cl^- concentration and pH range. The results presented in Fig. 1 show that the absorption spectra of the Au(III) complexes with I^- differ significantly from the absorption spectra of the Au(III) chloro complexes.

The stoichiometry of the Au(III) complexes with I^- was determined by the mole ratio method, keeping the $HAuCl_4$ concentration constant at 5×10^{-5} M, and varying the KI concentration. The experiments were performed in 1 M HCl and pH 2.8 in the presence of 1 M KCl (Fig. 2a), and pH 2.8 and pH 5.7 in the presence of 2.5×10^{-3} M KCl (Fig. 2b). The absorbance change as the function of $I^-/Au(III)$ ratio was followed at 250 nm in the presence of high (1 M) and 265 nm in the presence of low (2.5×10^{-3} M) Cl-concentration. These wavelengths were chosen for the complex stoichiometry determination because of the highest difference between the absorbance of Au(III) ionic forms and its iodo complex formed in the

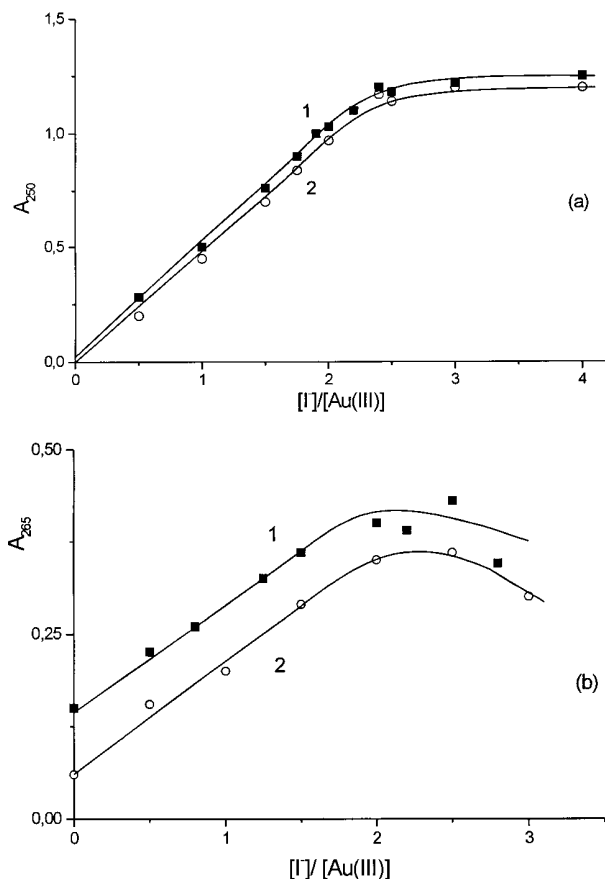


Fig. 2. Determination of the complex composition by the mole ratio method. $[HAuCl_4] = 5 \times 10^{-5}$ M. a) 1 – 1 M HCl, 2 – pH 2.8, 1 M KCl; b) 1 – pH 2.8, 2 – pH 5.3, 2.5×10^{-3} M KCl.

presence of high and low Cl^- concentration (see Fig. 1). The ratio $Au(III):I^- = 1:2$ in the complex was found in all cases. The changes of the absorption spectra as a function of KI concentration, which accompanied the formation of the complex under the present experimental conditions, showed well defined isobestic points. The results also showed that both complexes were formed in solutions where the concentration ratio was $KI:Au(III) \leq 2$. The absorption spectra of the solutions containing $KI:Au(III) > 2$ showed two absorption bands with the maximum at 288 nm and 355 nm, indicating the well known reduction of $Au(III)$ by I^- , followed by the formation of I_3^- ions.¹²

The comparison between the absorption spectra of $Au(III)$ complexes with I^- and the absorption spectra of $Au(III)$ ionic forms indicates that the complex formation in the presence of 1 M Cl^- caused the bathochromic shift of the absorption maximum. This would be in accordance with the substitution of two Cl^- ions by two I^- , suggesting the formation of $AuCl_2I_2^-$. The experimental results showed that the substitution of Cl^- by OH^- in $AuCl_4^-$ complex induced the hypsochromic shift

of the absorption maximum (data not shown). The complex formation in the presence of low Cl^- concentration was followed by the hypsochromic shift of the absorption maximum and the appearance of the bathochromically shifted shoulder. It suggests that the other complex may contain also $-\text{OH}$ ligands in its structure, having the composition $\text{Au}(\text{OH})_2\text{I}_2^-$.

Effect of Cl^- ions on the complexation equilibria

The effect of Cl^- ions on the absorption spectra of Au(III) complexes with I^- was investigated in the solutions containing 5×10^{-5} M Au(III) and 1×10^{-4} M KI at pH 2.8 and pH 5.3, by varying the Cl^- concentration from 2×10^{-3} to 1 M. The

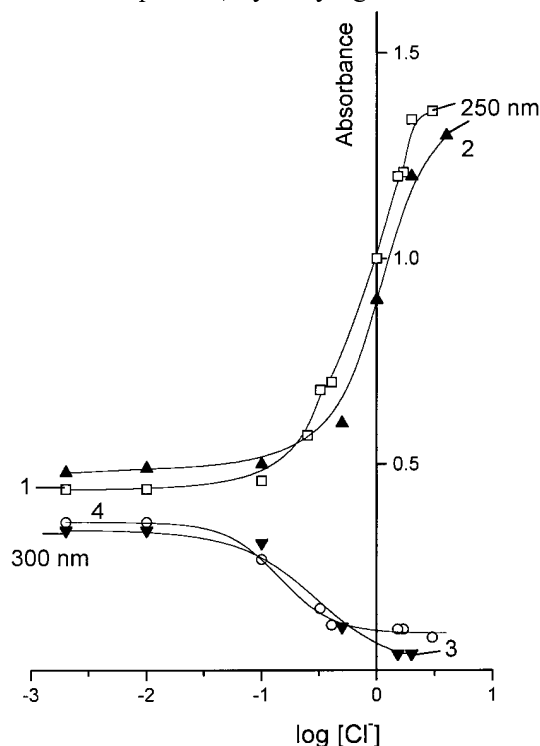


Fig. 3. Absorbance of $\text{AuCl}_2\text{I}_2^-$ (1,2) and $\text{Au}(\text{OH})_2\text{I}_2^-$ (3,4) as a function of Cl^- concentration. $[\text{Au(III)}] = 5 \times 10^{-5}$ M, $[\text{I}^-] = 1 \times 10^{-4}$ M. 1,3 – pH 2.8; 2,4 – pH 5.3.

absorbances at 250 nm and 300 nm are presented as a function of Cl^- concentration at pH 2.8 and pH 5.3 in Fig. 3. The results indicate that the formation of the $\text{AuCl}_2\text{I}_2^-$ complex is strongly dependent on the Cl^- concentration over a wide acidity range. A decrease in the Cl^- concentration was accompanied by the appearance of the $\text{Au}(\text{OH})_2\text{I}_2^-$ complex. The spectral changes formed a scattered isobestic point, indicating also that consecutive equilibria between $\text{AuCl}_{4-n}(\text{OH})_n^-$ forms occurred.

Complexation equilibria of Au(III) with I^-

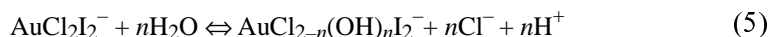
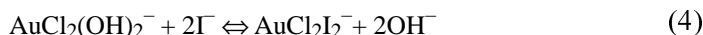
In the investigated ranges of acidity and Cl^- concentration a stepwise hydrolysis of AuCl_4^- takes place according to the equation:



The distribution of $\text{AuCl}_{4-n}(\text{OH})_n^-$ complexes was calculated using the known equilibria constants¹ for the hydrolysis of the AuCl_4^- ion (data not shown). On the basis of these results and the results obtained by the spectrophotometric investigations, it was concluded that $\text{AuCl}_{4-n}(\text{OH})_n^-$ ions react with I^- forming mixed complexes depending on the acidity and Cl^- concentration. The results indicate that in the presence of 1 M Cl^- in the acidity range from pH 0 (1 M HCl) to pH 6 equilibrium (2) exists, since under these experimental conditions Au(III) is in the form of AuCl_4^- :



The distribution diagram shows that AuCl_4^- , AuCl_3OH^- and $\text{AuCl}_2(\text{OH})_2^-$ complexes are in equilibria at pH 2.8 and 5.5. They probably form $\text{AuCl}_2\text{I}_2^-$ complex, which undergoes to the hydrolysis in the lack of the Cl^- ions, according to the equations:



The equilibrium constants corresponding to Eqs. (2) and (5), K and K_{eq} respectively, can be easily determined from the spectrophotometric data presented in Fig. 2 and Fig. 3. K and K_{eq} can be expressed as follows (the charges are omitted for simplicity):

$$K = \frac{[\text{AuCl}_2\text{I}_2] [\text{Cl}]^2}{[\text{AuCl}_4] [\text{I}]^2} \quad (6)$$

$$K_{\text{eq}} = \frac{[\text{AuCl}_{2-n}(\text{OH})_n\text{I}_2] [\text{Cl}]^n [\text{H}]^n}{[\text{AuCl}_2\text{I}_2]} \quad (7)$$

where the square brackets denote the equilibrium concentrations of the species. The Cl^- concentration was sufficiently high under the present experimental conditions that its changes during complex formation were negligible. The values of K for the formation of $\text{AuCl}_2\text{I}_2^-$ were determined from the changes of absorbance as a function of I^- concentration at pH 2.8 in the presence of 1 M KCl in 1 M HCl, assuming that under these experimental conditions only this type of complex is formed.

For equilibrium (5), the following equation is derived by simple manipulation of Eq. (7):

$$\log \frac{A_{\text{max}} - A}{A - A_{\text{min}}} = \log K_{\text{eq}} - n \log \text{Cl}^- + n\text{pH} \quad (8)$$

where A_{\max} and A_{\min} represent the absorbancies at the maximum or minimum of the absorbance vs. Cl^- curves (Fig. 3) and A is the absorbance at any Cl^- concentration. The equilibrium constant K_{eq} was obtained according to Eq. (8) from the dependence of the left hand side of Eq. (8) on $[\text{Cl}^-]$ at pH 2.8 and pH 5.3. Straight lines with the slope ≈ 2 were obtained in both cases. All obtained results are summarised in Table I.

TABLE I. Equilibria constants for the reactions between Au(III) and I^-

Equilibria	pH	Cl^-/M		Constant
(2)	0 (1 M HCl)	1	K	$(4.12 \pm 0.09) \times 10^{10}$
	2.8	1		$(7.09 \pm 0.08) \times 10^{10}$
(3)	2.8	2.5×10^{-3}	K_{eq}	$(1.69 \pm 0.09) \times 10^{-6}$
				$n = 2.1 \pm 0.1$
	5.3	2.5×10^{-3}		$(3.16 \pm 0.08) \times 10^{-11}$
				$n = 2.2 \pm 0.2$

Although the literature data indicate that AuCl_4^- is reduced by 1 M KI, the present study shows that it undergoes Cl^- substitution by I^- , forming $\text{AuCl}_2\text{I}_2^-$ and $\text{Au}(\text{OH})_2\text{I}_2^-$ complexes in the presence of low concentrations of KI. The substitution of Cl^- by I^- was confirmed by the shift of the charge transfer band to longer wavelengths, as was also found for the bromo complexes.³ The values of the equilibria constants, K , (Table I) indicate the formation of a very stable mixed complex, which undergoes hydrolysis in the presence of low concentrations of Cl^- . The slope ≈ 2 in Eq. (8) suggests that the composition of the complex is $\text{Au}(\text{OH})_2\text{I}_2^-$, since two Cl^- ions were replaced by OH^- in equilibria (5). As the values of the equilibria constant K_{eq} (Table I) show, the hydrolysis of $\text{AuCl}_2\text{I}_2^-$ is strongly dependent on the hydrogen ion concentration. This fact confirms that the reactions of $\text{AuCl}_2\text{I}_2^-$ in aqueous medium can be quite complex, leading to the formation of $\text{Au}(\text{OH})_2\text{I}_2^-$ through a complex reaction mechanism. A kinetic study of this complex system should give useful information about the reaction mechanism.

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ИЗВОД

СПЕКТРОФОТОМЕТРИЈСКО ИСПИТИВАЊЕ РЕАКЦИЈЕ ЗЛАТА(III) СА КАЛИЈУМ-ЈОДИДОМ

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Равнотеже образовања комплекса између $\text{AuCl}_{4-n}(\text{OH})_n$ и KI испитиване су спектрофотометријски у воденим растворима при односу концентрација $\text{KI}:\text{Au(III)} \geq 2$ у области киселости од 1 М HCl до pH 7 на 25 °C. Из промене апсорпционих спектра у зависности од киселости средине и концентрације Cl^- јона нађено је да се образују комплекси $\text{AuCl}_2\text{I}_2^-$ и $\text{Au}(\text{OH})_2\text{I}_2^-$. Одређене су константе равнотеже одговарајућих реакција.

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