The Interaction of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one with Platinum(IV) Ions

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Abstract – The work is devoted to the study of platinum(IV) ions with a new organic reagent – 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (HITO). The optimum conditions of interaction: pH = 5.0 (acetate buffer), 60 min heating in a boiling water bath, λ_{max} = 350 nm have been found. The ratio of components in complex Pt(IV):HITO = 1:1 at pH = 5.0 has been established. The molar absorptivity ($\varepsilon_{350} = 5.0 \cdot 10^3$ L·mol^{-1}·cm^{-1}) and detection limit of platinum ($C_{min} = 2.4 \cdot 10^{-6}$ mol·L^{-1}) are calculated.

Key words: platinum(IV), azolidons, 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one, spectrophotometry, complex.

I. Introduction

Among all metals of the platinum group platinum has many applications, since it has great chemical inertness and is one of the most frequently used platinoids. Due to the stability of electrical, thermoelectric, mechanical properties, high corrosion and heat resistance this metal is indispensable for modern electrical engineering, automation, precision instrument, glass, textiles, medical and jewelry industry. The most common use of platinum is as a catalyst in chemical reactions [1, 2].

Because of the widespread use of platinum in various facilities to researchers face the task of developing simple and affordable methods of spectrophotometric determination of this metal content.

The perspectives of organic substances are their complex compounds with metal ions. Among the large number of dyes, special interest have azolidons and their derivatives, which contain functional groups with electron donor atoms S, N, O [3]. Thiazolidon derivatives are a well-known class of biologically active compounds, which became the basis for an entire group of innovative medicines [4, 5]. However, azolidons are used not only in medicine but also in chemistry for identification of some elements. The thio-derivatives of azolidons are successfully used in analytical practice as reagents for the determination of noble metals [6, 7].

II. Experimental

The stock solution of Pt(IV) was prepared by dissolving metallic palladium (99.999%) in a mixture of concentrated HNO_3 and HCl (1:3). The standard working Pt(IV) solutions were prepared by dissolving an aliquot of platinum(IV) stock solution in 1.0 mol·L^{-1}·HCl.

The solution of 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was prepared by dissolving the exact mass of the reagent in 96% v/v ethanol.

Solutions of CH_3COONa, NaCl and NaOH were prepared by weight and HCl, CH_3COOH were prepared by dilution of concentrated HCl or CH_3COOH respectively. NaCl was selected to maintain the ionic strengths of the solutions. CH_3COONa, NaOH, CH_3COOH and HCl were used to vary the pH of the solutions.

All aqueous solutions utilized in the research have been prepared using distilled water. All chemicals used in the research were of analytical grade.

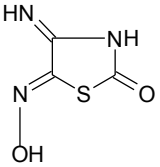
Absorption spectra were recorded using a 108 UV/ULAB spectrophotometer and a 1.0 cm quartz cell. Absorption spectra were obtained in the wavelength range 240–600 nm with a step of 2 nm using distilled water as a blank.

The pH measurements were carried out with pH-meter model pH-150 M equipped with a combination glass electrode, Gomelsky Plant of Measuring Devices, Belarus.

Activation of solutions was performed by thermal treatment in a boiling water bath.

III. Results and Discussion

For the study we used a new reagent – 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one, which belongs to the class of azolidons. The structural formula of HITO is:



It is a crystalline powder sand-colored, poorly soluble in water, but soluble in ethanol, methanol, ethylene glycol, glycerol, *n*-propanol, isoamyl alcohol dimethylformamide and dimethylsulfoxide. The spectrophotometric properties of HITO were investigated [8].

It was found that HITO is sensitive to the presence of Pt(IV) ions in the solution and forms with them a complex with the absorption maximum at λ_{max} = 350 nm (Fig. 1).

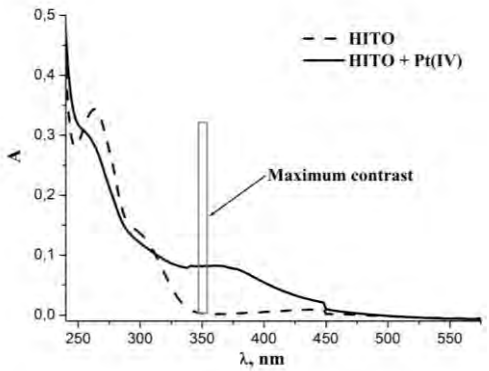


Fig. 1. Absorbance spectra of HITO and complex of Pt(IV) with this reagent, $C_{HITO} = 4.0 \cdot 10^{-5}$ mol·L^{-1}, $C_{Pt(IV)} = 2.0 \cdot 10^{-5}$ mol·L^{-1}, μ(NaCl) = 0.1 mol·L^{-1}, pH = 5.0, l = 1.0 cm

The process of complexation was carried out in acetate buffer at pH = 5.0, with the background sodium chloride solution (μ = 0.1 mol·L^{-1}) and 60 min of heating in a boiling water bath. Without heating the process is much slower and the same values of optical densities are not achieved even at twenty-four hours. Using two independent methods – the mole-ratio method and the

method of continuous variations, the correlation between the components in the system Pt(IV)-HITO was established and it is 1:1 (Fig. 2).

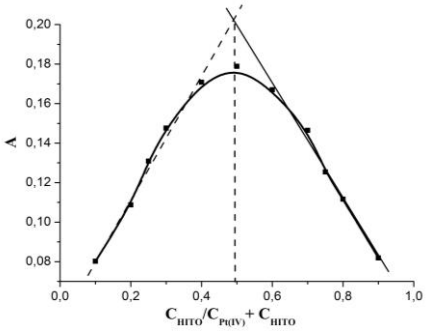


Fig. 2. The method of continuous variations:
$C_{Pt(IV)} + C_{HITO} = 1.0 \cdot 10^{-4}$ mol·L^{-1}, pH = 5.0, λ = 350 nm, μ(NaCl) = 0.1 mol·L^{-1}, l = 1.0 cm

It was found that the magnitude of the analytical signal in determining the Pt(IV) with this reagent depends linearly on the concentration of metal in solution at concentrations within $7.0 \cdot 10^{-6}$-$8.0 \cdot 10^{-6}$ mol·L^{-1}. The molar absorptivity is $5.0 \cdot 10^{3}$ L·mol^{-1}·cm^{-1}, the detection limit of platinum – $2.4 \cdot 10^{-6}$ mol·L^{-1}.

The selectivity of the developed spectrophotometric methods of the determination of Pt(IV) was investigated. The effect of the presence of platinum, heavy, alkaline earth cations and some anions on the ability to determine platinum(IV) with HITO were studied.

TABLE 1

TOLERANCE RATIOS OF INTERFERING IONS DURING THE SPECTROPHOTOMETRIC DETERMINATION OF PLATINUM(IV) IN THE PRESENCE OF HITO
($C_{HITO} = 8.0 \cdot 10^{-5}$ mol·L^{-1}, $C_{Pt(IV)} = 2.0 \cdot 10^{-5}$ mol·L^{-1}, μ(NaCl) = 0.1 mol·L^{-1}, pH = 5.0, l = 1.0 cm)

Extraneous ion	$C(M^{n+}) : C($ Pt(IV)	Extraneous ion	$C(M^{n+}) : C($ Pt(IV)
Ca(II)	200	Al(II)	8
Mg(II)	200	Pd(II)	0.15
Ba(II)	100	Ir(IV)	0.2
Pb(II)	75	Rh(III)	0.1
Cd(II)	75	Ru(IV)	0.25
Ni(II)	150	F^-	200
Co(II)	50	PO_4^{3-}	200
Mn(II)	200	$C_2O_4^{2-}$	200
Zn(II)	100	EDTA	200
Cu(II)	0.1	$Citr^{3-}$	200
Fe(III)	0.1	$Tart^{2-}$	200

On the formation of compound Pt(IV) with HITO do not interfere large excesses of Ca(II), Mg(II), Ba(II), Pb(II), Cd(II), Ni(II), Co(II), Mn(II), Zn(II) ions. However, the elaborated method possesses low selectivity towards Ir(IV), Ru(IV), Rh(III), Pd(II), Al(III), Fe(III) and Cu(II) ions (Table I).

Among the anions the influence of possible interfering ions and possible masking agents has been studied. Anions, which were investigated (Table I), do not interfere in large numbers, this suggests that they can be used to eliminate the interfering influence of foreign metal ions.

The accuracy of platinum(IV) spectrophotometric determination using HITO has been tested on model solutions. This method posses good reproducibility and the accuracy of the determination.

Conclusion

At first the existence of a new complex of platinum(IV) with 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one has been established. The optimum conditions for the formation of the complex Pt(IV)-HITO were found. The selectivity of the method for platinum(IV) spectrophotometric determination by means of HITO towards extraneous metals ions, including platinoids, has been investigated. This method is characterized by a wide range linearity, high enough sensitivity, reproducibility and expressivity. It allows us to use this spectrophotometric method for serial analytical determinations.

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