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SPECROPHOTOMETRIC INVESTIGATION OF PALLADIUM(II) IONS INTERACTION WITH 5-HYDROXYIMINO-4-IMINO-1,3-THIAZOLIDIN-2-ONE

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Abstract. The interaction of Pd(II) ions with 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one (HITO) in water solution has been investigated. The optimum conditions of the complexation for the complex of palladium(II) with 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one were found. The composition of the complex was determined. The method of spectrophotometric determination of palladium(II) ions with HITO was developed.

Keywords: palladium(II), 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one, azolidons, spectrophotometry, complex.

1. Introduction

The noble metals and compounds based on them always attracted the attention of scientists due to the unique physical and chemical properties and their wide application in various areas as catalysts, functional coatings, dental appliances *etc*.

Accumulation of platinum group elements in the environment has been increased as years pass. The concentration of these metals has increased significantly during the last decades in various environmental matrices: like airborne particulate matter, soil, roadside dust and vegetation, river, coastal and oceanic environment. Generally, platinum group elements are referred to behave in an inert manner and to be immobile. However, there is an evidence of spread and bioaccumulation of these elements in the environment. This necessitates the development of highly sensitive, selective, simultaneously expressive and cheap methods of their determination. The spectrophotometric method is one of the perspective methods for determination of the platinum metals [1-6].

Recently, the interest and the need for new highly sensitive reagents have sharply increased; newer elements and their compounds are beginning to be used in engineering and industry. This primarily applies to platinum group of metals, the quantitative determination of which usually requires considerable effort on all stages of analysis.

The purpose of our work is to find new selective reagents for the development of sensitive and express methods for determination of platinoids, such as palladium, in complex objects.

Azolidons as a new class of organic compounds were discovered in the mid of XX century [7]. These reagents are widely used in medicine, due to their wide range of biological activity [8-11]. Azolidons being promising reagents in analytical chemistry can be used to determine the platinoids. Rodanin, which belongs to the azolidons class and its derivatives are used for determination of noble metals [12].

2. Experimental

2.1. Materials

The stock solution of Pd(II) was prepared by dissolving metallic palladium (99.999 %) in the mixture of concentrated HNO_3 and HCl (1:3). The standard working Pd(II) solutions were prepared by dissolving an aliquot of palladium(II) 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 ethanol of 96 % v/v.

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

Universal buffer solutions were made by mixing solutions of phosphoric, boric and acetic acids and were used to maintain pH in constant acidity experiments (2.0–12.0 pH).

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

2.2. Equipment

Absorption spectra were recorded using 108 UV/ULAB spectrophotometer and 1.0 cm quartz cell. Absorption spectra were obtained in the wavelength range of 240–600 nm with the 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 combined glass electrode, Gomelsky Plant of Measuring Devices, Belarus.

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

2.3. Protolytic Equilibria Experiments

Volumes of $8.0 \cdot 10^{-3}$ mol·l^{-1} HITO, universal buffer (1.5 mol·l^{-1}), 2.0 mol·l^{-1} NaCl solutions were poured into 25.0 ml flask and the distilled water was added to a total volume of ~15–20 ml. Then pH was adjusted by means of 10.0 mol·l^{-1} NaOH (pH = 2.0–12.0). After that, distilled water was added to complete the volume and its absorption spectrum was measured. For pH = 1.0 the solution was prepared as follows: volumes of $8.0 \cdot 10^{-3}$ mol·l^{-1} HITO, 2.0 mol·l^{-1} NaCl solutions were poured into 25.0 ml flask and the distilled water was added to a total volume of ~15–20 ml; then pH was adjusted by means of 6.0 mol·l^{-1} HCl; after that, distilled water was added to complete the volume and its absorption spectrum was measured.

2.4. Investigation of the Interaction of Pd(II) with HITO in Water Solution

Volumes of $8.0 \cdot 10^{-3}$ mol·l^{-1} HITO, 2.0 mol·l^{-1} NaCl, $4.5 \cdot 10^{-4}$ mol·l^{-1} Pd(II) were put into 25.0 ml flasks and the distilled water was added to a total volume of ~15–20 ml. Then pH was adjusted by means of NaOH and HCl diluted solutions. After that, distilled water was added to complete the volume and its absorption spectrum was measured.

2.5. Effect of Heating time on the Maximum Yield of Complex Compound of Pd(II) with 5-Hydroxyimino-4-imino-1,3-thiazolidin-2-one

Volumes of $8.0 \cdot 10^{-3}$ mol·l^{-1} HITO, $4.5 \cdot 10^{-4}$ mol·l^{-1} Pd(II), 2.0 mol·l^{-1} NaCl, 4.0 mol·l^{-1} CH$_3$COONa were put into 25.0 ml flasks and the distilled water was added to a total volume of ~15–

20 ml. Then the pH was adjusted by means of CH$_3$COOH. After that, distilled water was added to complete the volume, and the solutions were heated on a boiling water bath (~ 371 K) for 2–60 min, cooled to 293–295 K and the absorbance of the solution was measured relative to a blank one at 350 nm. The blank solution contained all the components of the sample excepting Pd(II) and was thermally treated.

3. Results and Discussion

3.1. Protolytic Equilibria of HITO in Water Medium

At first the reagent, which belongs to the class of azolidons – 5-hydroxyimino-4-imino-1,3-thiazolidin-2-one was synthesized at the Department of Organic Chemistry, Ivan Franko National University of Lviv. The structural formula of HITO is:
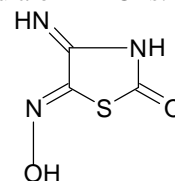
It is a crystalline powder sand-colored, poorly soluble in water, but soluble in ethanol, methanol, toluene, chloroform, carbon tetrachloride, dimethylformamide and dimethylsulfoxide.

As shown in the results of the experiment, the maximum absorption of the reagent depends on pH and accounts for a range of values of λ within 264–330 nm (Fig. 1). Baer law is performed at 264 nm (pH = 5.0) over the wide concentration range (Fig. 2), and the average effective value of molar absorption coefficient at $\lambda = 264$ nm – $1.6 \cdot 10^4$ l·mol^{-1}·cm^{-1}. HITO is unstable with time within pH = 6.0–12.0 (Fig. 3).

3.2. Investigation of the Interaction of Pd(II) with HITO in Water Solution

The ion of Pd(II) forms a complex compound with HITO sand color. Fig. 4 represents the absorbance spectra of the dye solutions and Pd(II)-HITO complex compound. As seen from the spectra of the absorption the maximum absorption of the dye is observed at 264 nm. The maximum absorption of the complex is in the same area wavelengths as the reagent, but it is characterized by the leverage within the wavelength range of 275–480 nm. According to Fig. 4 the investigation of the interaction between Pd(II) ions and HITO was conducted at $\lambda = 350$ nm, where there is virtually no absorption of the reagent and the maximum increases in the value of the shoulder complex.
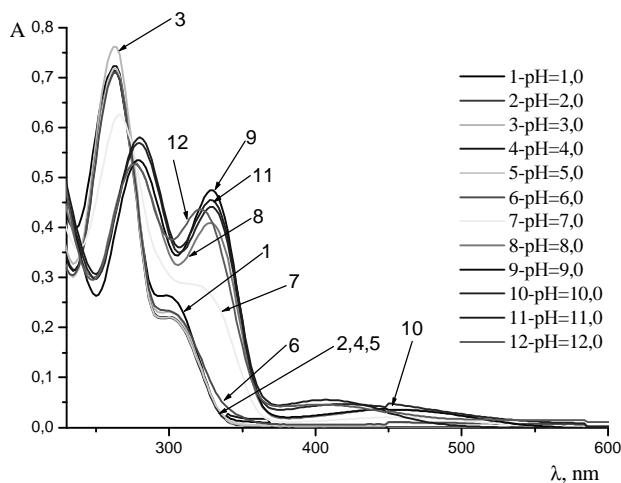
Fig. 1. Absorbance spectra of HITO at different pH; μ(NaCl) = 0.1; pH = 1.0–12.0; C_{HITO} = 4.0·10^{-5} mol·l^{-1}; C_{UBS} = 0.12 mol·l^{-1}

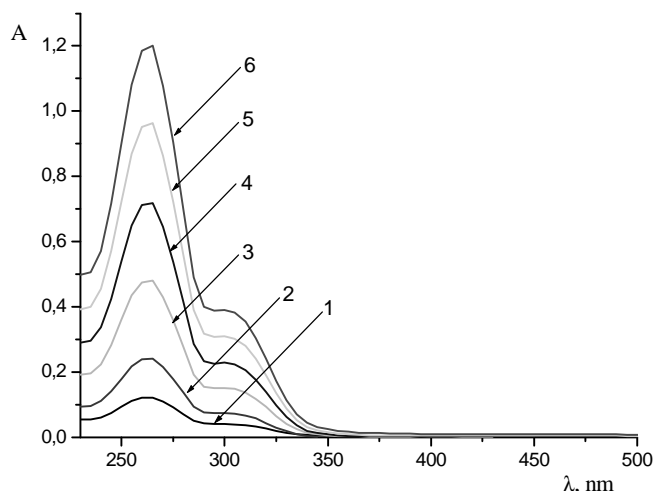**Fig. 2.** Absorbance spectra of HITO solutions of different molar concentration: 1.0·10^{-5} (1); 2.0·10^{-5} (2); 4.0·10^{-5} (3); 6.0·10^{-5} (4); 8.0·10^{-5} (5); 1.0·10^{-4} (6); (μ(NaCl) = 0.1; pH = 5.0
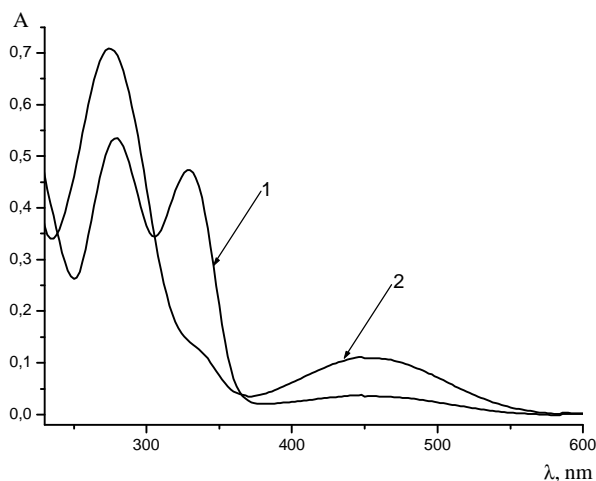
Fig. 3. Absorbance spectra of HITO at pH = 9.0; μ(NaCl) = 0.1; C_{HITO} = 4.0·10^{-5} mol·l^{-1}; C_{UBS} = 0.12 mol·l^{-1} immediately after preparation (1) and 30 min after preparation (2)
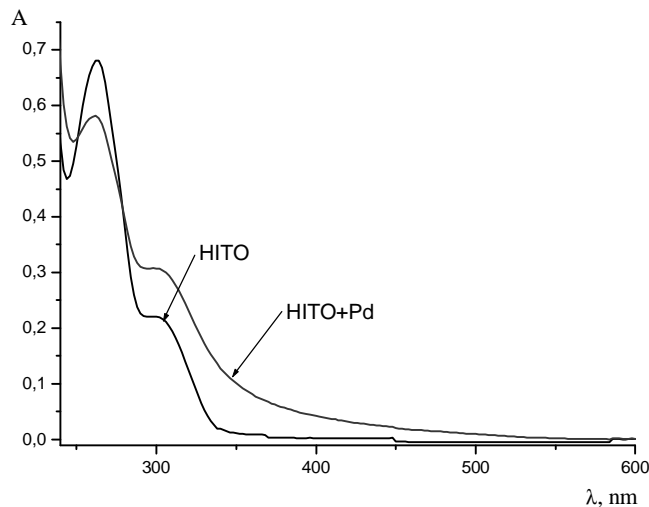

Fig. 4. Absorbance spectra of HITO and complex Pd(II) with the reagent; μ(NaCl) = 0.1; pH = 5.0; $C_{Pd(II)}$ = 2.0·10^{-5} mol·l^{-1}; C_{HITO} = 4.0·10^{-5} mol·l^{-1}

In case of establishing the optimal conditions of complexation of the system it is important to examine the influence of acidity. Fig. 5 shows the results of pH influence on the maximum yield of Pd(II)-HITO colored complex compound against the background of sodium chloride. The Pd(II) with HITO complex formed a fairly wide range of pH (Fig. 5).

The maximum yield of Pd(II)-HITO compound was achieved in the range of pH = 8.0–9.3 against the background of sodium chloride. But since its reagent is unstable in this pH region, so all subsequent studies we conducted at pH = 5.0.

To establish the optimal conditions for complexation, we examined the effect of heating time and standing on the yield of the colored complex compound. The process of complexation without heating passes slower than when heated, and the maximum yield of colored compounds is achieved after 5–10 min boiling on the water bath (Fig. 6). The rapid formation of the complex Pd(II) with HITO at heating is to reduce the kinetic inertness of the original complex $[PdCl_4]^{2-}$.

The maximum optical density without heating is achieved after 2.0–2.5 h. Thus, the following studies were carried out at ten minutes of boiling solutions on the water bath. Obviously prolonged heating leads to the destruction of the complex, possibly due to the oxidation.
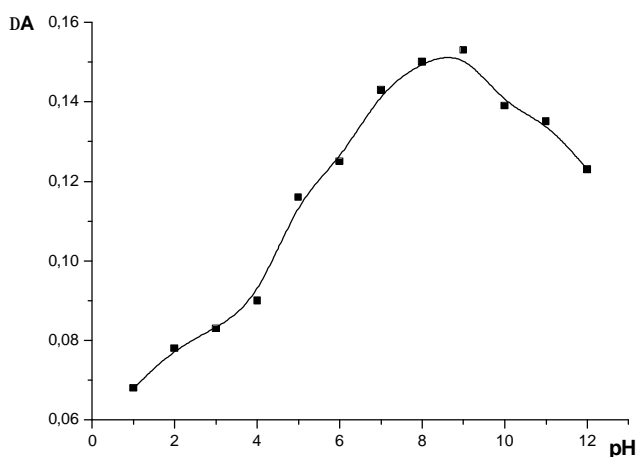
Fig. 5. Effect of acidity on the maximum yield of Pd(II) with
HITO colored complex;
$C_{Pd(II)} = 2.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{HITO} = 4.0 \cdot 10^{-5}$ mol·l⁻¹;
$\mu(NaCl) = 0.1$; $l = 350$ nm

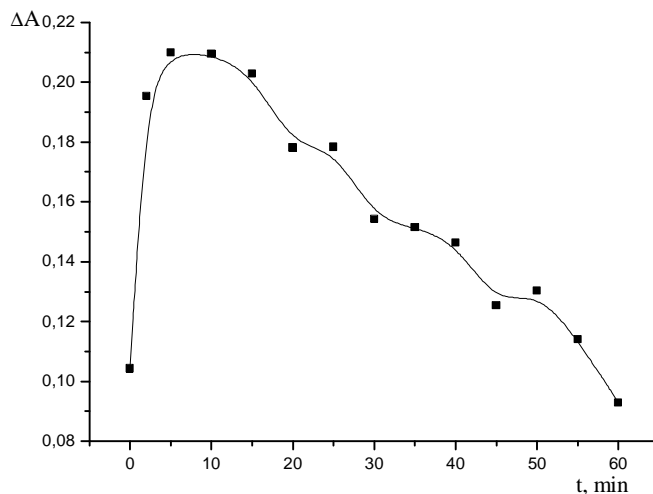**Fig. 6.** Effect of heating time on the maximum yield of the
palladium(II) with HITO colored complex;
$C_{HITO} = 4.0 \cdot 10^{-5}$ mol·l⁻¹; $C_{Pd(II)} = 2.0 \cdot 10^{-5}$ mol·l⁻¹; pH = 5.0;
$\mu(NaCl) = 0.1$; $l = 350$ nm
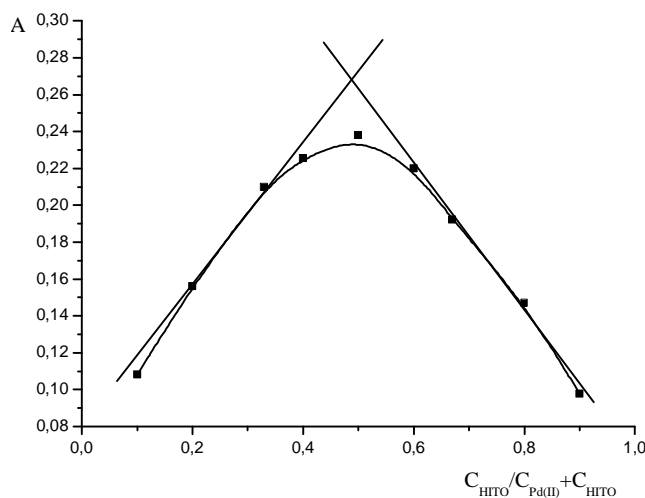
Fig. 7. The method of continuous variations:
$C_{Pd(II)} + C_{HITO} = 1.0 \cdot 10^{-4}$ mol·l⁻¹; pH = 5.0; $l = 350$ nm;
$\mu(NaCl) = 0.1$
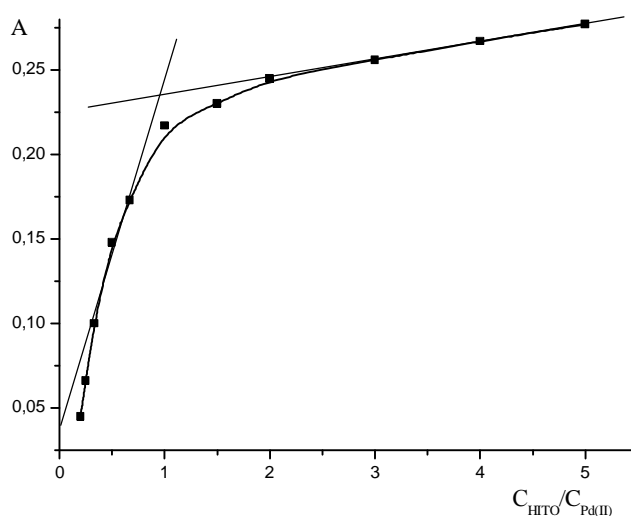
Fig. 8. The mole-ratio method: $C_{Pd(II)} = 5.0 \cdot 10^{-5}$ mol·l⁻¹;
$C_{HITO} = 1.0 \cdot 10^{-5} - 2.5 \cdot 10^{-4}$ mol·l⁻¹; $\mu(NaCl) = 0.1$; pH = 5.0;
$l = 350$ nm

Table

The metrological characteristics of spectrophotometric determination of the Pd(II) with HITO
($n = 5$; $P = 0.95$; $l = 350$ nm; $\mu(NaCl) = 0.1$; pH = 5.0; $C_{HITO} = 8.0 \cdot 10^{-5}$ mol·l⁻¹)

Characteristic	Value
Calibration equation	$\Delta A_{350} = a + b \cdot C_{Pd(II)}$, ($C_{Pd(II)}$, mol·l⁻¹)
Parameter a	$1.23 \cdot 10^{-2}$
Confidence interval Δa	$0.71 \cdot 10^{-2}$
Parameter b	$6.76 \cdot 10^{3}$
Confidence interval Δb	$2.16 \cdot 10^{2}$
Dispersion S_0^2	$1.15 \cdot 10^{-2}$
Correlation coefficient R	0.997
Limit of detection ($C_{Pd(II)}$, mol·l⁻¹)	$2.1 \cdot 10^{-6}$
Linearity range ($C_{Pd(II)}$, mol·l⁻¹)	$6.0 \cdot 10^{-6}$ to $6.0 \cdot 10^{-5}$

Using two independent methods – the mole-ratio method and the method of continuous variations, the correlation between the components in the system was established. The results are illustrated in Figs. 7 and 8. The calculations indicate the formation of the complex with a ratio of components Pd(II) : HITO = 1:1. The value of effective molar absorption coefficients is $5.9 \cdot 10^3$ l·mol^{-1}·cm^{-1}.

The metrological characteristics of spectrophotometric determination of Pd(II) with HITO are shown in Table. We found that the magnitude of the analytical signal in determining Pd(II) with this reagent depends linearly on the concentration of metal in the solution at concentrations within $6.0 \cdot 10^{-6}$–$6.0 \cdot 10^{-5}$ mol·l^{-1}.

Method for determination of palladium(II) with HITO: we selected the aliquot of Pd(II) test solution within $6.0 \cdot 10^{-6}$–$6.0 \cdot 10^{-5}$ mol·l^{-1} final volume, transferred to a flask 25.0 ml, added 0.25 ml of $8.0 \cdot 10^{-3}$ mol·l^{-1} HITO ethanolic solution , 2.0 ml of 4.0 mol·l^{-1} sodium acetate and 1.25 ml of 2.0 mol·l^{-1} sodium chloride. Then pH was adjusted by means (pH = 5.0) of CH$_3$COOH. After that, distilled water was added to complete the volume, and the solutions were heated on the boiling water bath (~ 371 K) for 10 min, cooled to 293–295 K and the absorbance of the solution was measured relative to the blank solution at 350 nm. The blank solution contained all the components of the sample excepting Pd(II) and was thermally treated.

4. Conclusions

Therefore, we investigated the spectrophotometric properties of HITO and found that this reagent forms a complex compound with Pd(II). Photometric methods found stoichiometric ratio of components: Pd(II) : HITO = 1:1. We have developed a method of spectrophotometric determination of palladium(II) ions with HITO characterized by a wide margin linearity, rather high sensitivity, reproducibility and expressivity and it allows to develop a spectrophotometric method for serial analytical determinations.

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СПЕКТРОФОТОМЕТРИЧНЕ ДОСЛІДЖЕННЯ ВЗАЄМОДІЇ ЙОНІВ ПАЛАДІЮ(II) З 5-ГІДРОКСИІМІНО-4-ІМІНО-1,3-ТІАЗОЛІДИН-2-ОНОМ

Анотація. Досліджено взаємодію йонів Pd(II) з 5-гідроксиіміно-4-іміно-1,3-тіазолідин-2-оном (ГІТО) у водному середовищі. Знайдено оптимальні умови комплексоутворення йонів паладію(II) з 5-гідроксиіміно-4-іміно-1,3-тіазолідин-2-оном. Визначено склад комплексу. Розроблено спектрофотометричний метод визначення йонів паладію(II) з ГІТО.

Ключові слова: паладій(II), 5-гідроксиіміно-4-іміно-1,3-тіазолідин-2-он, азолідони, спектрофотометрія, комплекс.