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HPLC AND SPECTROPHOTOMETRIC INVESTIGATION OF THE FORMATION OF Sn(II)-p-AMINOHIPPURIC ACID COMPLEX IN PERCHLORATE MEDIUM

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Abstract

The complex equilibrium in tin(II)-p-aminohippuric acid (PAH) solutions in perchlorate medium was investigated. HPLC, spectrophotometric and pH-metric methods were used. The experimental results have shown that week mononuclear complex of the general composition PAH/Sn(II)=1/1 was formed.

Introduction

o-Iodohippuric acid labelled with isotope ^{131}I (OIH) has been used in clinical evaluation of renal tubular function. The greatest disadvantage of OIH is relatively high-absorbed radiation dose of ^{131}I to the patient, even at low diagnostic doses. In order to replace it, numerous chelate reagents labelled with technetium-99m (^{99m}Tc), were developed, but none of these radiopharmaceuticals could completely replace OIH. Therefore, we attempted to label p-aminohippuric acid ($H_2NC_6H_4CONHCH_2COOH$, PAH), "gold standard" for renal tubular function diagnostic, with ^{99m}Tc using Sn(II) chloride method [1]. In this process, Sn(II)-ion reduces technetium from non-reactive, +7 (in $^{99m}TcO_4^-$) in lower +3, +4 or +5 oxidation states. However, the possibility of interaction between some ligand and Sn(II)-ion existed too [2-4]. In this paper the possibility for formation of Sn(II)-PAH complexes were studied.

Experimental

All chemicals used in our experiments were of analytical purity grade (p.a. Merck). The stock solution of PAH and was prepared by dissolving of the measured amount of pure acid in doubly distilled water. The stock solution of $SnCl_2x2H_2O$ was prepared by dissolving of the measured amount of the pure salt in concentrated HCl and then diluting it with doubly distilled water until the definite volume.

HPLC analysis was performed by isocratic HPLC. All measurements were made on Liquid Chromatograph, Hewllet Packard 1050, S/N with UV and Raytest gamma flow detector RP and C18 column (250x4.6 mm). The different methanol/water mixtures prepared from HPLC grade water, were used like mobile phases. UV spectra of 10 μl PAH ($1x10^{-4}$ mol dm^{-3}) as well as PAH-Sn(II) mixture with different molar rations: 1/1; 1/10, and 1/25, pH≅3, were obtained at wavelength of 220 nm and 295 K.

All spectrophotometric measurements were performed using Uvicon 810/820 (Kontron Instruments, Austria) spectrophotometer. The absorbency of solutions was measured in wavelength range 190 nm to 350 nm, in 10-mm quartz cells. UV spectra of PAH ($4x10^{-6}$ mol dm^{-3}-$2x10^{-4}$ mol dm^{-3}, pH≅3) and Sn(II) ($4x10^{-6}$ mol dm^{-3}) in 0.1 mol dm^{-3} $NaClO_4$ ionic medium, were recorded using 0.1 mol dm^{-3} $NaClO_4$ in doubly

distilled water as a reagent blank. UV spectra of the mixtures of PAH and Sn(II) in 0.1 mol dm^{-3} $NaClO_4$ ionic medium, in concentration rations: [Sn]/[PAH]=1/1; 1/2; 1/5; 1/10; pH≅3, were recorded too, using corresponding Sn-free solution as a reagent blank.

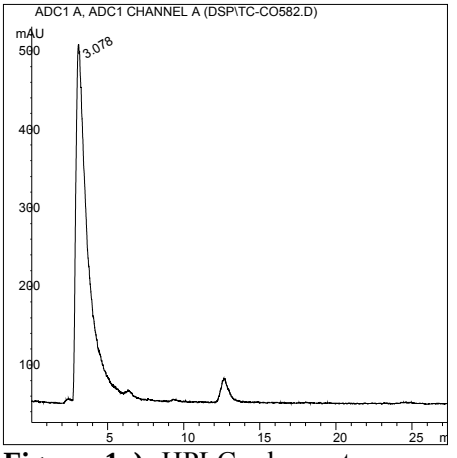

Figure 1a) HPLC chromatograms of PAH obtained with 10 %CH_3OH:90 % H_2O as mobile phase (0.7 ml/min)

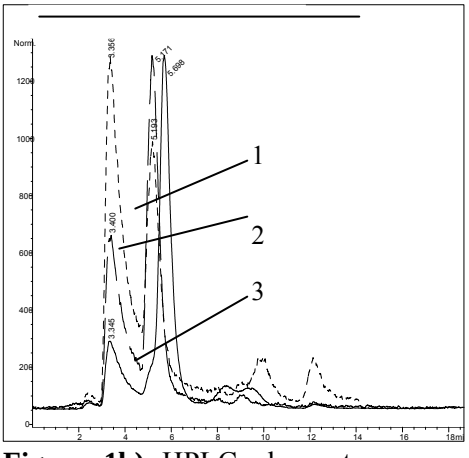

Figure 1b) HPLC chromatograms of PAH/Sn(II) with different molar rations: 1/1 (1); 1/10 (2), and 1/25 (3)

Results and Discussion

V spectra of PAH obtained with at 220 nm point to a peak with retention time 3.078 min and some impurity at ~12.7 min. The HPLC chromatograms for PAH/Sn(II) solutions, exhibit two well separated peaks for each chromatogram: peak at 3.345-3.400 min for PAH and peak at 5.171-5.698 min for PAH-Sn(II) complexes. The position and intensity of these peaks vary upon changing the concentration ratio of PAH and Sn(II). The best results were for concentration ratio PAH/Sn(II)=1/1 where peak for Sn(II)-PAH complex was the highest.

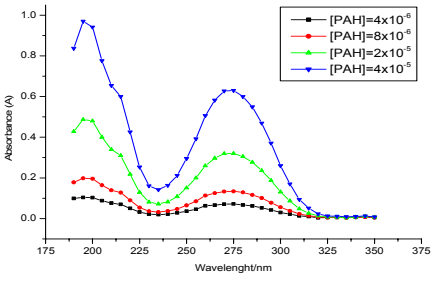

Figure 2. UV spectra of PAH ($4x10^{-6}$ mol dm^{-3}-$2x10^{-4}$ mol dm^{-3}) in 0.1 mol dm^{-3} $NaClO_4$, pH≅3

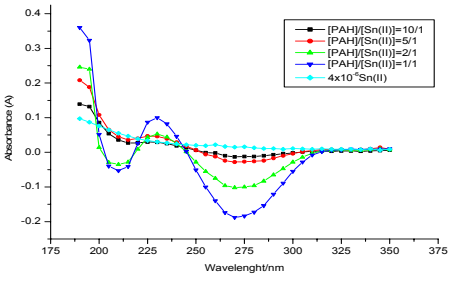

Figure 3. UV spectra of Sn(II)-PAH solutions in 0.1 mol dm^{-3} $NaClO_4$: [PAH]/[Sn]=10/1; 5/1; 2/1; 1/1

Spectrophotometric measurements were performed with the aim to examine the possibility of complex formation in PAH-Sn(II) solutions and the nature of complexes. UV spectra made on the series of PAH with different concentration, in 0.1 mol dm^{-3} $NaClO_4^-$ ionic medium, have shown two peaks: at 200 nm and 275 nm. UV spectra of Sn(II)-PAH-solutions showed the disappearance of a peak at 275 nm and a new peak at 228 nm. The appearance of a new peak at 228 nm confirmed the complexion between Sn(II)-ion and PAH in investigated conditions. The negative absorbance of the spectra at wavelength 275 nm were consequence of the use of PAH solutions with the same concentration as a reagent blank. The highest absorbance possessed the spectrum of PAH/Sn(II) solution with concentration ratio 1/1.

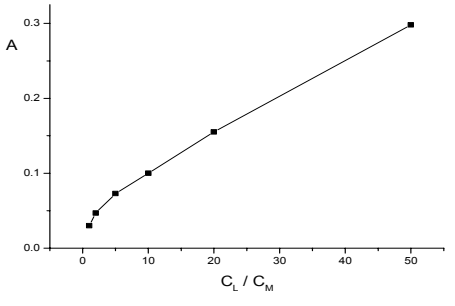

Figure 4. Dependence of absorbency on molar ratio metal and ligand

The UV spectra obtained with different concentrations of PAH and constant concentration of Sn (II) made possible the application of the molar-ratio method. (Fig 4.). From the form of the curve it could be concluded that one weak complex with high degree of dissociation was obtained

The application of Bent-French method at this low stabile complex enable the calculation not only the stoichiometric coefficients *p* and q, but also the stability constant $\beta_{p,q,r}$ of complexes, forming in reaction:

$$pSn^{2+} + qH^{+} + r\,PAH^{-} \Leftrightarrow \left[Sn_pH_q\left(PAH\right)_r\right]$$

In the case $q=0$, pure [Sn-PAH] complexes was formed, while for $q<0$ mixed complex $[Sn_p(OH)_q(PAH)_r]$.If log A is presented as a function of log C_M, the number of metal or ligand ion, as well as stability constant could be obtained. The slope of the curve on the graph have shown that the mononuclear complex of the general composition PAH/Sn(II)=1/1 was formed.

Acknowledgment

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