

DETERMINATION OF PALLADIUM /II/ IN ACETATE BUFFERS
WITH E D T A AND THIOGLYCOLLIC ACID

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Pd /II/ forms with glacial acetic acid a trimer, insoluble in water, acetic acid, aqueous solutions of CH_3COONa , NaCl and NaNO_2 , but soluble in some organic solvents /benzene, chloroform, acetonitrile/ /1/. However, if to the solution of $\text{Pd}/\text{ClO}_4/2$ or $\text{Pd}/\text{NO}_3/2$ containing HClO_4 in excess, a large amount of acetate buffer is added, so that the ratio Pd : acetate is very large /e.g. 1:80 to 1:2.000/, precipitation can not be observed. This points to the formation of a water-soluble complex, the anionic character of which was proved by electrophoresis / a movement of 35 mm was observed after 2 hours at a potential gradient of 10 V/cm/. Spectrophotometric measurements showed increase in absorbance when to the Pd-perchlorate solution /pH 0.5/ acetate buffer /pH 4/ was added. Polarographically obtained curves in 1 M acetate buffer had the half-wave potential of 0.22 V/SCE. The polarographic wave is diffusion controlled, but poorly defined, because it continues after the mercury dissolution wave and measurements must be made from the galvanometer zero-line.

The most convincing results to prove the existence of the mentioned Pd-complex were obtained potentiometrically, using a bright Pd foil electrode /20 cm^2 / for Pd activity measurements. Acetate buffers of 4.10 ± 0.05 with an ionic strength of 1 /by addition of

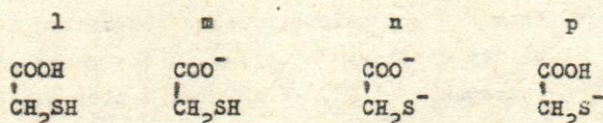
NaClO_4 were used, and the ratio Pd : acetate was varied. Solutions with a ratio lower than 1:40 showed reddish-brown colour, while above 1:80 were yellow. Relatively reproducible potentials were obtained in solutions without stirring and deaeration, at 20°C /after 15 minutes, the potential changed for less than ± 5 mV in the following 3 hours/. By application of the Leden method /2/ for determining the average ligand number linked to one Pd-ion, 4.4 was obtained. Having in mind uncertainties and difficulties in potential measurements, this value points to the formula $[\text{Pd}/\text{CH}_3\text{COO}/_4]^{2-}$, for solutions with Pd : acetate ratio above 1:80. The proposed formula is in accordance with other palladium complexes obtained with a large excess of ligand, having the coordination number 4. The stability constant calculated for the complex of the proposed formula is $1.2 \cdot 10^{12}$, indicating an unusual stability of the complex as compared to other metal-acetate complexes, and almost reaching the value of $[\text{PdCl}_4]^{2-}$ complex $K_s = 1.6 \cdot 10^{13}$ /. The high stability of the Pd-acetate complex is also confirmed by the observation, that from the acidified $\text{Pd}/\text{ClO}_4/2$ solutions, after addition of NaOH, the hydroxide precipitates at a pH as low as 1; on the contrary, after the addition of acetate buffer, the solution remains clear for weeks. Only after prolonged heating a dark precipitate can be observed in the solution.

In the complex mentioned Pd /II/ was determined spectrophotometrically or potentiometrically with EDTA; in the former case the titration was carried out at the wavelength of 337 nm with 0.01 M EDTA. By titrating about 3 mg of Pd, an average deviation of 0.3% was found. In the latter case, the new method developed for determining Pd by potentiometric titration is based on the use of mercury electrode in an acetate buffer, containing 10^{-3} M Hg-EDTA as well. The stability constant of Pd-EDTA complex in 0.5 M acetate buffer was determined and amounted to 10^{18} , in agreement with the spectrophotometrically obtained value /3/. The difference between the stability constant of $\text{Pd}/\text{ac}/_4$ and $\text{Pd}/\text{EDTA}/$ allowed successful potentiometric titrations of Pd /II/ at the Hg-electrode in acetate buffers.

Amounts from 10 to 50 mg Pd are determined and $99.5 \pm 0.3\%$ of the metal was found.

A controversy exists in the literature about the composition of the Pd-complex with thioglycollic acid. Widtman /4/ established a 2:3 metal to ligand ratio. We could not confirm this, while Pilipenko and Moslei /5/, in a study published after our report /6/, give the stoichiometric ratio as 1:2, which agrees with our findings. We isolated after that the palladium-thioglycolate complex /7/, made its elemental analysis, recorded its IR spectrum and compared it with those of its components, determined the stability constants of the complexes formed at various pH and from the electrochemical behavior of the complex we worked out procedures for the determination of palladium by potentiometric and amperometric titration.

The determination of stability constants of Pd-thioglycolate complexes was performed in the pH range 0 - 10. Assuming that thioglycollic acid in aqueous solution exists in the forms:



and the corresponding dissociation constants are:

$$K_1 = \frac{a_{\text{H}^+} \cdot m}{1} = \frac{n \cdot a_{\text{H}^+}}{p} \quad /1/ \quad \text{and}$$

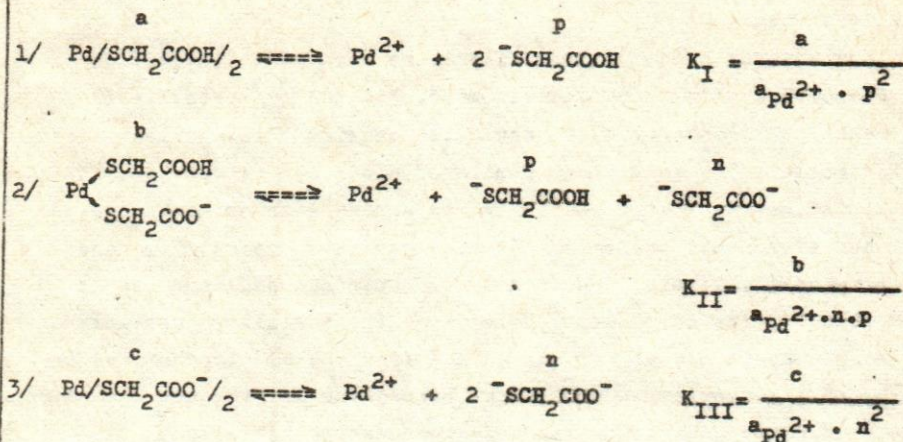
$$K_2 = \frac{n \cdot a_{\text{H}^+}}{m} = \frac{p \cdot a_{\text{H}^+}}{1} \quad /2/$$

the total concentration of thioglycollic acid is given by:

$$1 + m + n + p = n / \frac{a_{\text{H}^+}^2}{K_1 \cdot K_2} + \frac{a_{\text{H}^+}}{K_2} + 1 + \frac{a_{\text{H}^+}}{K_1} /$$

By substitution of K_1 and K_2 , given by Kolthoff and al /8/ and the activities of H^+ , the values for 1, m, n and p can be calculated.

Depending on the pH, the Pd-complexes can exist in following forms:



In the pH range of 0 - 2 the complex a exists in solution; between pH 2 and 5 predominantly b with little amounts of a and c are present; above pH 5 the complex c exists practically alone.

From l,m,n,p and from the potentiometrically determined activities of Pd^{2+} the stability constants obtained in the range pH 0 - 10, at 25°C, in the atmosphere of N_2 , at the ionic strength of 1, are as follows:

pH 0 - 2	$K_{\text{I}} = /1.96 \pm 0.93/.10^{44}$
pH 2 - 5	$K_{\text{II}} = /3.04 \pm 1.72/.10^{44}$
pH 5 - 10	$K_{\text{III}} = /1.57 \pm 0.29/.10^{42}$

In all measurements 10^{-4} M PdCl_2 and 10^{-2} M thioglycollic acid were used.

A procedure was developed for inverse determination of 1 - 20 mg of Pd by titrating thioglycollic acid with Pd /II/ potentiometrically on Pt electrode. The potential jump at the equivalence point is very pronounced; the mean of 10 determination was 100.1%, the

average deviation \pm 0.5%.

Using Hg electrode, potentiometric titrations of thioglycollic acid with $\text{Pd}/\text{NO}_3/2$ or $\text{Pd}/\text{ClO}_4/2$ were also performed. In the vicinity of the equivalence point a very pronounced potential jump occurs /about 110 mV/ 0.03 ml of 0.02 M Pd^{2+} /, which allows high precision even in diluted $/2 \cdot 10^{-4} \text{ M/}$ solutions. Quantities of 0.5 to 5 mg-Pd with $99.7 \pm 0.9\%$ recovery of the metal were performed.

By inverse titration, Pd was also determined with thioglycollic acid on anodically polarized rotating Pt-electrode. Titrations were done at 0.9 V/SCE, since establishment of constant diffusion current takes a long time at higher potentials. The errors were lower than 1%. By the dead-stop method the inverse determinations of Pd were carried out; amounts of 0.2 to 5 mg of metal with an error below $\pm 1\%$ were determined.

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