

p-nitroso arylamines as reagents for the spectrophotometric determination of palladium

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Received on June 19, 1978; Revised on September 1, 1978

Abstract

The effect of substitution in *p*-nitroso arylamines has been studied. Two reagents, *viz.*, *p*-nitrosodiphenylamine sulphonic acid and *p*-nitrosophenyl α -naphthylamine have been synthesised and investigated as possible reagents for the determination of palladium. The first compound gives a water soluble complex which can be used directly for the quantitative estimation of palladium. The latter reagent *p*-nitrosophenyl α -naphthylamine shows greater selectivity as compared to *p*-nitrosodimethylaniline.

Key words: *p*-nitroso diphenylamine sulphonic acid, *p*-nitrosophenyl α -naphthylamine, palladium determination.

1. Introduction

Organic compounds containing *p*-nitrosophenylamino group are known to form highly coloured complexes with palladium and have been used for its colourimetric estimation^{1,2}. Of these, *p*-nitrosodiphenylamine and *p*-nitrosodimethylaniline have been extensively used. *p*-nitrosodiphenylamine is more suited for colourimetric work as it permits higher limiting concentration of the presence of salts and interfering ions³. The diphenyl derivatives, although very sensitive, have an upper limit to their application for the palladium complex and require very careful and rigorous control of the conditions for colour development. Being colloidal in nature, the palladium complex starts settling down soon after the complex is formed. The complex can be extracted by organic solvents and the estimation of the metal has been carried out by measurement of the colour of the organic phase⁵. *p*-nitrosodimethylaniline can be used over a wide range of palladium concentrations, but it shows less tolerance for foreign ions and the absorption due to the reagent is also appreciable.

In the present work, substitution in *p*-nitrosophenylamine has been carried out with a view to improve the properties of the reagent. It is well known that the introduction of a sulphonic acid group in a reagent makes it water soluble. Two new reagents, which are essentially *p*-nitrosoarylamines, have been synthesised and studied for their

The following solutions were prepared:

(a) Palladium solution

0.25 gm of palladium metal was dissolved in aqua-regia. It was subsequently treated three times with hydrochloric acid to remove nitric acid. The solution thus obtained was made to 250 ml. The palladium content of the solution was checked by the dimethyl glyoxime method. The metal concentration was found to be 1 mgm/ml. Subsequent dilutions were made from this solution.

(b) p-nitrosodiphenylamine sulphonic acid solution

100 mgm of the reagent was dissolved in water and the volume made to 100 ml.

(c) p-nitrosophenyl α -naphthylamine and p-nitrosodiphenylamine solution

10 mgm of each of the reagent was dissolved in 50 ml of alcohol and the volume made to 100 ml with water.

(d) Sodium acetate—hydrochloric acid buffer (pH 4.9)

80 ml of 1M HCl was mixed with 200 ml of 1M sodium acetate and the volume was made to 1 litre.

(e) 80 ml of 1M nitric acid was mixed with 200 ml of 1M sodium acetate and the volume was made to 1 litre.

Absorption spectra of palladium-p-nitrosodiphenylamine sulphonate

1 ml of palladium solution containing 100 gm of palladium was taken in a beaker, 2 ml of reagent solution added and the volume was made to 90 ml and pH adjusted to 3.0.

Similarly, the reagent solution was taken as blank and the pH adjusted. The volume of the two solutions was made to 100 ml and the absorption was measured from 400 $m\mu$ to 700 $m\mu$. The absorption spectra (a) of palladium complex against the reagent as blank, (b) of the reagent against water as blank, (c) of the palladium complex against water as blank are shown in Fig. 1. The palladium complex shows a maximum at 530 $m\mu$, against the reagent whereas the reagent shows maximum absorption at 435 $m\mu$. The reagent shows negligible absorption at 530 $m\mu$. The palladium complex thus formed is highly soluble in water. The colour of the complex reaches its maximum almost immediately and remains stable for one hour after which it starts fading gradually.

Effect of pH on the optical density of the complex

In a set of experiments known quantities of palladium solutions were taken, the reagent was added and the pH value was also adjusted in steps of 0.5 units,

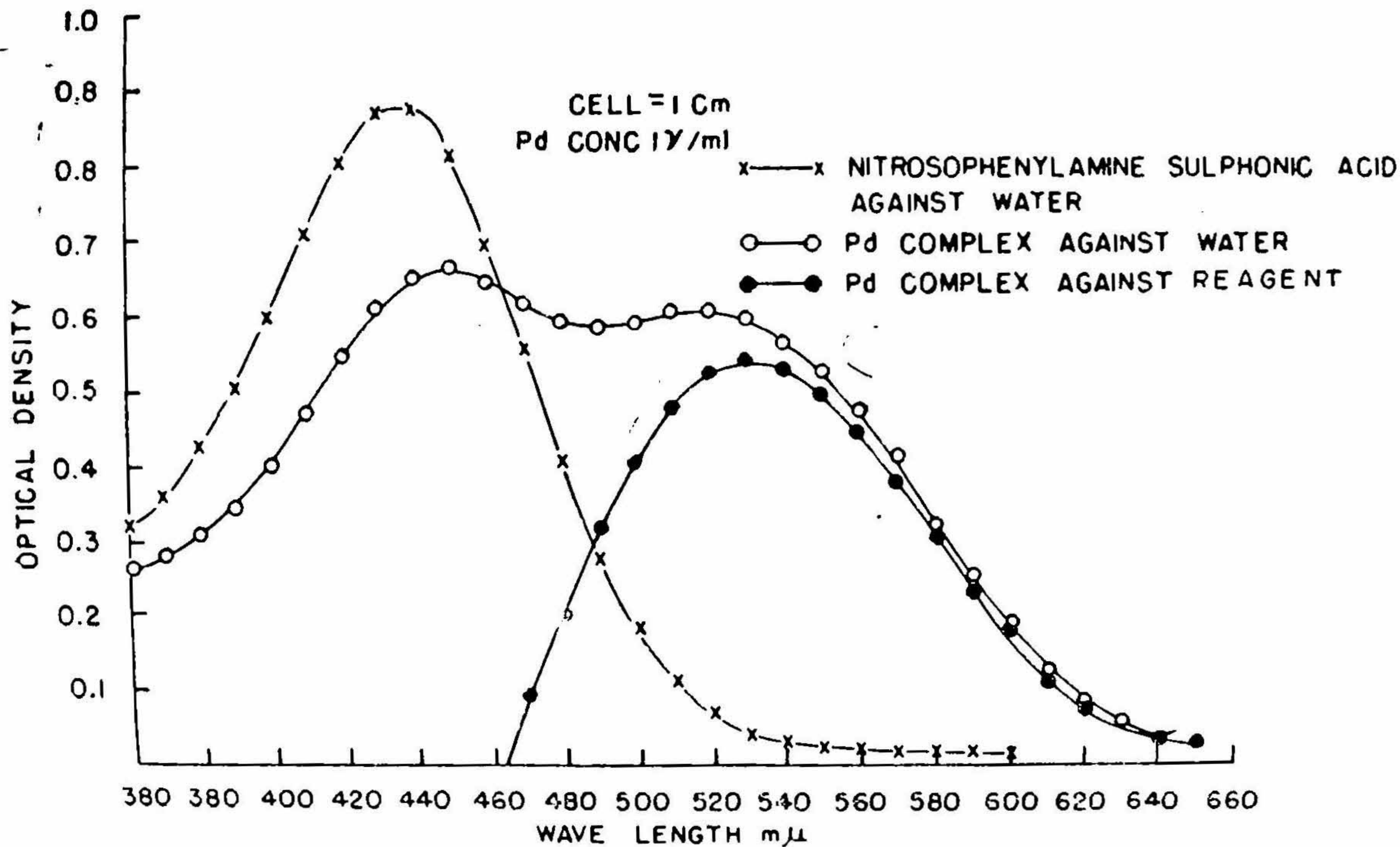


FIG. 1. Absorption spectra of nitrosophenylamine sulphonic acid and its palladium complex.

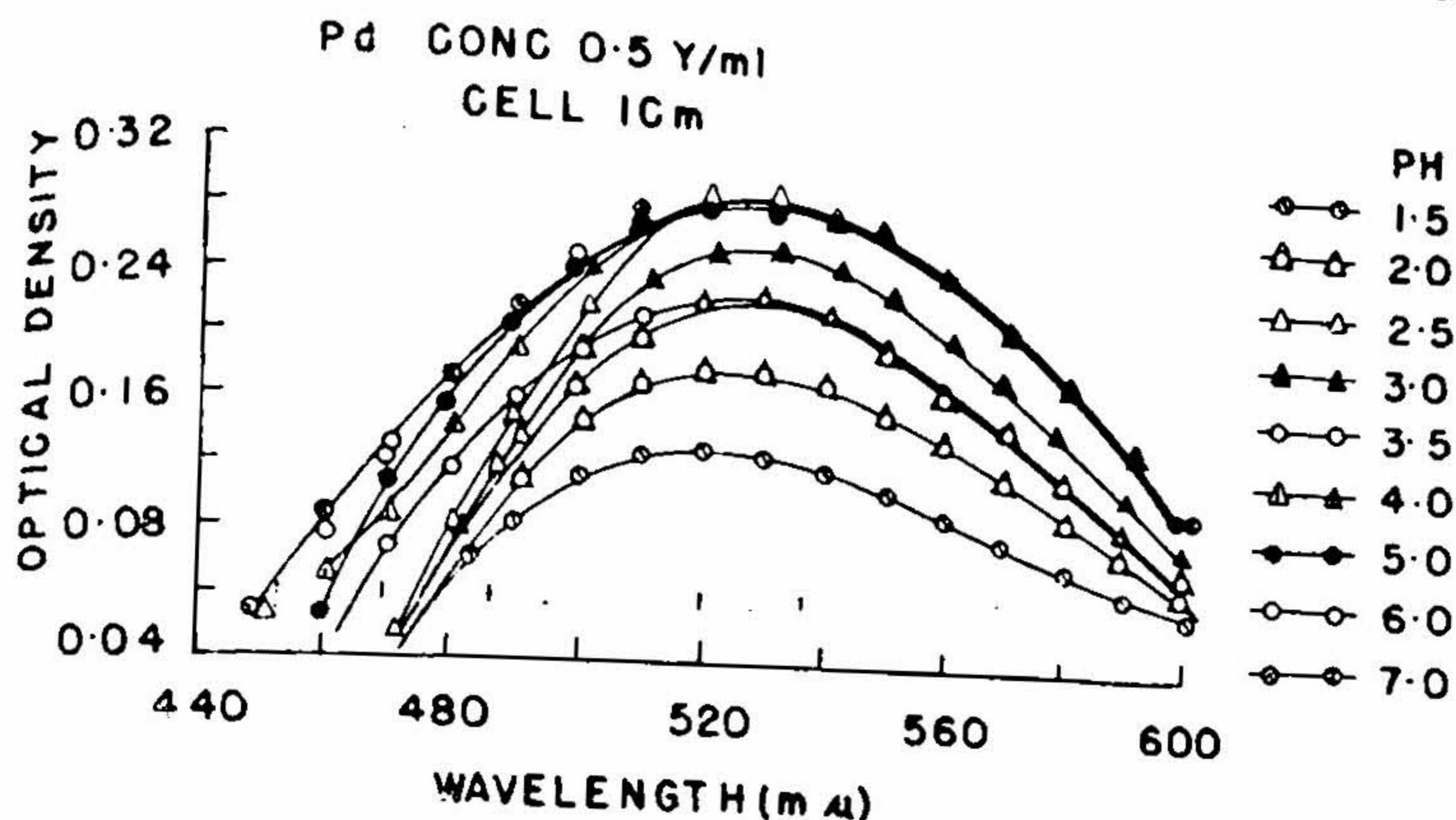


FIG. 2. Effect of pH on the absorption spectra of palladium nitrosodiphenylamine sulphonic acid.

pH values for the blank were also adjusted similarly. It may be seen that the complex shows maximum absorption between pH 2.0 to 3.5.

Effect of salts

The presence of salts greatly affects the colour of the complex. Known quantities of sodium chloride were added to the palladium complex solution and it was found that the solution starts fading when the total salt concentration exceeds 0.03 M.

Calibration curve

Palladium solution was diluted suitably to make it 10 mgm/ml. Different quantities of this solution ranging from 1–20 ml were taken, the reagent was added and the colour developed in the usual manner and the absorbance was measured. The calibration curve is shown in Fig. 3. Even when larger quantities of palladium are taken, no turbidity appears. This shows that after suitable adjustment of metal reagent ratio, the linear relationship can be extended to the higher concentrations of palladium.

Absorption spectra of palladium p-nitrosophenyl α -naphthylamine

The same procedure outlined as above was followed. 20 mgm of palladium was transferred to a 100 ml volumetric flask, 25 ml of buffer solution of pH 4.8 (Sodium acetic-nitric acid) was added to it and then 2 ml of the alcoholic solution of the reagent was mixed with it. The volume was made and the contents were mixed thoroughly.

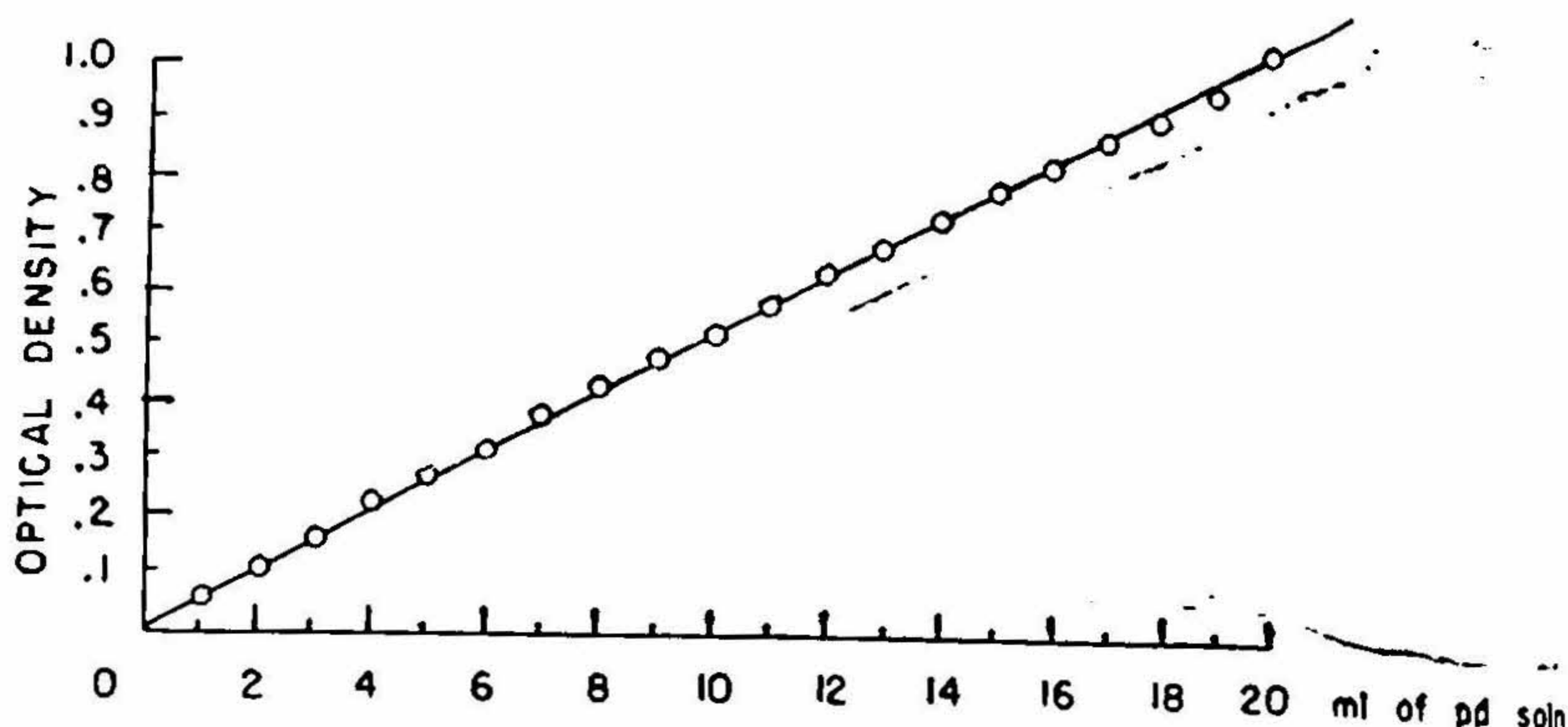


FIG. 3. Calibration curve of Pd complex of nitrosodiphenylamine sulphonic acid. Cell—1 cm, Pd solution—1 γ /ml.

The solution was left for 15 minutes and the absorbance measured. Spectra were drawn as in the previous case, and are shown in Fig. 4.

Interference of metal ions

One drop each of solution of (a) *p*-nitrosodiphenylamine sulphonic acid, (b) *p*-nitrosophenyl α -naphthylamine was added to a drop of metal on a spot plate solution containing approximately 0.1 mgm of the metal ion, the following metals did not show any interference:

Al⁺⁺⁺, Bi⁺⁺⁺, Ca⁺⁺, Cd⁺⁺, Co⁺⁺, Cr⁺⁺⁺, Cu⁺⁺, Mg⁺⁺, Mn⁺⁺, Ni⁺⁺, Pb⁺⁺, Fe⁺⁺,

Rh⁺⁺⁺ Sn⁺⁺, Sr⁺⁺ Ti⁺⁺⁺⁺, Th⁺⁺⁺⁺, UO₂⁺⁺, VO⁺, Zr⁺⁺⁺⁺, WO₄⁻⁻⁻, Sn⁺⁺, SO₄⁻,

CO₃⁻⁻⁻, NO₂⁻, NO₃⁻, PO₄⁻⁻⁻.

Platinum does not cause interference in cold but when it is warmed with the reagents, rose red colour develops. Gold does not cause interference in case of *p*-nitrosophenyl α -naphthylamine when present up to 200 ppm quantity but in case of *p*-nitrosodiphenylamine sulphonic acid its interference is observed. Silver ions do not cause interference when nitric acid sodium acetate buffer is used but in the presence of chloride ions the interference is understandable.

The point of maximum absorption of the palladium complexes with different reagents and their molar extension coefficients are given in Table I.

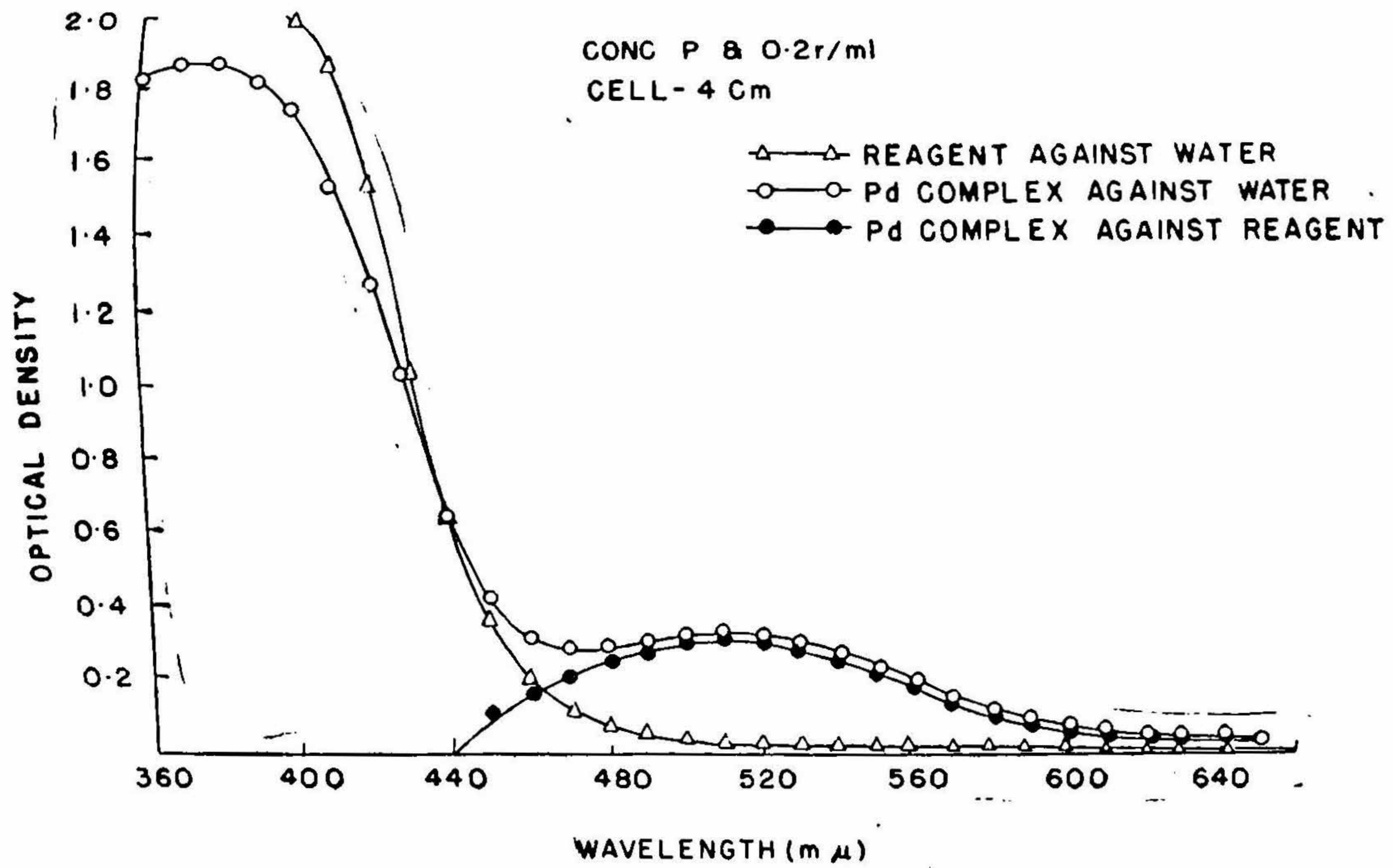


FIG. 4. Absorption spectra of nitrosophenyl α -naphthylamine and its palladium complex.

Table I

Palladium complex of the reagent	Maximum absorption of complex	Molar extinction coefficient
(a) <i>p</i> -nitrosodiphenylamine	520 m μ	38,730
(b) <i>p</i> -nitrosophenyl α -naphthylamine	510 m μ	42,300
(c) <i>p</i> -nitrosodiphenylamine sulphonic acid	535 m μ	54,800

3. Discussion

A comparison of the absorption spectra of the palladium complex of *p*-nitrosodiphenylamine with (a) *p*-nitrosodiphenylamine sulphonic acid, (b) *p*-nitrosophenyl α -naphthylamine shows that the latter reagents have definite advantages over the reagent hitherto used. These reagents show negligible absorption at the point of maximum absorption of the palladium complex and are more suited for spectrophotometric work; *p*-nitrosodiphenylamine sulphonic acid forms a water soluble palladium complex thus permitting estimation of larger quantities of palladium. Moreover, it does not require a close control of pH as is in the case of *p*-nitrosodiphenylamine. *p*-nitrosodiphenyl α -naphthylamine exhibits greater selectivity than *p*-nitrosodiphenylamine. In this case, gold does not interfere in the estimation of palladium when present up to 200 ppm quantity. As may be seen from the table both the reagents show greater sensitivity and selectivity than *p*-nitrosodiphenylamine.

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