
INTRODUCTION

1-(2-pyridyl-azo)-2-naphthol (PAN) is a well known complexing agent. It gives characteristic reactions with a number of ions such as Bi, Cd, Cu, Pt, Sn²⁺, U⁴⁺, Hg, Th, Pb, Fe³⁺, Ni, Zn, Ce⁴⁺, the rare earths, Co, and Pd¹. Moreover it is successfully utilized for the spectroscopic determination of uranium², and cobalt³, as well as a complexometric indicator for the determination of rare earths⁴. K.L. Cheng & R.H. Bray⁵ also used PAN as a colorimetric reagent, as well as a metal indicator for the determination of indium. Although they state that rhodium fails to react with PAN we tried this reaction, and we succeeded, under certain conditions, to make it possible.

In this paper the interaction of PAN with rhodium (III) chloride is studied, and the reaction is applied in the spectroscopic determination of rhodium.

EXPERIMENTAL

Solutions of rhodium: For the preparation of the rhodium solutions the chloride salt (Fluka AG product) was used. The salt was dissolved in 0.2 F hydrochloric acid and the resulting solution was standardized by the 2,5-dimercapto-1,3,4-thiodiazole method⁶.

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Solutions of PAN: Merck p.a. grade product was used and its solutions were prepared by direct weighing of the substance in the needed volume of 95% alcohol.

Solutions of sodium acetate: Merck p.a. grade product was used and its solutions were prepared by dissolving the salt in the appropriate volume of de-ionized water.

The optical density was measured by a Carl Zeiss M4 QII spectrophotometer. Quartz cells were used with thickness of the liquid of 0.5 - 1 cm. depending on the concentration of the solutions. The infra-red spectra were taken by a Perkin-Elmer model 137 spectrophotometer with prism of sodium chloride, using potassium bromide pellet technique. Magnetic susceptibility measurements were made by the Gouy's method using a Newport electromagnet and a Mettler B6 balance. A Jouan type pHmeter was used for pH measurements.

**INTERACTION OF PAN WITH RHODIUM (III) CHLORIDE**

By adding alcoholic PAN solutions to acid solutions of rhodium (III) chloride no change is observed, and on heating this mixture, again no change is observed. If the acidity of the mixture is adjusted at a range of pH 6, by

![Graph showing optical density vs. time of heating](image_url)

*Fig. 1.—Curve A = f (t of heating) for solutions of PAN-Rh (III) at λ = 5850 Å (Quartz cells 1 cm. thickness were used).*

adding sodium acetate solution, upon heating, a green colour is developed, due to interaction of PAN with rhodium (III) chloride. This green colour
is not stable in aqueous solutions and soon a dark green precipitate is formed, but it may be stabilized by adding a small amount of alcohol.

Fig. 1 shows the dependence of the optical density on the time of heating.

An examination of this curve indicates that the reaction is completed after heating the solution for 10 min. in a boiling water bath. Therefore the following procedure is adopted for the interaction.

Into a 50 ml. volumetric flask, 5 ml. of Rh (III) $1 \times 10^{-3}$F solution, 5 ml. of PAN 0.03% solution, 10 ml. of alcohol 95%, and 10 ml. of sodium acetate 10% solution are added. The resulting solution is heated for 10 min. in a boiling water bath, and after cooling at room temperature, it is made up with de-ionized water.

**SPECTROSCOPIC STUDIES**

In a series of experiments alcoholic-acetate solutions of PAN were investigated, and it was found that these are characterized by one absorption maximum at 4900 Å.

The absorption spectra of PAN-Rh (III) solutions were then studied. These solutions are characterized by three absorption maxima at 4500 Å, 5850 Å, and 6300 Å.

Fig. 2 shows the change of the optical density ($A$) as a function of the wave length ($\lambda$), $A = f (\lambda)$, of a number of acetate buffer solutions (pH = 6) of I. PAN $1 \times 10^{-4}$M, II. PAN-Rh (III) $8 \times 10^{-5}$M, and III. Rh (III) $1 \times 10^{-4}$F. Quartz cells of 0.5 cm. thickness were used.

From the above curves it is evident that the complex formed absorbs strongly at 4500 Å, 5850 Å, and 6300 Å, while the absorbance of the reagents is negligible at and above 5600 Å. Therefore the study of the formation of the complex can be made either at 5850 Å, or at 6300 Å.

In order to characterize the complex compound formed between PAN and rhodium (III) chloride, the absorption spectra of mixtures of PAN and Rh (III) were studied, according to the method of continuous variations, and that of molar ratio.

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Fig. 2.—Curves $A = I(\lambda)$ for solutions of I. PAN, II. PAN-Rh (III), and III. Rh (III).
By the method of continuous variations, the change of the optical density of PAN-Rh (III) mixtures obtained from equimolar solutions of PAN and Rh (III) was studied as a function of X of the mixtures. (X is the volume in ml. of Rh (III) solution that was mixed with (1 - X) ml. of PAN solution).

This study was extended at wave lengths between 5850 Å and 6300 Å and in solution of pH around 6; the concentration was ranging from \( 1 \times 10^{-3} \) F to \( 1 \times 10^{-5} \) F. In all cases studied the curves \( A = f(X) \) present a maximum, whose position is independent of the wave length, of the pH, and of the concentration of equimolar solutions. For this maximum the corresponding value of X is \( X = 0.5 \). From this value it is found that at the concentration and the pH studied only one complex is formed in a ratio of PAN : Rh (III) = 4 : 1.

Fig. 3 shows a series of curves \( A = f(X) \) of PAN-Rh (III) solutions.

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**Fig. 3.**—Curves \( A = f(X) \) for PAN-Rh (III) solutions.

I. Concentration \( 1 \times 10^{-2} \) F, pH 6, Wave length 5850 Å.
II. Concentration \( 1 \times 10^{-3} \) F, pH 5.5, Wave length 6300 Å.
III. Concentration \( 6 \times 10^{-4} \) F, pH 6, Wave length 5850 Å.
IV. Concentration \( 6 \times 10^{-4} \) F, pH 6.2, Wave length 6300 Å.
By the method of molar ratio, the change of the optical density of solutions of constant concentration of Rh (III) and of continually increasing concentration in PAN is investigated. I.e. the curves $A = f (\text{PAN} : \text{Rh (III)})$ are studied, which represent the change of the optical density as a function of the ratio of the molar concentrations of the solutions of PAN and Rh (III).

In this case the point of inflexion of experimental curves determines the molar ratio of PAN and Rh (III) in the complex formed. The study of a number of solutions of various concentrations and pH, and at different wavelengths, reveals that under the conditions studied the formation of only one complex takes place between PAN and Rh (III) solutions, at a molar ratio 1 : 1. The same results were obtained by the method of continuous variations, as it has already been stated above.

Fig. 4 shows a series of curves $A = f (\text{PAN} : \text{Rh (III)})$.

Fig. 4.—Curves $A = f (\text{PAN} : \text{Rh (III)})$ for PAN-Rh (III) solutions.

I. Concentration $1 \times 10^{-4}$F, pH 6, Wave length 5850 Å.

II. Concentration $1 \times 10^{-4}$F, pH 5.7, Wave length 6300 Å.

III. Concentration $4.8 \times 10^{-5}$F, pH 6, Wave length 5850 Å.

IV. Concentration $4.8 \times 10^{-5}$F, pH 6.2, Wave length 6300 Å.
ISOLATION OF THE COMPLEX COMPOUND

Into a 250 ml. beaker, 50 ml. of rhodium (III) chloride 0.2F solution, 50 ml. of PAN 0.2M solution and 5 g. of solid sodium acetate are added. The resulting solution is heated for 1 hr. on a steam bath and then is allowed to stand overnight. Under these conditions a dark green precipitate is formed, which is filtered, washed with water and alcohol, and finally is dried under vacuum for three days.

INFRA-RED SPECTRA

The infra-red spectra of the isolated solid substance were taken using potassium bromide pellet technique.

Figures 5 and 6 show the infra-red spectra of PAN and the complex compound PAN-Rh (III) respectively.

A close examination of the above spectra reveals that the main changes due to the complex formation occur at the frequencies 685 cm\(^{-1}\), 753 cm\(^{-1}\), 1235 cm\(^{-1}\), 1350 cm\(^{-1}\), which belong to the phenolic group\(^9,10\), and at 843 cm\(^{-1}\), 990 cm\(^{-1}\), 1040 cm\(^{-1}\), 1090 cm\(^{-1}\), which belong to the C-N group\(^11\). The charac-

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teristic frequencies of the pyridine ring at 1479 cm\(^{-1}\), 1572 cm\(^{-1}\), and 1598 cm\(^{-1}\) remain unchanged and therefore the pyridyl group of the reagent does not participate in the complexation. It may be assumed therefore, that coordi-

![Infrared spectra of the complex PAN-Rh (III).](image)

Fig. 6.—Infrared spectra of the complex PAN-Rh (III).

nation takes place through the phenolic group and the \(-N=N-\) group of the reagent. That the phenolic group participates in the coordination is confirmed by allowing the reagents to react in an unbuffered solution, and measuring the pH of it before and after the reaction. Such measurements showed that the reaction takes place with an increase in the acidity, which is due to the release of hydrogen ions from the hydroxyl group.

The interaction, therefore, between rhodium (III) chloride and 1-(2-pyridyl-azo)-2-naphthol may be represented by the following equation.

\[
\text{RhCl}_3 + \begin{array}{c}
\text{N} \\
\text{H}
\end{array} - \text{N} = \text{N} - \begin{array}{c}
\text{H}
\end{array} \quad \Rightarrow \quad \begin{array}{c}
\text{N} \\
\text{H}
\end{array} - \text{N} = \text{N} - \begin{array}{c}
\text{H}
\end{array} \downarrow \quad \text{Cl}_3 + \text{HCl}
\]

The analysis of the solid substance is as follows, found \(\text{Rh} = 24.32\%\), \(\text{Cl} = 16.78\%\). required \(\text{Rh} = 24.38\%\), \(\text{Cl} = 16.90\%\).

and it confirms the results obtained by the spectroscopic data which have been stated above.
DISASSOCIATION AND FORMATION CONSTANTS
OF THE COMPLEX IN SOLUTION

The formation constant of the complex in solution has been calculated
from Fig. 3. It may be assumed that at the points A and B of the ascending
portion of the curves (I) and (III), the observed optical density (0.35) is
mainly due to the colour of the complex; there the amounts of the complex
are identical. For the system:

\[ \text{Rh} (\text{H}_2\text{O})_\text{Cl}^+ + \text{PAN}^- = \text{RhPANCl} + 4 \text{H}_2\text{O} \]

the formation constant is:

\[ K_f = \frac{(X)}{(a - X)(b - X)} \]  \hspace{1cm} (1)

in which \( X \) is the concentration of the complex, \( a \) and \( b \) are the initial concen-
trations of rhodium and PAN respectively. With the two concentrations \( a_1 \),
\( a_2 \) and \( b_1 \), \( b_2 \) of the reactants, for which the optical density is the same, the
values due to \( X_1 \) and \( X_2 \) are the same, therefore:

\[ K_f = \frac{(X)}{(a_1 - X)(b_1 - X)} = \frac{(X)}{(a_2 - X)(b_2 - X)} \]  \hspace{1cm} (2)

or

\[ X = \frac{a_1 b_1 - a_2 b_2}{(a_1 + b_1) - (a_2 + b_2)} \]  \hspace{1cm} (3)

The value of \( K_f \) is found from equation (1) by substituting the value
of \( X \) as obtained from equation (3); thus the formation constant can be calcu-
lated, and it was found to be:

\[ K_f = 2 \times 10^8, \text{ at } 20^\circ\text{C, and at pH = 6.} \]

The dissociation constant also can be calculated from the curvature
around the end point of the molar ratio plot (Fig. 4) and it was found to be:

\[ K_d (\text{mean}) = 1.09 \times 10^{-6}, \text{ at } 20^\circ\text{C, and at pH = 6.} \]

Using the mean value of the constant formation \( K_f \), it is possible to
determine the standard free energy change by substituting the values of the
various symbols in the equation:

\[ \Delta F^0 = - 2.303 RT \log K_f \]

from which is found that:

\[ \Delta F^0 = - 10.5 \text{ Kcal. mol.}^{-1} \]
Magnetic susceptibility measurements of the complex in solid state as well as in solution showed that it is diamagnetic.

**ANALYTICAL APPLICATIONS**

The spectroscopic study of the reaction showed that the colour system follows Beer's law for the concentration range 40 μg. to 400 μg. of rhodium per ml., and this is evident from the fact that when the optical densities at 5850 Å or 6300 Å, are plotted against the respective concentrations, as it is indicated in Fig. 7, a straight line is obtained. Spectroscopic studies also showed that the colour system remains stable for more than 48 hr.

Procedure: The pH of the rhodium solution is adjusted at about 6 by adding solution of sodium acetate 10%, after the addition of solution
0.03% of PAN (3 mg. of PAN per mg. of rhodium) and 10 ml. of alcohol 95%. The resulting solution is heated for 10 min. in a boiling water bath and then after cooling at room temperature it is made up to 50 ml. with deionized water. After thorough mixing, a portion of the solution is transferred into a 0.5 cm. absorption cell, and its optical density is measured at either 5850 Å, or 6300 Å.

ΠΕΡΙΔΗΨΗΣ

Μελετάται η αντίδραση μεταξύ χλωριούχου ροδίου (III) και 1-(2-πυρι-δυλάζο)-2-ναφθιλίνη (PAN). Δι’ ἔφαρμογής φασματοσκοπικῶν μεθόδων, ἀπε- δείχθη ὅτι σχηματίζονται μία καθαρισμένη σύμπλοκος ἐνώσεως ὑπὸ ἀναλογίαν PAN:RhCl, 1:1. Μελέτη τοῦ ὑπερθύρου φάσματος τῆς συμπλόκου ἐνώσεως ἀπεδείχθη ὅτι η σύμπλοξ συντελεῖται μέσω τῆς φαινολικής ὁμάδος καὶ τῆς ὁμάδος -N= N- τοῦ ἀντιδραστηρίου. Ἐκ φασματοσκοπικῶν δεδομένων ὑπολο- γίσθησαν ή σταθερὰ σχηματισμοῦ τῆς συμπλόκου ἐνώσεως καὶ η μεταβολὴ ἐλευ- θέρας ἐνεργείας, εὑρέθησαν δὲ 3,2,10⁻⁶ καὶ 10,5Kcal/mole ἀντιστοίχης. Μετρή- σεις τῆς μαγνητικῆς ἐπιδεικτικότητας ἀπεδείχθη ὅτι η νέα σύμπλοκος ἐνώσεως εἶναι διαμαγνητική. Φασματοσκοπικῶς εὑρέθη ὅτι η ἀντίδρασις εἶναι κατάλληλης ὅταν τὸν προσδιορισμὸν τοῦ ροδίου διὰ τὴν περιοχὴν συγκεντρώσεων ἀπὸ 40 μg ἕως 400 μg Rh ἀνὰ χιλιοστόλυτρον.