Solvent Extraction of Palladium(II) from Aqueous Chloride Medium by Triphenylphosphine, Triphenylphosphine Oxide or Triphenylphosphine Sulphide in Benzene

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Abstract: *Solvent extraction of Palladium(II) [Pd(II)] from chloride solution has been investigated by using triphenylphosphine (Ph₃P), triphenylphosphine oxide (Ph₃PO) and triphenylphosphine sulphide (Ph₃PS) as extractants in benzene. Under similar experimental conditions, Ph₃P showed relatively better extraction of Pd(II) compared to the other two extractants. Therefore, detailed investigations on the effects of different parameters on the extraction of palladium by Ph₃P were then carried out. The stripping of the extracted metal species using different stripping agents solutions was investigated and the selective removal of Pd was found to be when using 1 M stabilised thiosulfate solution. Based on the experimental results, an equilibrium model is proposed and the stoichiometry of the extracted species was found to be [Pd(Cl)₂.2Ph₃P]. Thermodynamic parameters including ΔG, ΔH and ΔS for the Pd-Ph₃P extraction system were determined. IR spectrum analysis of the extracted complex indicates the direct extraction of Pd as chloride and bonding to phosphorus.*

Keywords: Solvent extraction, triphenylphosphine, triphenylphosphine oxide, triphenylphosphine sulphide

1. INTRODUCTION

Palladium (Pd) has been used in various ways as a hydrogenation catalyst, micro contactors in the electronics, hard alloy in dentistry and in the last few years as a component in the three-way catalysts in automobile exhaust catalytic beads.[1,2] Platinum group metals (PGMs) and their compounds have been widely used as catalysts in the automobile, chemical and petroleum industries. PGMs are also used as conductors in the electrical and electronic industries, in extrusion devices, in dental and medical prostheses, and in jewellery.

Due to their characteristics such as the resistance to corrosion and oxidation, high melting points, electrical conductivity, and catalytic activity, PGMs are extremely useful in different industries. For these reasons, establishing rapid and accurate methods for the determination of palladium for industrial process, quality and pollution control is important.[3] The triphenylphosphine

chalcogenides, Ph_3PX (X = O & S) are all well known as ligands.[4,5] However, an examination of the Cambridge Crystallographic Database[6] shows an imbalance in the number of structural characterisations. Triphenylphosphine (TPP) is a reagent that is routinely employed in organic synthesis.

There are only 16 examples of metal complexes with X = S and nearly 300 with X = O. Furthermore, most of those for X = O involve metals in higher oxidation states, whereas those for X = S are for metals in low oxidation states, especially Au(I). This is understandable since Ph_3PO is a hard Lewis base preferring hard acids, while Ph_3PS is a soft base.[4] The solvent extraction of palladium from nitrate medium by different extractants has been studied by different authors.[7–11] Ahmed et al. studied the extraction of Pd from nitric acid medium using CYANEX 471X in kerosene. The results indicate the possibility of separation of Pd from a synthetic chloride solution similar in composition to that expected from the leaching of spent automotive catalyst.[12]

Solvent extraction separation and recovery of Pd and platinum (Pt) from hydrochloric acid leach liquors of spent automobile catalyst employing precipitation and solvent extraction methods were also studied.[13] Separation of Pd from high level liquid waste (HLLW) solution originated from the reprocessing of spent fuel by the PUREX process was carried out by solvent extraction and precipitation methods using oximes.[14] The solvent extraction and separation performances of Pd(II) and Pt(IV) from hydrochloric acid solutions were investigated using dibutyl sulfoxide (DBSO) diluted in kerosene.[15] The extraction behaviour of Pd(II) was studied with LIX 84I (2-hydroxy-5-nonylacetophenone oxime) in HCl medium[16] and was found to be 97%.

The present paper describes the extraction and back extraction of Pd(II) using Ph_3P as extractant in benzene as well as with Ph_3PO and Ph_3PS. The effects of various parameters like hydrogen ion concentration, extractant concentration, chloride concentration, HCl concentration and metal ion concentration on the distribution ratios of the Pd-Ph_3P system have been studied. The composition of Pd-Ph_3P complex was elucidated using slope analysis method and verified by IR measurements. Thermodynamic data was generated for the Pd-Ph_3P system.

2.   EXPERIMENTAL

2.1   Chemicals and Reagents

All chemicals and reagents used are of analytical reagent (AR) grade. The extracting ligands used, Ph_3P, Ph_3PO and Ph_3PS were supplied from Fluka and used as received without further purification. Ph_3P is a common

organophosphorus compound with the formula $P(C_6H_5)_3$ often abbreviated to PPh_3 or Ph_3P ($Ph = C_6H_5$). It is widely used in the synthesis of organic and organometallic compounds. PPh_3 is in the form of colourless crystals at room temperature. It dissolves in non-polar organic solvents such as benzene and diethyl ether (Figure 1). Ph_3PO is the chemical compound with the formula $(C_6H_5)_3PO$ often abbreviated to Ph_3PO or PPh_3O. This white crystalline compound is a common side product in reactions involving Ph_3P. It is a popular reagent to induce the crystallisation of chemical compounds (Figure 1).
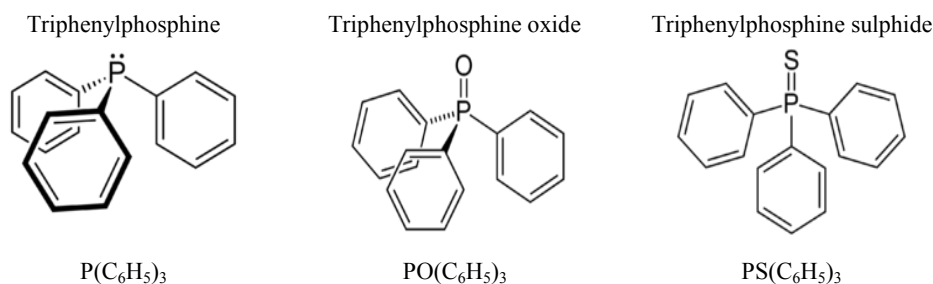

Figure 1: The structure and formula of Ph_3P, Ph_3PO and Ph_3PS.

Ph_3PS is the organophosphorus compound with the formula $(C_6H_5)_3PS$, usually written as Ph_3PS. It is a colourless solid, which is soluble in a variety of organic solvents (Figure 1). Benzene used as a diluent is an AR product of Prolabo. The Pd salt used is $PdCl_2$ of pure grade (Fluka) and was dissolved in hydrochloric acid solution (Aldrich). The concentration of Pd stock solution thus obtained was 9.4×10^{-3} M (1 g l^{-1}) in 1 M HCl, unless otherwise stated.

2.2   Procedure

During batch experiments, a good shaking was carried out for 5 cm^3 of an aqueous hydrochloric acid solution containing Pd(II) of known concentration with 5 cm^3 of the organic phase containing Ph_3P, Ph_3PO or Ph_3PS at the desired concentration. The extraction equilibrium was attained after 30 min (sufficient to attain equilibrium) in glass-stoppered tubes using a shaking water bath shaker type Julabo SW-20C, Germany controlled within ± 1°C adjusted at 25 ± 1°C (except when studying the effect of temperature).

The concentration of Pd(II) in the aqueous acid chloride solution was determined spectrophotometrically by the iodide method[17] using a Shimadzu, UV/visible recording spectrophotometer type UV-160A at λ = 407 ± 3 nm. The concentration of the metal in the organic phase was calculated from the difference between its concentration in the aqueous phase before and after

extraction. The distribution ratio D was calculated as the ratio of the concentration of the metal in the organic phase to its concentration in the aqueous phase.

Stripping experiments were carried out by shaking 10 ml of the organic phase loaded with the extracted metal for 30 min with the same volume of distilled water and other different stripping solutions. The palladium extracted in the organic phase was characterised by measuring the infrared spectra, using FT-IR JASCO 6300 instrument.

3.   RESULTS AND DISCUSSION

3.1   Investigations on the Extraction of Pd(II) with Ph_3P, Ph_3PO and Ph_3PS

In order to choose the suitable extractant for the extraction of 9.4×10^{-3} M (1g l^{-1}) Pd(II) from acid chloride medium, three different and related extractants, namely Ph_3P, Ph_3PO and Ph_3PS dissolved in benzene have been investigated.

The results obtained with these extractants under similar experimental conditions and given in Table 1 reveal a lower influence of Ph_3PS concentration and consequently lower values for Pd(II) extraction, which can be attributed to the electron withdrawing characteristics of the aromatic ring with a decrease of the solvating power of the S atom for Ph_3PS.[18] On the other hand, use of the soft donor acceptor property of palladium to interact with the soft donor property of (Ph_3P) ligand is explored in the extraction of Pd from chloride medium by Ph_3PO.

Table 1: Extraction of Pd(II) (1 g l^{-1}) from 1 M HCl solution using different extractants dissolved in benzene at 25°C.

Extractant, 0.1 M	Distribution ratio, D	Extraction percent, %
Ph_3P	6.5	86.7
Ph_3PO	0.08	7.4
Ph_3PS	0.13	11.5

Extraction of Pd(II) from aqueous chloride solution using Ph_3PO in benzene was poor due to the low tendency of the soft acid Pd(II) to be associated with, and extracted by, the hard oxygen donor base (Ph_3PO).[7] The results obtained indicate that the extraction of Pd(II) with Ph_3P as extractant seems to be the most promising compared to Ph_3PO and Ph_3PS. Therefore, further detailed

investigations were carried out on the extraction of Pd(II) from chloride medium with Ph$_3$P in benzene.

3.2   Etraction of Pd(II) from Chloride Medium with Ph$_3$P in Benzene

The effects of [H$^+$], [Cl$^-$], [extractant] and [HCl] on the extraction of 9.4 × 10^{-3} M (1 g l^{-1}) Pd(II) were separately investigated in the respective concentration range.

3.2.1   Effect of extractant concentration

The extraction of Pd(II) (1 g l^{-1}) was carried out from 1M HCl solution using different concentrations of Ph$_3$P in the range of (1 × 10^{-3})–0.2 M. A traditional and effective means of obtaining both the stoichiometric and equilibrium constant and information about the extraction processes, called "slope analysis," is based on an examination of the variation of the distribution ratio as a function of the relevant experimental variables in a log-log scale.

As shown in Figure 2, the log-log relation between the distribution ratio increases linearly with the increase in the extractant concentration with slope ~2 indicating the participation of two Ph$_3$P molecules in the extracted palladium species.
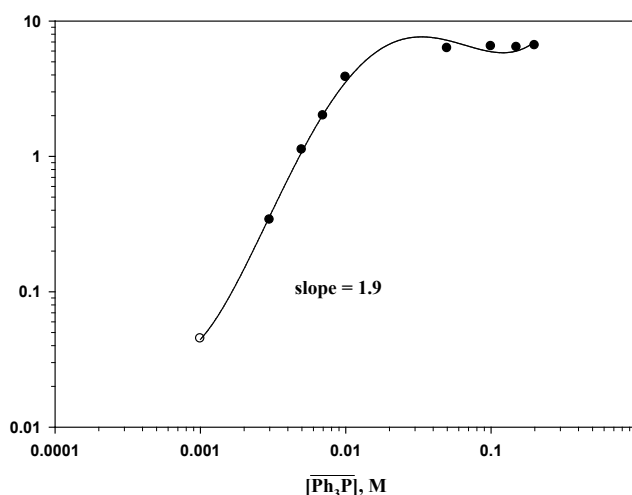

Figure 2: Effect of Ph$_3$P concentration in benzene on the extraction of 9.4 × 10^{-3} M (1 g l^{-1}) Pd(II) from 1 M HCl medium at 25°C and phase ratio (O/A) = 1.

3.2.2   Effect of hydrogen ion concentration

The effect of hydrogen ion concentration on the extraction of Pd(II) by Ph_3P in benzene at constant $[Cl^-]$ of 1 M using sodium chloride was investigated in the 0.1–1 M range. The increase in H^+ concentration in the investigated range had almost no influence on the extraction under the used experimental conditions (Figure 3). This is because the used extractant is neutral and contains no hydrogen ions.
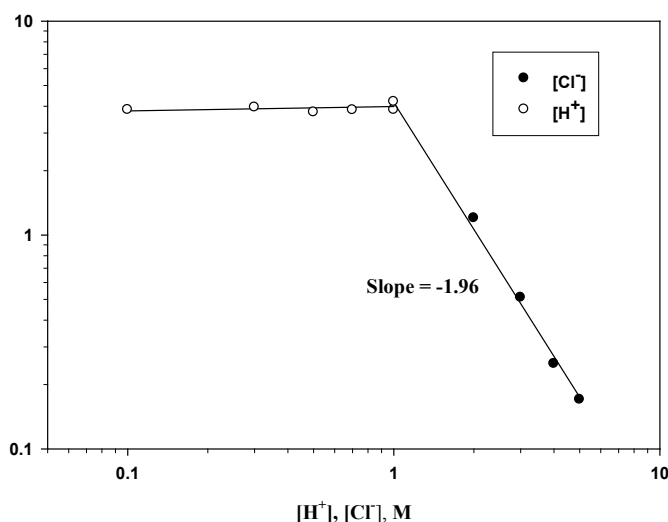

Figure 3: Effect of $[H^+]$ and $[Cl^-]$ on the extraction of 9.4×10^{-3} M (1 g l^{-1}) Pd(II) by 0.01 M Ph_3P in benzene at 25°C and phase ratio (O/A) =1.

3.2.3   Effect of chloride concentration

Distribution ratios of Pd(II) were measured by varying the chloride concentration range of 1–5 M at constant $[H^+]$ of 1 M. It can be observed from the data that when the chloride concentration increases, the distribution ratio decreases; the increase in the chloride concentration favours the formation of $PdCl_4^{2-}$ complex which leads to the decrease in the concentration of free Pd(II) ions. The plot of log D versus log $[Cl^-]$ was found to be a straight line with negative slope of about 2 (Figure 3).

3.2.4   Effect of hydrochloric acid concentration

The influence of hydrochloric concentrations in the 0.1–5 M range on the extraction of 9.4×10^{-3} M Pd (II) by 0.01 M Ph_3P is illustrated in Figure 4. The results obtained show that the extraction efficiency decreases as the hydrochloric

acid concentration increases and the extraction percentage of Pd(II) has a maximum value at 1 M HCl. With further increase in HCl concentration, the extraction percentage of Pd decreases to a minimum value at 2 M HCl and remains constant with further increase in HCl concentration. This decrease may be attributed to the probable extraction of hydrochloric acid at high acidity together with the formation of extractable species $PdCl_4^{2-}$.
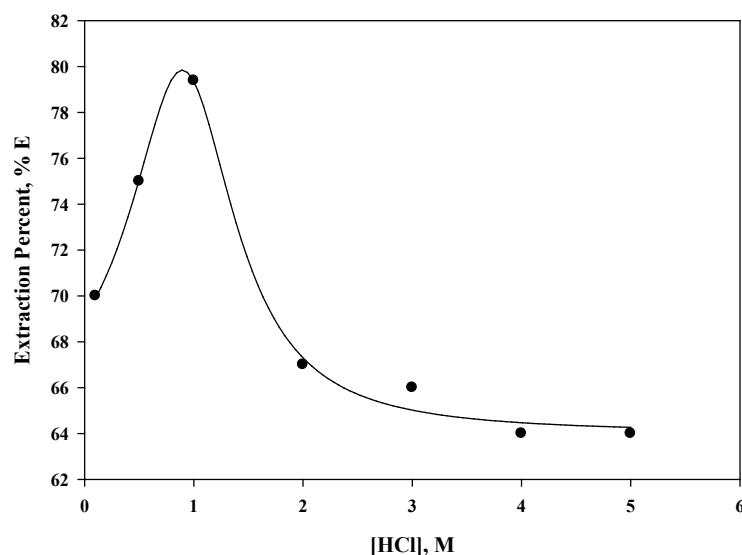

Figure 4: Effect of hydrochloric acid concentration on the extraction of 9.4×10^{-3} M (1 g l^{-1}) Pd(II) by 0.01 M Ph_3P in benzene at 25°C and phase ratio (O/A) =1.

3.2.5 Effect of metal concentration

The effect of Pd(II) concentration on its extraction with 0.01 M Ph_3P in benzene from 1 M aqueous hydrochloric acid solution was investigated in the range of (4.7×10^{-3})–0.023 M. The results obtained are represented in Figure 5 as a relation between the equilibrium palladium concentration in organic and aqueous phases. From this figure, it is clear that the concentration of Pd in the organic phase increases with its equilibrium concentration in the aqueous phase to reach a maximum value around 0.015 M. The ratio between this value and its equilibrium concentration in the aqueous phase indicates the formation of 1:2 (metal to extractant) complexes, which supports the results obtained in Figure 2.
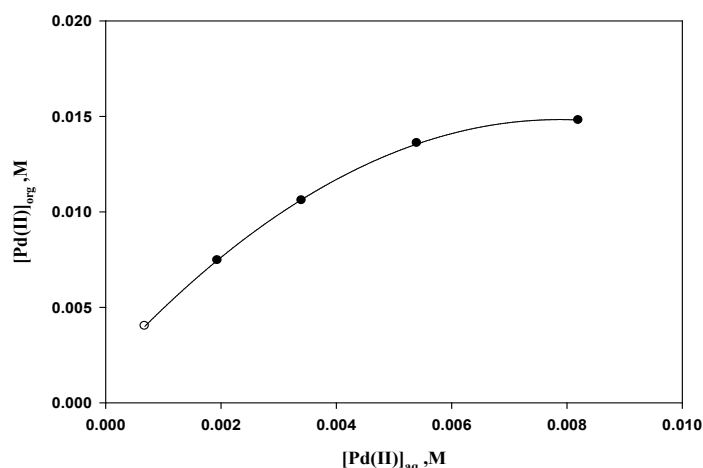
Figure 5: Relation between equilibrium concentration of metal in the organic and aqueous phase from 1 M HCl medium by 0.01 M Ph$_3$P dissolved in benzene at phase ratio (O/A) = 1 and 25°C.

3.2.6   Effect of phase ratio

The effect of change of organic to aqueous (O/A) phase ratio on the extraction trend of Pd(II) and 1 M HCl medium using 0.01 M Ph$_3$P extractant in benzene was carried out. The extraction percent for Pd(II) was found to increase when the phase ratio increases from 0.25 to 2 and then becomes constant afterwards. Further, the separation factor falls in its maximum value at equal volumes of the two phases (O/A =1).

3.3   Extraction Equilibrium

Palladium can form stable chloro-complexes such as PdCl$^+$, PdCl$_2$, PdCl^{3-} and PdCl$_4^{2-}$ in acidic chloride solutions. At about 0.1 M Cl$^-$ and higher, the predominant palladium species in solution[19] is PdCl$_4^{2-}$.

Based on the above results, the following extraction equilibrium is proposed as:

$$PdCl_4^{2-} + 2\overline{Ph_3P} \leftrightharpoons \overline{Pd.2(Ph_3P)} + 2Cl^-$$

(1)
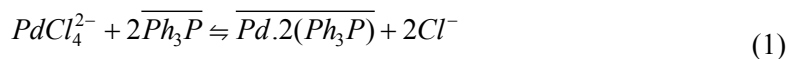
Thus, the extraction constant can be calculated from the relation:

$$K_{ex} = \frac{[\overline{Pd.2(Ph_3P)}][Cl^-]^2}{[PdCl_4^{2-}][\overline{Ph_3P}]^2} \quad (2)$$

$$= \frac{D[Cl^-]^2}{[\overline{Ph_3P}]^2} \quad (3)$$

The average value of K_{ex} calculated at different Cl^- and Ph_3P concentrations was found to be $(4.22 \pm 0.34) \times 10^4$ for Pd(II).

3.4 Temperature Effect

The increase of temperature in the range 15°C–45°C was found to decrease the extraction of 9.4×10^{-3} (1 g l^{-1}) Pd(II) when extracted by 0.01 M Ph_3P in benzene from 1 M HCl solution. Plotting ln K_{ex} values against the reciprocal of the respective absolute temperatures experimented (1/T) K^{-1} yielded a straight line (Figure 6). The temperature effect on the metal extraction could be evaluated in terms of its thermodynamic parameters given in Table 2. The negative value of the enthalpy change (ΔH) indicates that the extraction process is exothermic. The negative value of the free energy change (ΔG) means that the extraction of palladium in the investigated system takes place via a spontaneous reaction and the positive entropy change (ΔS) indicates the increase in the randomness of the system during extraction.
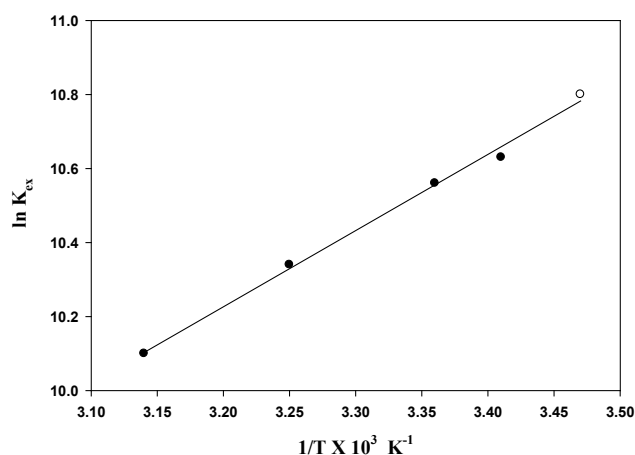

Figure 6: Effect of temperature on the extraction of 9.4×10^{-3} M (1 g l^{-1}) Pd(II) from 1 M HCl medium 0.01 M Ph_3P in benzene at 25°C and phase ratio (O/A) =1.

Table 2: Thermodynamic parameters for 9.4×10^{-3} M Pd(II) extracted from 1 M HCl by 0.01 M Ph_3P in benzene.

Thermodynamic parameter	Calculated value
Enthalpy change (ΔH)	-17.13 ± 0.65 kJ mol^{-1}
Free energy change (ΔG)	-26.16 ± 0.20 kJ mol^{-1}
Entropy change (ΔS)	30.32 ± 2.27 J mol^{-1} K^{-1}

3.5   Stripping Investigations

Screening of stripping reagents such as distilled water, HCl (0.1–6 M), H_2SO_4 (0.1–5 M), HNO_3 (0.1–5 M), NaOH (0.01–1 M), oxalic acid (0.1–1 M) and ascorbic acid (1–10%) was carried out at unit phase ratio to learn about the stripping behaviour of Pd(II) from the loaded Ph_3P. It was observed that, the stripping percentage with the different investigated reagents is generally very poor. The use of 1 M stabilised thiosulfate solution[20] was found to be efficient and the stripping percentage reached 70%.

3.6   Infrared investigations

To verify the chemical composition of the resulted palladium complex extracted by Ph_3P, IR spectrum of Ph_3P in benzene as diluent was carried out before and after palladium extraction from 1 M HCl. As shown in Figure 7, the absorption band in the spectrum of Ph_3P at 914 cm^{-1}, pointing to phenyl ring vibrations, disappeared after palladium extraction. This may be attributed to the change in the symmetry of the three phenyl groups and loss of the induced dipole moment by coordination of palladium to phosphorus, which restricts the phenyl ring vibrations.

The strong phosphorus stretching vibration band observed at 1313 cm^{-1} was shifted to lower frequency at 1188 cm^{-1} when palladium was extracted which is in agreement with direct bonding of the palladium to phosphorus. The broad band at 3448 cm^{-1} observed for Ph_3P in benzene has disappeared from the IR spectrum of the extracted palladium complex. This absorption band is referred to the hydrogen bond of Ph_3P with little water in the diluent. As a result, most probably palladium is mainly bonded to the phosphorus atom of Ph_3P, which restricts the stretching vibrations of phenyl groups of Ph_3P, supporting the extraction equilibrium proposed.
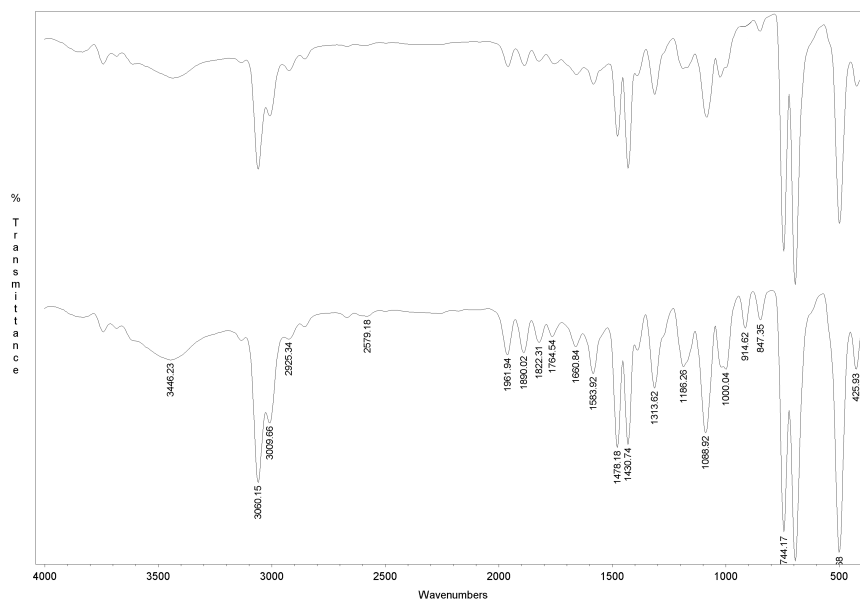
Figure 7: IR spectrum of the extracted PdCl$_2$ by Ph$_3$P in benzene before and after extraction.

4.   CONCLUSION

The extraction studies of palladium from hydrochloric acid medium with Ph$_3$P, Ph$_3$PO and Ph$_3$PS show high extraction with Ph$_3$P. The experimental results indicate that the extracted palladium species when using Ph$_3$P is $\overline{[Pd.2(Ph_3P)]}$. Increasing the temperature had a negative effect on the extraction of palladium metal giving an idea about the exothermic nature of the extraction process. Palladium could be separated in a pure form based on its trend in the extraction and stripping procedures. The use of 1 M stabilised thiosulfate solution was found to be efficient for stripping palladium from its loaded Ph$_3$P-benzene solution and the stripping percentage reached 70%.

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