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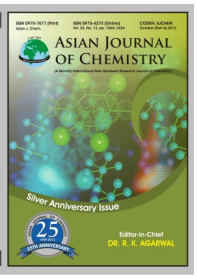

Diisopentyl Sulphide as an Extractant for Palladium(II) and the Crystal Structure of Palladium(II) Complex

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Diisopentyl sulphide (DIS) was used in an extractant for Pd(II) from hydrochloric acid media. Palladium(II) was extracted quantitatively from 0.1 M HCl with diisopentyl sulphide in kerosene. Ammonia solution could be used as stripping agent. Extraction parameters of Pd(II), including diisopentyl sulphide concentration, contact time of aqueous and organic phases, organic/aqueous (O/A) phase ratio, ammonia concentration and hydrochloric acid concentration of aqueous phase, were studied. Diisopentyl sulphide and Pd(II) form a 2:1 adduct $Pd(DIS)_2Cl_2$ in the extraction. X-Ray crystal structure determination revealed that $Pd(DIS)_2Cl_2$ is square-planar complex in which diisopentyl sulphide acts as a neutral unidentate ligand coordinated with palladium(II) *via* the sulphur atom of the diisopentyl sulphide.

Key Words: Palladium, Solvent extraction, Diisopentyl sulphide.

INTRODUCTION

Palladium is extensively used in automobile, chemical and electronic industry owing to its specific physical and chemical properties. Besides, it is also used in the field of photography and aviation[1,2]. Since natural resources for palladium metal are limited and the demand for palladium in industry will continue to grow, it is important to find an effective method for the recovery of palladium from secondary sources.

The hydrometallurgical methods, including solvent extraction, ion exchange resin and the reduction of palladium precipitate by reagents, are more applicable to palladium recovery[3-5]. In industrial process streams, palladium occurs in the divalent oxidation state and forms chloride complexes, of which the tetrachlorinated palladium anion $[PdCl_4]^{2-}$ is the most common species. Solvent extraction has been considered as a most efficient technique for the recovery of palladium in chloride media[6-9]. Extensive investigations have been made to extract Pd(II) using highly selective extractants[10-15]. However the corresponding extractants usually have complicated molecular structures and difficult to synthesize, which hinders their further applications. In industry, it is mainly extracted by solvent extraction with straight-chain sulphide through the formation of inner-sphere complexes[16].

In the present work, we have investigated the extraction of Pd(II) from hydrochloric acid medium with a diisopentyl sulphide (DIS), by controlling important parameters like extractant concentration, acidity, contact time, phase ratio and concentration of stripping agent. The crystal structure of $Pd(DIS)_2Cl_2$ showed that DIS acts as a neutral unidentate ligand coordinated with Pd(II) *via* the S atom of the DIS.

EXPERIMENTAL

A Z-2000 polarized zeeman atomic absorption spectrophotometer (Hitachi High-Technologies Corpotation, Japan) was used to measure the concentration of Pd(II). The operating conditions were carried out according to the recommendations of manufacturer. The wavelengths selected were as follows: Pd 247.6 nm. The pH values were measured with a PHS-3C precision pH meter (REX Instrument Factory, Shanghai, China).

Pd(II) stock solution (1.0 g L^{-1}): A weighed portion of palladium metal was dissolved in aqua regia (120 mL). When the metal was completely dissolved, the solution was evaporated to nearly dryness. Residual HNO_3 was removed by adding 30 mL of 6 mol L^{-1} HCI and evaporated to nearly dryness again and this was repeated 3 times. The solution was transferred into a 250 mL of volumetric flask and the final volume was adjusted by adding 0.1 mol L^{-1} HCl solution. The organic phases with desired extractant concentration were obtained by dissolving a definite volume of diisopentyl sulphide (DIS) in kerosene.

General extraction procedure: Equal volumes (10 mL) of both phases were mixed and vigorously shaken for 15 min, which was sufficient enough to attain equilibrium in a

preliminary experiment. After phase separation, the concentration of Pd(II) in aqueous solution was determined by an atomic absorption photometer. These results were further used to estimate the extraction efficiency of metal. The amount of extracted metal ion was calculated according to the differences in the metal concentrations of the aqueous phase between, before and after the extraction.

RESULTS AND DISCUSSION

Influences of the extractant concentration: To investigate the effect of diisopentyl sulphide (DIS) concentration on the extraction performances of Pd(II), the experiments were performed at the fixed conditions. The results are shown in Fig. 1. As can be seen from Fig. 1, DIS dissolved in kerosene with the extractant concentration varying from 0.002 to 0.02 mol L^{-1}. The percentage extraction of Pd(II) increased in the range from 77.3 to 99.5 % by increasing DIS concentration from 0.002 to 0.008 mol L^{-1}. Further increasing DIS concentration from 0.008 to 0.02 mol L^{-1}, the percentage extraction of Pd(II) only had a slight increase (from 99.5 to 99.9 %). 0.008 mol L^{-1} DIS was needed for quantitative extraction of Pd(II) from a 0.1 mol L^{-1} HCI aqueous solution containing 100 mg L^{-1} palladium.

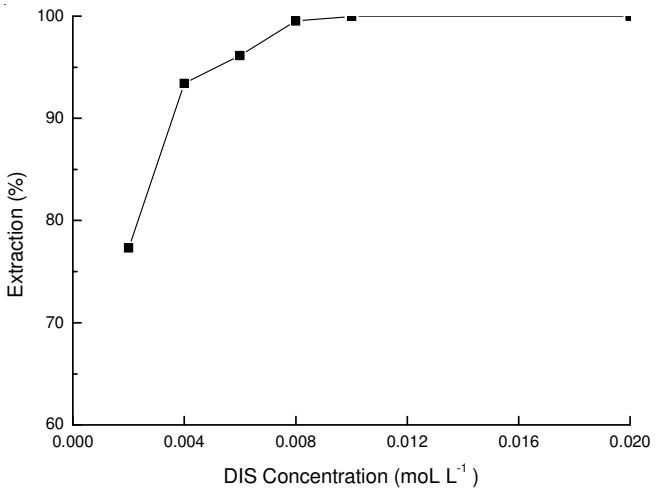

Fig. 1. Effect of extractant concentration on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{HCl}: 0.1 mol L^{-1}, O/A: 1.0, contact time: 15 min

Influences of hydrochloric acid concentration: In industrial application for extraction of Pd(II), the acidity of stock solution usually influences significantly. The effect of hydrochloric acid concentration on the extraction of Pd(II) is shown in Fig. 2. The extraction curve indicated the percentage of extraction of Pd(II) decreased drastically with the increase of HCl concentration. The percentage extraction of Pd(II) decreased in the range from 99.5 to 34.5 % by increase of HCl concentration from 0.1-2.0 mol L^{-1}. Quantitative extraction of palladium occurred at 0.1 mol L^{-1} HCl. Therefore, 0.1 mol L^{-1} HCl was used in all subsequent experiments.

Influences of contact time: To extract Pd(II) efficiently by controlling an optimal contact time of aqueous and organic phases, the experiments were carried out with different contact time at other fixed extraction parameters. The results are shown in Fig. 3. Contact time was determined by measuring the metal

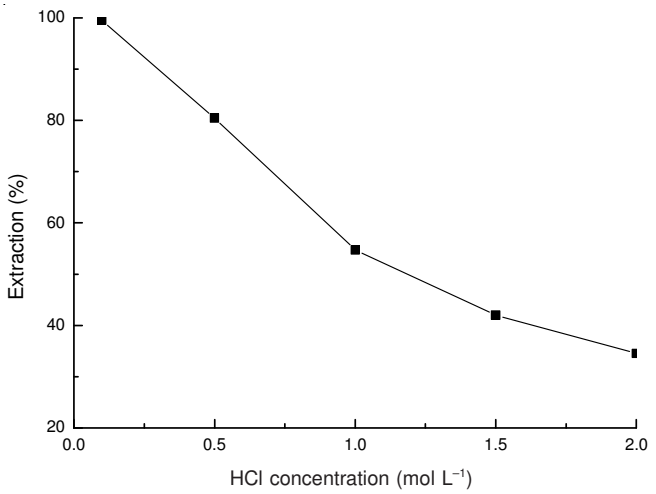

Fig. 2. Effect of HCl concentration on the extraction of Pd(II) $C_{Pd(II)}$: 100 mg L^{-1}, C_{DIS}: 0.008 mol L^{-1}, O/A: 1.0, contact time: 15 min

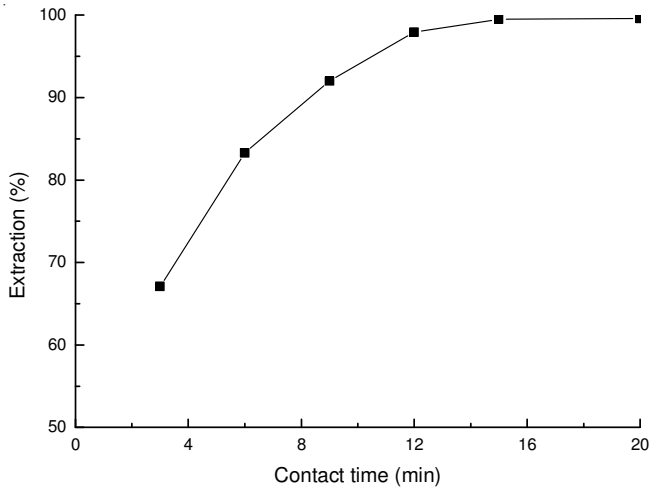

Fig. 3. Effect of contact time on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{DIS}: 0.008 mol L^{-1}, O/A: 1.0, C_{HCl}: 0.1 mol L^{-1}

content in the aqueous phase as a function of time until the metal concentration in the aqueous solution did not vary. The two phases were shaken for a period ranging from 3 to 20 min. The percentage extraction of Pd(II) increased in the range from 67.1 to 99.5 % by in increased of contact time from 3 to 15 min. Further increasing contact time from 15-20 min, the percentage extraction of Pd(II) kept constant. Therefore, the minimum period of equilibration required for the quantitative extraction of palladium was found to be *ca.* 15 min.

Influences of organic/aqueous (O/A) phase ratio: To obtain optimal organic/aqueous phase ratio for extraction of Pd(II), the following experiments were performed at other fixed extraction parameters (Fig. 4). As can be seen from Fig. 4, by increasing organic/aqueous phase ratio from 0.4-1.0, the percentage extraction of Pd(II) increased from 90.0-99.5 %. By further increasing organic/aqueous phase ratio from 1.0-2.0, the percentage extraction of Pd(II) kept constant. Therefore, Pd(II) can be extracted efficiently by controlling organic/aqueous phase ratio, 1.0.

Stripping properties of palladium: Palladium loaded in the organic phase was stripped with various stripping agents, such as nitric acid, sodium sulfite and ammonia as stripping

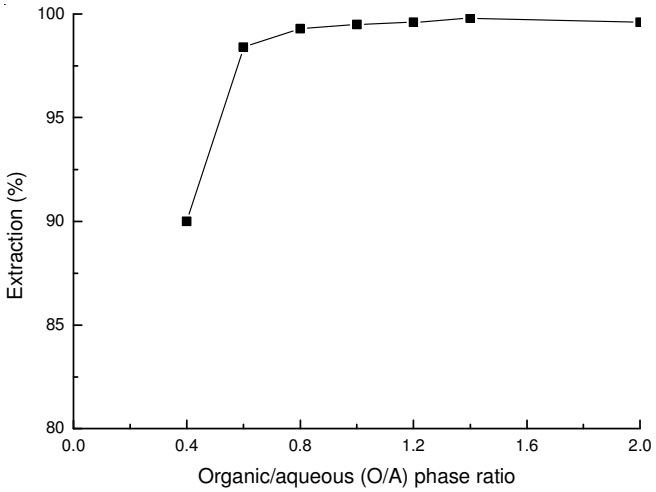

Fig. 4. Effect of O/A on the extraction of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{DIS}: 0.008 mol L^{-1}, contact time: 15 min, C_{HCl}: 0.1 mol L^{-1}

agents. In the following experiments, the organic phase loaded with 100 mg L^{-1} Pd(II) was used. The experiments were carried out at the following fixed parameters: contact time of the two phases, 15 min; organic/aqueous (O/A) phase ratio, 1.0. The results show that palladium can not be stripped from organic phase with acid solution and sodium sulfite. Ammonia solution can be used as the effective stripping agent. As can be seen from Fig. 5, by increasing ammonia concentration from 0.1 to 1.0 % (v/v), the percentage stripping of Pd(II) increased from 51.9 to 96.4 %. By further increasing concentration of ammonia from 1.0 to 2.0 % (v/v), the percentage stripping of Pd(II) kept constant. The stripping was quantitative when 1 % (v/v) ammonia solution was used.

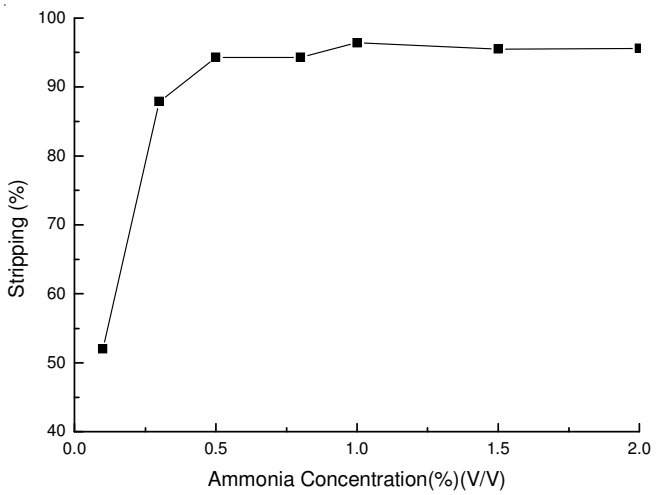

Fig. 5. Effect of stripping reagent concentration on the stripping of Pd(II). $C_{Pd(II)}$: 100 mg L^{-1}, C_{DIS}: 0.008 mol L^{-1}, O/A: 1.0, contact time: 15 min

IR spectra of extracted Pd(II)-DIS complex: Extracted Pd(II)-DIS adduct may be prepared by following procedure: 0.2 mol L^{-1} DIS in kerosene was shaken with Pd(II) aqueous solution (1.0 g L^{-1} in 0.1 M HCl) many times until a saturated extraction organic phase was obtained. Fig. 6 shows the IR spectra of DIS and Pd(II)-DIS complex. The C-S stretching vibration observed at 1460 cm^{-1} for DIS is shifted to 1450 cm^{-1} in the Pd(II)-DIS complex. This fact indicated the DIS is coordinated with Pd(II) *via* sulphur atom.

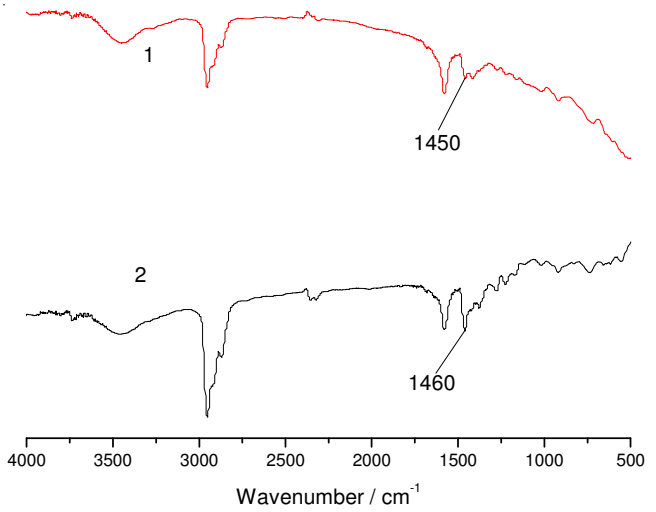

Fig. 6. Infrared spectra of Pd(II)-DIS complex (**1**) and DIS (**2**)

X-Ray crystallography of $Pd(DIS)_2Cl_2$: The crystal structure of $Pd(DIS)_2Cl_2$ is shown in Fig. 7. Crystallographic data and some experimental conditions used to obtain the intensity data are given in Table-1. As expected, in Pd(II)-DIS complex, DIS acts as neutral unidentate ligand coordinating to palladium *via* the sulphur atom. The complex is of trans-conformation and Pd(II) is coordinated by two Cl atoms and two DIS at opposite position. Two opposite Pd-S and Pd-Cl bond distances are equivalent, respectively. The Pd-atom and two S-atoms are coplanar (S(1)-Pd(1)-S(1)# = 180.00°). Thus, the palladium-DIS complex as a whole is in complete symmetry with palladium atom at the symmetry center of the square-planar complex.

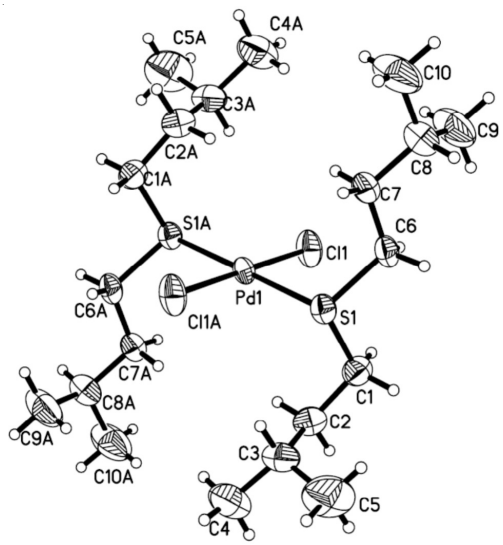

Fig. 7. Crystal structure of DIS-Pd(II)

Conclusion

The solvent extraction of Pd(II) from hydrochloric acid solutions were investigated using diisopentyl sulphide (DIS) diluted in kerosene. Extraction parameters of Pd(II) were obtained and summarized as the following: DIS concentration, 0.008 mol L^{-1}; organic/aqueous (O/A) phase ratio, 1.0; hydrochloric acid concentration of aqueous solution, 0.1 mol L^{-1}; contact

TABLE-1
CRYSTAL DATA AND STRUCTURE PARAMETERS FOR DIS-Pd(II)

Parameters	Data
Empirical formula	$C_{20}H_{44}Cl_2PdS_2$
Formula weight	525.97
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	P2(1)/c
Unit cell dimensions	a = 12.0690(14) Å α = 90º
	b = 10.9888(13) Å β = 99.5650(10) Å
	c = 10.3636(12) Å γ = 90º
Volume	1355.4(3) $Å^3$
Z	2
Calculated density	1.289 mg/m^3
$F_{(000)}$	552
Crystal size	0.36 mm × 0.18 mm × 0.06 mm
Theta range for data collection	1.71-28.15º
Reflections collected	8117
Goodness-of-fit on F^2	1.008
Final R indices [I > 2σ(I)]	R_1 = 0.0350, wR_2 = 0.0729
R indices (all data)	R_1 =0.0632, wR_2 =0.0868
Largest diff. peak and hole	0.726 and -0.696 e $Å^{-3}$

time of two phases 15 min. Pd(II) loaded in organic phase could be stripped efficiently using an ammonia solution. X-Ray crystal structure determination revealed $Pd(DIS)_2Cl_2$ square-planar complex in which DIS acts as a neutral unidentate ligand coordinated with palladium(II) *via* the S atom of the DIS.

ACKNOWLEDGEMENTS

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