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Study on Mechanism of Extraction of Palladium(II) with 2-Ethylhexyl Benzimidazole Sulfide

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The mechanism of extraction of Pd(II) with 2-ethylhexyl benzimidazole sulfide was studied. Experimental results show that the distribution coefficient of Pd(II) was not affected by the H^+ concentration, but decreased dramatically with the increase of Cl^- concentration in hydrochloric acid. $PdCl_2$·2-ethylhexyl benzimidazole sulfide complex has been identified with the infrared spectrum, UV-visible spectrum and slope. The possible mechanism of palladium extraction with 2-ethylhexyl benzimidazole sulfide determined to be neutral coordination. It reveals that 2-ethylhexyl benzimidazole sulfide coordinates with Pd(II) *via* the benzimidazole N atom and the molar ratio of 2-ethylhexyl benzimidazole sulfide to Pd(II) was 2:1.

Keywords: Palladium(II), Extraction, Mechanism, 2-Ethylhexyl benzimidazole sulfide.

INTRODUCTION

Palladium, as an element of the most important noble metals, plays a decisive role in the performance of exhaust systems and is widely used in the synthesis of many materials, from polymers to pharmaceuticals[1-3]. As Pd(II) can form a number of complexes which are soluble in organic solvents, solvent extraction has become an advanced technique in the recovery and separation of palladium from aqueous solutions.

Various reagents, including trialkyl amines, Schiff base, 8-hydroxyquinoline, sulphur-containing extractants phosphor-containing extractants, have been studied on the solvent extraction of Pd(II)[4-15]. Sulphur-containing extractants have been considered as a most efficient extractant for extraction of Pd(II) from hydrochloric acid solution. Palladium(II) was strongly extracted by 2-ethylhexyl benzimidazole sulfide which was dissolved in toluene in a lower concentration of hydrochloric acid solution[16]. The mechanism of extraction Pd(II) with 2-ethylhexyl benzimidazole sulfide was studied and the results show that 2-ethylhexyl benzimidazole sulfide acts as a neutral unidentate ligand coordinated with Pd(II) *via* the benzimidazole N atom. This is quite different from general Pd(II) dialkyl sulfide complexes in which sulfides are coordinated with palladium *via* the S atoms of the ligand[17-20].

EXPERIMENTAL

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} HCl 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 weight of 2-ethylhexyl benzimidazole sulfide in different diluents.

Synthesis of the 2-ethylhexyl benzimidazole sulfide: 2-Ethylhexyl benzimidazole sulfide was synthesized according to a simple route and the structure of 2-ethylhexyl benzimidazole sulfide was verified by elemental analysis, ^{1}H NMR, ^{13}C NMR and mass spectra. These results of elemental analysis, ^{1}H NMR, ^{13}C NMR and mass spectra were as same as the document[16].

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. Percentage extraction of Pd(II) was calculated according to eqn. 1:

$$E\ (\%) = \frac{(C_{ini} - C_{fin})}{C_{ini}} \times 100$$

where C_{ini} is metal ion concentration of organic phase, C_{fin} is the metal concentration of stock solution before extraction.

RESULTS AND DISCUSSION

Extraction behavior of 2-ethylhexyl benzimidazole sulfide (EHBMS): Extractions were carried out by shaking equal volumes (10 mL) of the Pd(II) aqueous solution and 2-ethylhexyl benzimidazole sulfide dissolved in toluene with the 2-ethylhexyl benzimidazole sulfide concentration varying from 0.001 to 0.01 mol L^{-1}. It was found the percentage extraction of Pd(II) increases as the 2-ethylhexyl benzimidazole sulfide concentration increases and 0.005 mol L^{-1} 2-ethylhexyl benzimidazole sulfide was needed for quantitative extraction of Pd(II) from HCl aqueous solution containing 100 mg L^{-1} Pd(II) (Fig. 1). The effect of HCl 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, showing that quantitative extraction of Pd(II) occurred at 0.2 mol L^{-1} HCl.

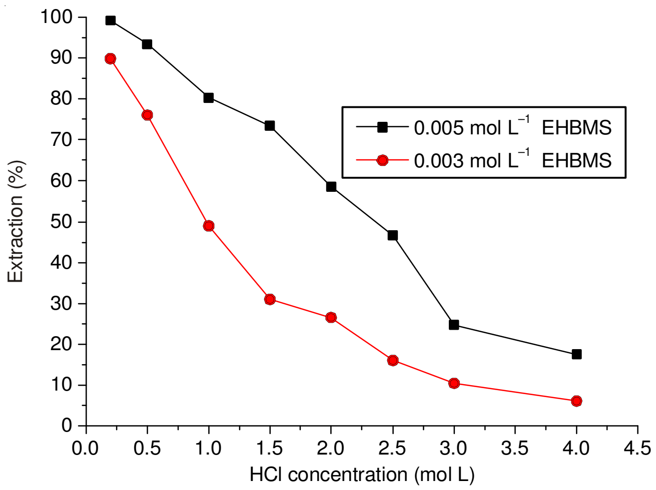

Fig. 1. Effect of EHBMS concentration on the extraction of Pd(II)

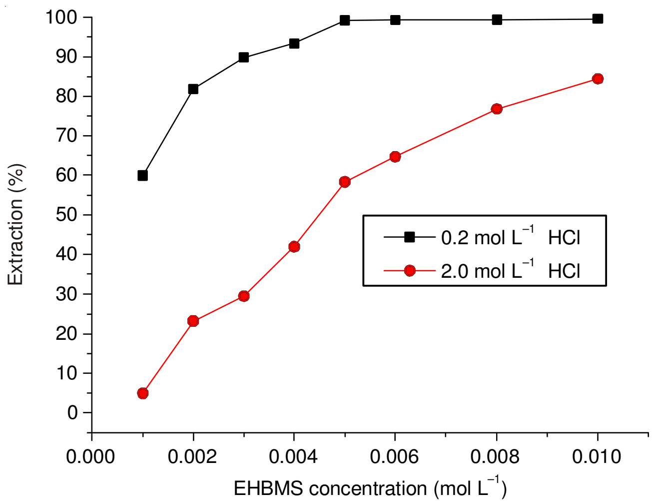

Fig. 2. Effect of HCl concentration on the extraction of Pd(II)

Mechanism of extraction Pd(II) with 2-ethylhexyl benzimidazole sulfide: There are two different mechanism of extraction Pd(II) from hydrochloric acid solution with different extractant. It is possible that coordinate compound was formed between Pd(II) and 2-ethylhexyl benzimidazole sulfide, the chemical reaction equation may be depicted as:

$$PdCl_4^{2-} + 2EHBMS_{(O)} \rightleftharpoons [Pd(EHBMS)_2Cl_2]_{(O)} + 2Cl^- \quad (2)$$

Furthermore, another chemical reaction would carry out and the chemical reaction equation was showed as:

$$PdCl_4^{2-} + 2EHBMS + 2H^+ \rightleftharpoons [EHBMSH^+]_2{\cdot}PdCl_4^{2-} \quad (3)$$

It is obvious that H^+ did not participate in the chemical reaction eqn. (2) and can not affect the distribution ratio, while H^+ was reactant in chemical reaction eqn. (3), affecting the distribution ratio. We have studied the dependence of Pd(II) extraction upon the acidity to determinate which reaction acted. H^+ concentration was varied from 0.2 to 2.0 mol L^{-1} while maintaining a constant ionic strength (Cl^- = 2.0 mol L^{-1}) by adding NaCl. Experimental results are shown in Fig. 3, indicating plot of log D *vs.* log [H^+] yielded a straight line with a slope about 0 respectively. Experimental results showed the variation of H^+ concentration did not affect the distribution ratio, as is similar to petroleum sulfoxide and dialkyl sulfoxide cases in the extraction of Pd(II) at low acidity[21,22]. So the extraction of Pd(II) by 2-ethylhexyl benzimidazole sulfide may form coordinate compound of [Pd(2-ethylhexyl benzimidazole sulfide)$_2Cl_2]_{(O)}$.

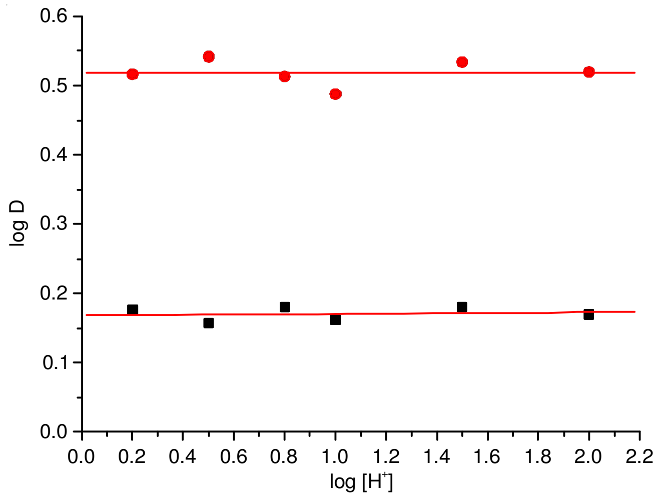

Fig. 3. log D as a function of log [H^+]

Stoichiometry of Pd(II)-EHBMS complex: The ratio of metal ion extractant in the extracted species can be determined by plotting log D (D: distribution ratio) *vs.* log [extractant] at constant pH[23]. As can be seen in Fig. 4, plots of log D *vs.*

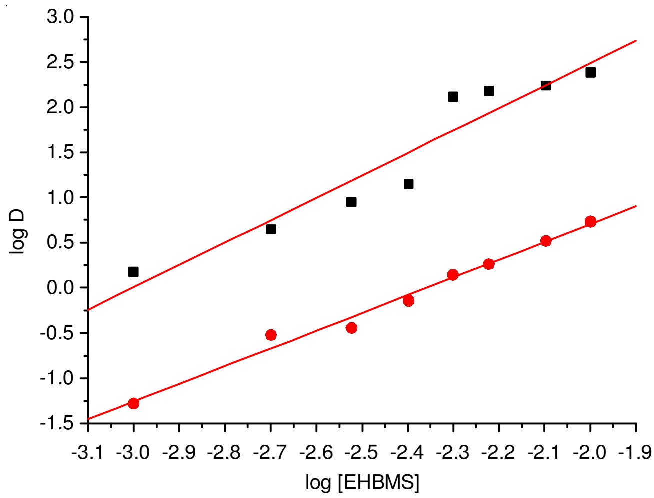

Fig. 4. log D as a function of log [EHBMS]

log [EHBMS] for the extraction of Pd(II) at 0.2 and 2.0 mol L^{-1} HCl yield slopes of 2.47 and 1.96, respectively, indicating that two 2-ethylhexyl benzimidazole sulfide molecules were involved in the extracted Pd(II)-EHBMS adduct.

Furthermore, we have studied the dependence of Pd(II) extraction upon the acidity. Since the extraction percentage of Pd(II) decreased drastically with the increasing of hydrochloric acid concentration, while the extraction was independent on acidity, an increase in Cl^- concentration should have a negative effect on the extraction of Pd(II). Such a tendency was actually observed by adding NaCl to the extraction system. A plot of log D *vs*. log [Cl^-] yielded a straight line with a slope of about -2.05 (Fig. 5), showing that two Cl^- ions were released during the extraction of Pd(II) and formed coordinate compound of $[Pd(EHBMS)_2Cl_2]_{(O)}$.

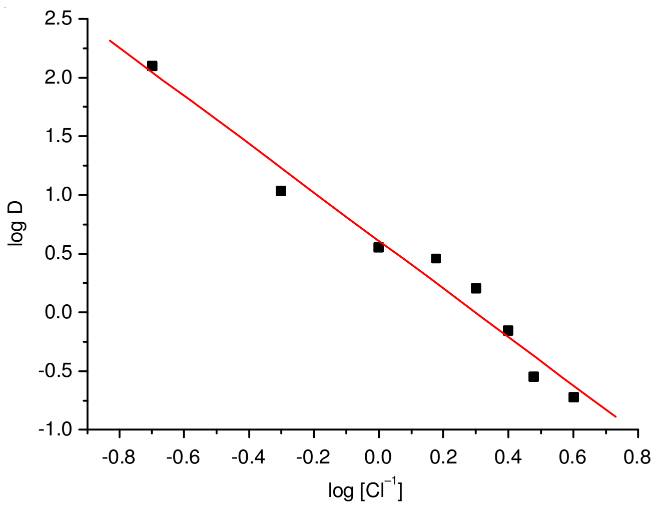

Fig. 5. log D as a function of log [Cl^-]

IR spectra of extracted Pd(II)-EHBMS adduct: Extracted Pd(II)-EHBMS adduct may be prepared by following procedure: 0.05 mol L^{-1} EHBMS in toluene was shaken with aqueous solution of Pd(II) (1.0 g L^{-1} in 0.2 mol L^{-1} HCl) many times until a saturated extraction organic phase was obtained. After removing toluene by distillation, a yellowish solid complex was obtained and dried in vacuum. IR spectra of 2-ethylhexyl benzimidazole sulfide and Pd(II)-EHBMS complex is shown in Fig. 6. The ν(C=N) of free 2-ethylhexyl benzimidazole sulfide ligand appears as a absorption at 1621 cm^{-1}, while the characteristic ν(C=N) absorption appears at 1618 cm^{-1} in Pd(II)-EHBMS complex and it does shift to low frequency, indicating that 2-ethylhexyl benzimidazole sulfide is coordinated with Pd(II) *via* N atom on the benzimidazole ring[24-25].

In addition, the ν(C-N) of free 2-ethylhexyl benzimidazole sulfide ligand appears as a strong absorption at 1402 cm^{-1}, while the characteristic ν(C-N) absorption weakens in extracted complex, which is similar to the binding of benzimidazole derivatives to a number of other metals reported previously[26,27], indicating that 2-ethylhexyl benzimidazole sulfide is coordinated with Pd(II) *via* N atom on the benzimidazole ring.

Ultraviolet and visible spectra of 2-ethylhexyl benzimidazole sulfide and Pd(II)-EHBMS complex: 0.1 mol L^{-1} EHBMS in toluene was shaken with Pd(II) aqueous solution (1.0 g L^{-1} in 0.2 mol L^{-1} HCl) many times until a saturated

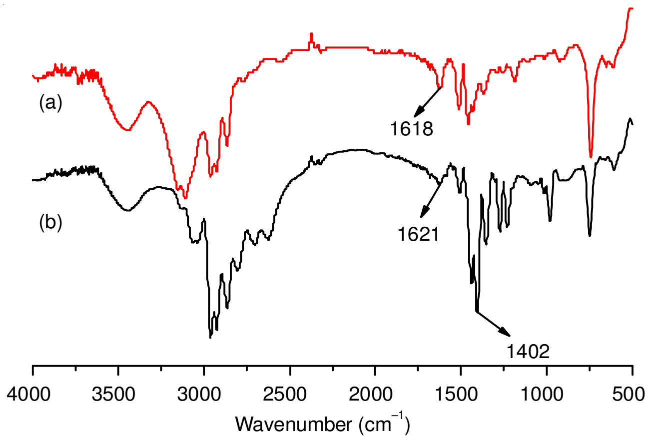

Fig. 6. Infrared spectra of EHBMS; (a) and Pd(II)-EHBMS complex (b)

extraction organic phase was obtained. After removing toluene by distillation, a yellowish solid complex was obtained and dried in vacuum. Visible spectra of Pd(II), 2-ethylhexyl benzimidazole sulfide and Pd(II)-EHBMS complex are shown in Fig. 7 and ultraviolet spectra of 2-ethylhexyl benzimidazole sulfide and Pd(II)-EHBMS complex is showed in Fig. 8.

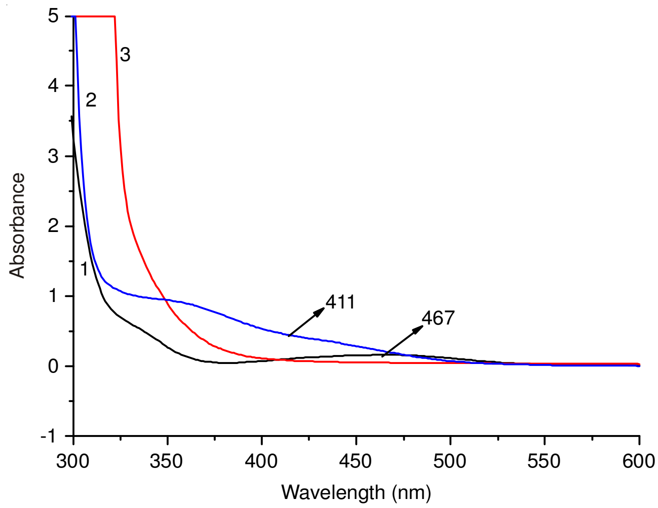

Fig. 7. Visible spectra of Pd(II), EHBMS and Pd(II)-EHBMS complex 1-Pd(II) in 0.2 mol L^{-1} HCl; 2-Pd(II)-EHBMS complex; 3-EHBM

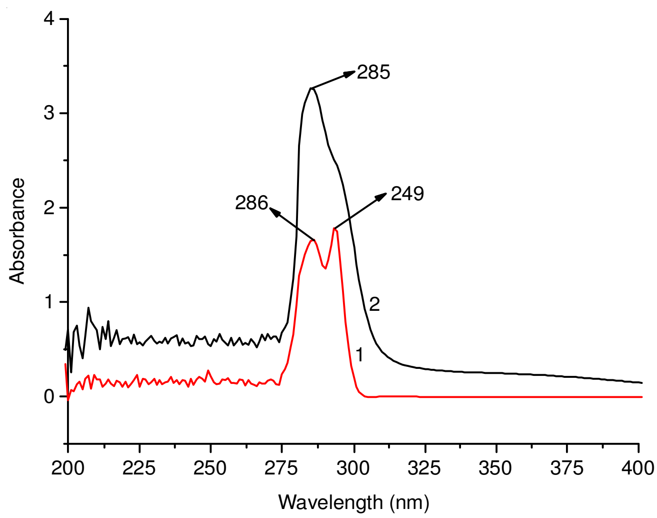

Fig. 8. Ultraviolet spectra of EHBMS (1) and Pd(II)-EHBMS complex(2)

As can be seen in Fig. 7, the aqueous solution of Pd(II) (1.0 g L^{-1} in 0.2 mol L^{-1} HCl) appears as a absorption at 467 nm and 2-ethylhexyl benzimidazole sulfide does not absorption in 400-600 nm, while the new weak absorption peak appears in extracted complex at 411 nm, which is indicated that 2-ethylhexyl benzimidazole sulfide is coordinated with Pd(II) and formed Pd(II)-EHBMS complex[28].

Fig. 8 showed that 2-ethylhexyl benzimidazole sulfide appears as a strong absorption at 249 nm, 286 nm and the new absorption peak appears at 285 nm of Pd(II)-EHBMS complex, indicating that the extraction of Pd(II) by 2-ethylhexyl benzimidazole sulfide may form coordinate compound of Pd(II)-EHBMS complex[28].

$PdCl_2$·2EHBMS complex has been identified with the infrared spectrum, UV-visible spectrum and slope and the characteristic was as same as the document[27-29]. The possible structure of $PdCl_2$·2EHBMS is shown in Fig. 9.

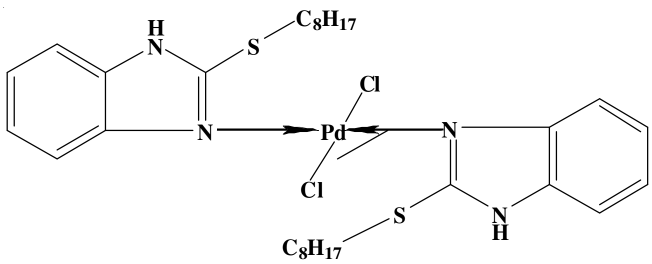

Fig. 9. Structure of Pd(II)-EHBMS complex

Conclusion

The mechanism of extraction Pd(II) with 2-ethylhexyl benzimidazole sulfide was studied. The percentage extraction of Pd(II) increases as the extractant concentration increases and 0.005 mol L^{-1} 2-ethylhexyl benzimidazole sulfide was needed for quantitative extraction of Pd(II) from HCl aqueous solution containing 100 mg L^{-1} Pd(II). Experimental results show that the distribution coefficient of Pd(II) was not affected by the H^+ concentration, but decreased dramatically with the increase of Cl^- concentration in hydrochloric acid. Pd(II)-EHBMS complex has been identified with the infrared spectrum, UV-visible spectrum and slope. The possible mechanism of palladium extraction with 2-ethylhexyl benzimidazole sulfide determined to be neutral coordination and formed $PdCl_2$·2EHBMS complex. It reveals that 2-ethylhexyl benzimidazole sulfide coordinates with Pd(II) *via* the benzimidazole N atom and the molar ratio of 2-ethylhexyl benzimidazole sulfide to Pd(II) was 2:1 respectively.

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