

Mechanism of extracting palladium(II) with cyclic sulfoxide derivatives^①

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Abstract: The extraction ability of palladium(II) from acidic media with cyclic sulfoxide derivatives — α -Dodecyltetrahydrothiophene 1-Oxide (DTMSO), α -octyltetrahydrothiophene 1-Oxide (OTMSO) and α -butyltetrahydrothiophene 1-Oxide (BTMSO) was investigated. The extracting efficiency of cyclic sulfoxide derivatives decreased with the increasing of acidity in the lower acidity, and the efficiency became stable with the change of acidity in the higher acidity. The extraction reaction of palladium(II) with DTMSO is exothermic, and extraction reaction of palladium(II) is endothermic when OTMSO or BTMSO were used as extracting reagents. The coordination number was studied by slope method. The results indicate that coordination number is 2, and the composition of complex is $(PdCl_2) \cdot 2RTMSO$. FT-IR spectra were used to analyze the structure of complex and coordinated atom in complex, Pd is coordinated with both oxygen and sulfur atom in $S=O$ group in sulfoxide derivatives.

Key words: cyclic sulfoxide; palladium; solvent extraction; tetrahydrothiophene 1-Oxide

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1 INTRODUCTION

Extraction reagents containing sulfur have been attracting much attention for their excellent extraction ability to precious metals^[1]. The dialkyl sulfides have been chosen as extractant of precious metals because of their good physical properties for solvent extraction^[2-4]. Nevertheless, slow extraction kinetic is an obvious problem in the extraction of Pd(II) with dialkyl sulphides. Symmetrical sulfoxides RSO (where R = alkyl) were proposed for using in separation of rare metals by YUAN et al^[5]. The extraction of palladium(II) from hydrochloric acid solution with α -butyloctyl sulfoxide was studied by XIANG et al^[6]. The mechanism of extracting palladium(II) with dialkyl sulfoxide from hydrochloric acid was discussed by ZHANG et al^[7]. The far-infrared spectrum, visible, and violet spectrum of KSO-Pd(II) complex show that the extractive exists as the structure of chloride-bridged binuclear trans-(PdL-Cl₂)₂. Both sulfur and oxygen atom in KSO can coordinate with palladium(II). CHEN et al^[8] investigated the extraction of Gold(III), palladium(II) and platinum(IV) with PSO. The separation of palladium from solutions containing platinum(IV) was discussed. The synthesis of cyclic sulfoxide derivative DTMSO as novel reagent to investigate its extraction behavior for Gold(III) and palladium(II) from chloride media was reported^[9, 10]. The reagents are expected to be much higher selectivity and reactivity for

precious metal ions classified as soft acid than conventionally used dialkyl sulfoxides because of their asymmetrical structure.

2 EXPERIMENTAL

2.1 Reagents

Synthesis of cyclic sulfoxide derivatives was described in Ref. [10]. Determined by element analysis, the purity of sulfoxides is more than 98%. Their chemical structure is shown in Fig. 1. An organic solution was prepared by diluting each extractant into sulfonated kerosene to a desired concentration. An aqueous solution was prepared by dissolving palladium chloride to a desired concentration into aqueous hydrochloric acid. The other reagents are AR grade.

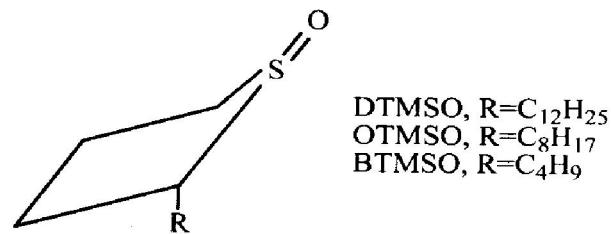


Fig. 1 Configuration of sulfoxides(RTMSO)

2.2 Procedure

Equal volume(3 ml) solution of both phases were mixed and shaken vigorously for fifteen minutes, which was sufficient enough to attain equilibrium in a

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preliminary experiment. After phase separation, aqueous concentration of palladium(II) in aqueous phase was determined by WFX-IB atom absorption spectrophotometer. These results are further used to estimate the extraction efficiency ($E\%$) of palladium(II). The amount of extracted metal ions were calculated from the differences of the metal concentrations in the aqueous phase between before and after the extraction. The loaded organic phases were determined with a Vextor 33 FT-IR spectrophotometer.

3 RESULTS AND DISCUSSION

3. 1 Influential factors of extracting palladium with cyclic sulfoxide derivatives

3. 1. 1 Effects of concentration of RTMSO on extraction efficiency

The effects of the concentration of RTMSO on percentage extraction of palladium(II) are shown in Fig. 2. In the concentration region of cyclic sulfoxide derivatives below 0.4 mol/L, as can be seen from these figures, the extraction efficiency of palladium(II) by three cyclic sulfoxide derivatives all increases with increasing extractant concentration at the low hydrochloric acid concentration (0.1 mol/L). The palladium(II) is extracted to the extent of only about 30% in the sulfoxides concentration region lower than 0.025 mol/L while it increases up to 99% in the concentration region higher than 0.2 mol/L by DTMSO and OTMSO. The extraction efficiency of palladium(II) with BTMSO is different from other two sulfoxides. The extraction efficiency of palladium(II) by BTMSO is less than 80% over the whole sulfoxide concentration region, and the extraction efficiency of palladium with the maximum of 77% is at 0.3 mol/L. As described above, the extracting efficiency of Pd(II) by cyclic sulfoxide derivatives is arranged that the order from large to small is DTMSO, OTMSO and BTMSO. This means that the extracting efficiency of palladium(II) by sulfoxides decreases with decreasing branch chain length.

3. 1. 2 Effects of concentration of HCl on extraction efficiency

The effects of the concentration of hydrochloric acid on extraction efficiency of palladium(II) are shown in Fig. 3. In the concentration region of HCl below 4 mol/L, the extraction of palladium(II) from hydrochloric acid solutions with cyclic sulfoxide derivatives in sulfonated kerosene was compared. As can be seen from Fig. 3, the extraction efficiency order of palladium(II) is DTMSO, OTMSO and BTMSO at the same concentration of hydrochloric

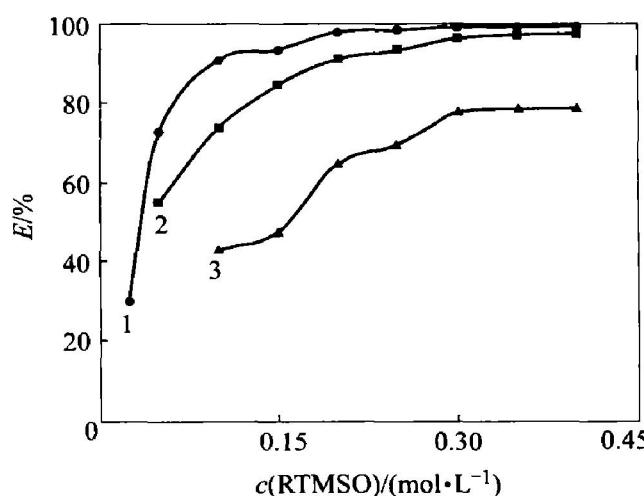


Fig. 2 Dependence of extraction efficiency of Pd on sulfoxide concentration
1—DTMSO; 2—OTMSO; 3—BTMSO

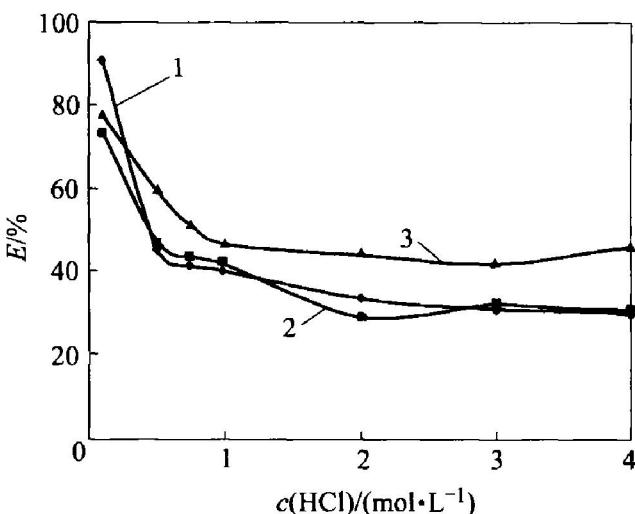


Fig. 3 Extraction of 0.89 g/L Pd from different concentration of hydrochloric acid solution by RSO in sulfonated kerosene
1—0.1 mol/L DTMSO; 2—0.1 mol/L OTMSO;
3—0.3 mol/L BTMSO

acid. The plots of the extraction efficiency of palladium(III) appear the minimum value of extraction efficiency at 1–2 mol/L. The extraction efficiency increases in the small extent with increasing hydrochloric acid concentration in the concentration region higher than 2 mol/L. It is predicted that the mechanism of extracting palladium(II) may change in the whole acid scope when DTMSO and OTMSO would be used as extractants. Extraction efficiency of palladium(II) does not change in the low concentration region of acidity (less than 3 mol/L) when BTMSO was used as extractant, while the extraction efficiency of palladium(II) decreases with increasing aqueous acidity because of the competing extraction being brought from hydrochloric acid.

3. 1. 3 Effects of temperature on extraction efficiency

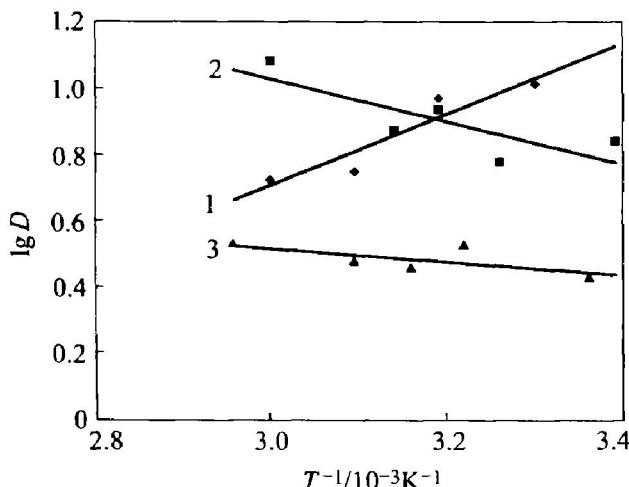


Fig. 4 Effect of temperature on distribution ratio

1—0.1 mol/L DTMSO; 2—0.1 mol/L OTMSO;
3—0.3 mol/L BTMSO

The effects of the temperature (T) of extraction on distribution ratio (D) are shown in Fig. 4. The extraction of 890 mg/L palladium was carried out at different temperatures with different amounts of extractant at the same acidity (0.1 mol/L).

In accordance with thermodynamic equilibrium equation:

$$\frac{K_{ex}}{T} = \frac{-\Delta H^\ominus}{RT^2} \quad (1)$$

When the concentration of extractants and aqueous acidity is fixed, K_{ex} can be replaced by D . The relation of distribution ratio D and T can be shown as the following equation:

$$\ln D = \frac{-\Delta H^\ominus}{RT} + C \quad (2)$$

Plots of the distribution ratio vs temperature have excellent linearity from Fig. 4. For DTMSO, the distribution ratio decreases with increasing temperature. It can be seen that the extracting reaction is an exothermal reaction. However, for OTMSO or BTMSO, the distribution ratio increases with the increasing of temperature. This shows that extraction reaction of palladium(II) is endothermic when OTMSO or BTMSO is used as extracting reagent.

Based on the reaction isotherm, the reaction heat can be calculated as follows:

$$\Delta H_{DTMSO}^\ominus = -20.7 \text{ KJ/mol}$$

$$\Delta H_{OTMSO}^\ominus = 12.2 \text{ KJ/mol}$$

$$\Delta H_{BTMSO}^\ominus = 3.6 \text{ KJ/mol}$$

3.2 Discussion of mechanism of extracting palladium(II)

3.2.1 Determination of coordination number

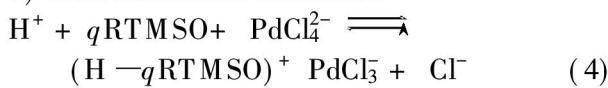
Because sulfoxide type materials are neutral extractants as TBP, the extraction mechanism of them is similar to TBP. Considering the chemical behavior of palladium in aqueous phase, there are two following ways to extract palladium(II) from hydrochloric

acid solutions with cyclic sulfoxide derivatives:

1) Neutral solvent extraction:



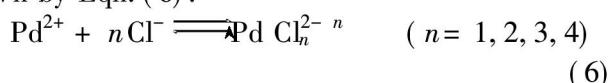
2) Acid association extraction:



$$K_{ex} = \frac{[(PdCl_2) \cdot qRTMSO]}{[Pd^{2+}] [Cl^-]^2 [RTMSO]^q} \quad (5)$$

The corresponding equilibrium constant K_{ex} of Eqn. (3) is defined by Eqn. (5).

Ion equilibrium of Pd(II) in aqueous phase is shown by Eqn. (6):



The cumulative stability constants as follows:

$$\beta_n = \frac{[PdCl_n^{2-n}]}{[Pd^{2+}] [Cl^-]^n};$$

$$\lg \beta_1 = 4.40; \lg \beta_2 = 7.74; \lg \beta_3 = 10.12;$$

$$\lg \beta_4 = 11.50$$

The concentration of palladium in aqueous phase can be shown as Eqn. (7):

$$c(Pd) = [Pd^{2+}] + [PdCl^+] + [PdCl_2] + [PdCl_3^-] + [PdCl_4^{2-}] = [Pd^{2+}] (1 + \sum \beta_n [Cl^-]^n) \quad (7)$$

The distribution ratio of palladium is defined as:

$$D = \frac{c(Pd_{(0)})}{c(Pd)} = \frac{[(PdCl_2) \cdot qRTMSO]}{c(Pd)} \quad (8)$$

In accordance with Eqns. (5), (7) and (8), Eqn. (9) can be obtained.

$$\lg D = \lg K_{ex} + q \lg [RTMSO] + \lg \frac{[Cl^-]^2}{1 + \sum \beta_n [Cl^-]^n} \quad (9)$$

The metal-distribution data for concentration of extractant is plotted in the form of $\lg D$ vs $\lg [RTMSO]$, then a straight line should be obtained with a slope equal to the number of molecules of incorporated into the extracted complex (see Eqn. 10).

$$\lg D = \lg K_{ex} + q \lg [RTMSO] + C \quad (10)$$

For the same reason to Eqn. (4), the relation between D and $[RTMSO]$ can be shown as Eqn. (11).

$$\lg D = \lg K_{ex} + q \lg [RTMSO] + \lg [H^+] + C \quad (11)$$

Representative plots are shown in Fig. 5 for the extraction of palladium(II) is 0.1 mol/L hydrochloric acid solutions by DTMSO, OTMSO and BTMSO. The slopes of these plots are obtained as follows: $q_{DTMSO} = 2.2$, $q_{OTMSO} = 2.2$ and $q_{BTMSO} = 1.87$. The results show that the coordination number is 2 when DTMSO, OTMSO or BTMSO is used as extractant.

3.2.2 Confirmation of coordination atom in complex

The structure of extracted complexes was discussed by FT-IR spectra. It was reported that the

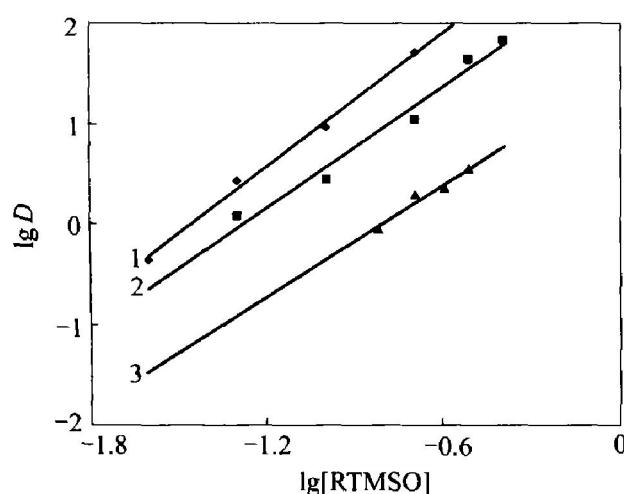


Fig. 5 Dependence of distribution ratio on sulfoxide concentration for extraction
from $0.1 \text{ mol} \cdot \text{L}^{-1}$ HCl
1—DTMSO; 2—OTMSO; 3—BTMSO

electron structure of sulfoxide could be shown in the form of vibration mode as follows (see Fig. 6).

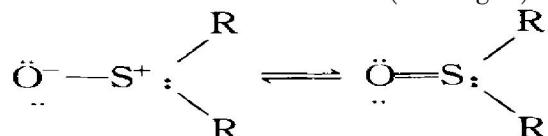


Fig. 6 Electron structure of sulfoxide

It is generally accepted that there is a higher frequency $\text{S}=\text{O}$ stretch of RSO bonded to metal through the sulfur atom because of the increase of the $\text{S}=\text{O}$ bond order. Conversely, co-ordination through the oxygen atom is considered to lower the $\text{S}=\text{O}$ bond order and hence lower the frequency of the SO stretch. FT-IR of organic phase before and after extracting could be compared to confirm the chemical bond between palladium and sulfoxide in the extracted complexes (see Figs. 7, 8 and 9).

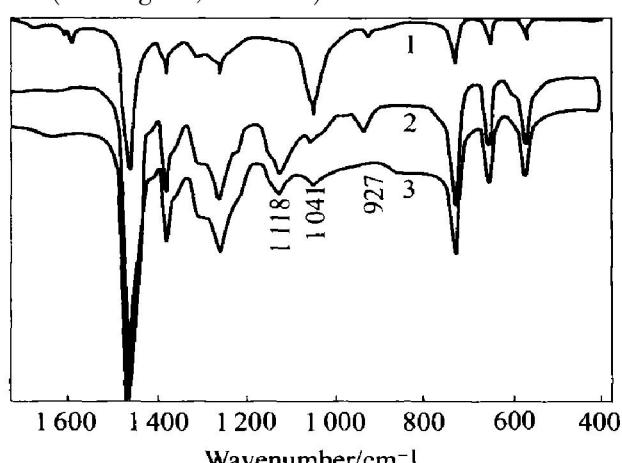


Fig. 7 FT-IR spectra of organic phases
1—Unloaded DTMSO;
2—Loaded DTMSO of Pd(II) (0.1 mol/L HCl);
3—Loaded DTMSO of Pd(II) (2 mol/L HCl)

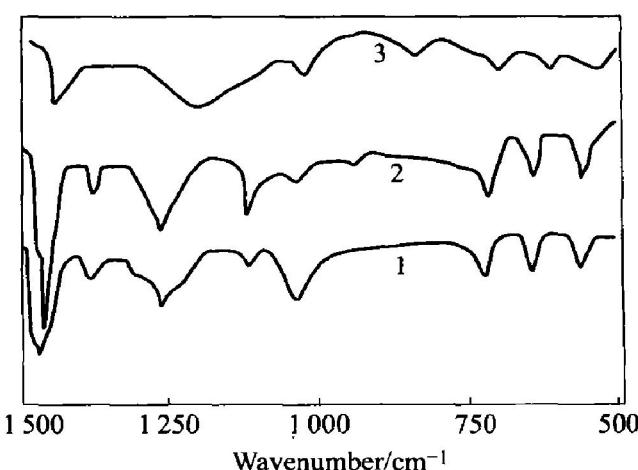


Fig. 8 FT-IR spectra of loaded OTMSO
1—Loaded organic phase of HCl;
2—Loaded organic phase of palladium (0.1 mol/L HCl);
3—Loaded organic phase of palladium (2 mol/L HCl);

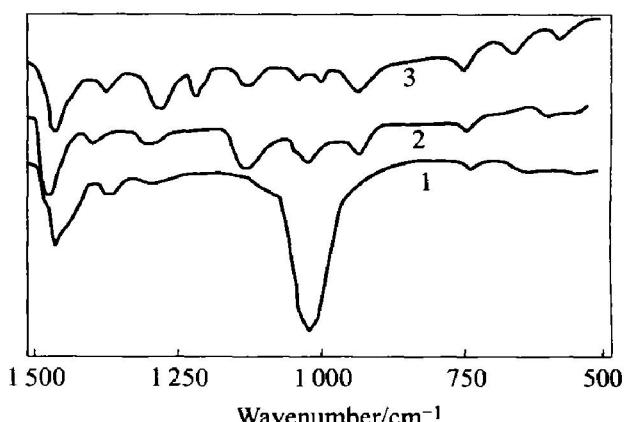


Fig. 9 FT-IR spectra of loaded BTMSO
1—Loaded organic phase of palladium (0.1 mol/L HCl);
2—Loaded organic phase of HCl;
3—Loaded organic phase of palladium (2 mol/L HCl);

The characteristic absorption peak of sulfoxide derivatives is in the region from 1010 cm^{-1} to 1045 cm^{-1} before extracting palladium (II) from Fig. 7. The characteristic absorption peak of DTMSO is at 1041 cm^{-1} . The loaded DTMSO got from low acidity media has two new absorption peaks at 927 cm^{-1} and 1118 cm^{-1} . From both their situation and strength, they could be unambiguously assigned as SO stretch of oxygen-bonded complexes and sulfur-bonded complexes. The complex with oxygen-palladium bond contributed the former, and the complex with sulfur-palladium bond contributed the latter. After pre-reaction with 2 mol/L HCl hydrochloric acid, the situation and strength change of characteristic absorption peak was not clear. The absorption peak becomes blunt at 1095 cm^{-1} . In higher acidity region, DTMSO extracts palladium(II) in the form of acid association extraction^[8], which the extraction of palladium(II) is therefore ion-pair formation between solvated hydronium cations and the chlorometallate anion. The

reaction mode is consistent with Eqn. (2). Palladium competes with hydrion in the extracted complex, then inter-coordination transfer occurs because of the stronger binding energy of palladium-sulfur, thus the peak at 1118 cm^{-1} appears. It was reported that the *cis*-, *trans*-configuration of complex can be estimated on the basis of the symmetry of characteristic absorption peak of sulfoxides. There is excellent symmetry peak at 927 cm^{-1} , then it seems to show that the *trans*-sulfoxide exists in complex coordinated with oxygen in SO group.

The FT-IR spectra of loaded OTMSO are shown in Fig. 8. From Fig. 8, the characteristic absorption peak of OTMSO is at 1016 cm^{-1} . The character of the loaded OTMSO got from low acidity media is similar to that of DTMSO. The peak brought from the complex with oxygen-palladium bond is at 934 cm^{-1} , and the peak brought from the complex with sulfur-palladium bond is at 1117 cm^{-1} . After pre-reaction with 2 mol/L hydrochloric acid, the peak shifts from 1016 cm^{-1} to 1033 cm^{-1} due to the extraction of hydrochloric acid. The inter-ligand transfer occurs in complexes which were obtained from high acidity media. There is difference between DTMSO complex and OTMSO complex. In complex with inter-ligand exchange, the peak contributed by the complex coordinated with oxygen atom of OTMSO is at 860 cm^{-1} , and the peak contributed by the complex coordinated with sulfur atom of OTMSO is at 1224 cm^{-1} .

It can be seen that the characteristic absorption peak of BTMSO is at 1012 cm^{-1} from Fig. 9. The character of the loaded BTMSO got from low acidity media is similar to that of DTMSO and OTMSO. The peak from the complex with oxygen-palladium bond is at 922 cm^{-1} , and the peak contributed by the complex with sulfur-palladium bond is at 1116 cm^{-1} . The peak shifts from 1012 cm^{-1} to 1029 cm^{-1} after pre-reaction with 2 mol/L hydrochloric acid solutions. The peak of 1029 cm^{-1} disappears, and two new blunt peaks appear at 954 cm^{-1} and 1180 cm^{-1} after extraction of palladium (II). The complex with sulfur-palladium bond contributes to the former, and the complex with oxygen-palladium bond contributes to the latter. Comparing the two peaks, the absorbance of complex with oxygen-palladium bond seems more than another with sulfur-palladium bond.

3.2.3 Discussion of extracting palladium mechanism

The results from FT-IR spectra and slope method indicate that the reactions are neutral solvent complexing extraction in lower acidity when DTMSO or OTMSO is used as extractant, in which the composition of extracted complexes is $\text{PdCl}_2(\text{RTMSO})_2$,

and palladium is coordinated with sulfur atom and oxygen atom in S—O bond. The reaction mode is consistent with Eqn. (1). In higher acidity region, DTMSO or OTMSO extracts palladium (II) in the form of acid association extraction. Palladium competes with hydrion in the extracted complex, then inter-coordination transfer occurs, and the composition of complex is $[\text{PdCl}_2(\text{RTMSO})_2] \cdot [\text{H} \cdot (\text{RTMSO} \cdot n\text{H}_2\text{O}) \text{Cl}]$. The reaction mode is consistent with Eqn. (2). BTMSO extracts palladium (II) in the mode of neutral solvent complexing extraction in the studied region. The reaction mode is consistent with Eqn. (1). Both sulfur-palladium bond and oxygen-palladium bond appear in extracted complex when BTMSO is used as extractant.

In accordance with soft-hard acid-base rule, sulfur atom in SO bond seems easier to coordinate with palladium(II), while oxygen atom seems difficult to coordinate with palladium(II). However, the situation of oxygen was very protruded. The stronger steric effect was favorable for coordination of oxygen and palladium when the cyclic sulfoxide derivative had longer branch chain. In extracted complex produced by cyclic derivatives with longer branch chain, such as DTMSO and OTMSO, palladium coordinated with oxygen in both extraction modes. As to BTMSO with four carbon in its branch chain, the ability of coordination through sulfur increased with the decreasing space hindrance. On the other hand, the coordination ability of oxygen increased with increase in density charge when branch chain length decreased. This means that the coordinating ability of oxygen and sulfur both increased, thus oxygen and sulfur could both coordinate with palladium when BTMSO was used as extractant.

The order of extraction of palladium (II) from weak to strong is BTMSO, OTMSO and DTMSO, that is to say, the extracting ability decreases with the decreasing branch chain length. The order can be explained as follows: although the larger charge density of oxygen and smaller space hindrance of sulfur mean stronger complexing ability that it is favorable for producing complex, the solubility of extracted complex increases with decreasing branch chain length. The final result is that percentage extraction decreases when the number of branch chain carbon decreases.

4 CONCLUSIONS

On the basis of experimental results and the analysis of FT-IR spectra, the following results can be obtained.

- 1) The extraction of Pd(II) is in the same mechanism, i. e. neutral solvent extraction in lower acidity media and acid association extraction in higher acidity media, when DTMSO and OTMAO act as ex-

tractants.

2) The mechanism of extracting Pd(II) is neutral solvent extraction when BTMSO is used as extractant.

3) In complex, the inter-ligand transfer occurs. The rule of transfer follows the soft-hard acid-base theory, space hindrance theory and induction effect theory.

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