

EXTRACTION EQUILIBRIUM OF PALLADIUM IN AQUEOUS ACID SOLUTION WITH DI(2-ETHYLHEXYL) AMINE IN TOLUENE

YOSHINOBU KAWANO, RYOUSUKE MORITA AND TAKANAO MATSUI

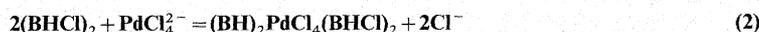
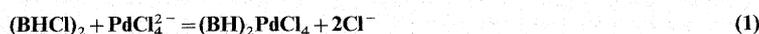
Faculty of Engineering, Miyazaki University, Miyazaki 889-21

KAZUO KONDO AND FUMIYUKI NAKASHIO

Department of Organic Synthesis, Kyusyu University, Fukuoka 812

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Extraction equilibria of hydrochloric acid by toluene solution of a long-chain secondary alkyl amine, di(2-ethylhexyl) amine, and of palladium from aqueous hydrochloric acid by the toluene solution of the amine were studied under various experimental conditions. The results were analyzed by the following reaction model:



Water content and IR spectra for alkyl ammonium chloride salt solution equilibrated with aqueous palladium chloride solution were also measured to estimate the complexes formed by the reactions. The amine reacts with hydrochloric acid to form dimer of ion-paired ammonium chloride salt together with water as $(\text{BHCl})_2 \cdot (2/3)\text{H}_2\text{O}$. The results for the extraction equilibrium of palladium by the amine were interpreted by a reaction model in which two kinds of ion-paired species, $(\text{BH})_2\text{PdCl}_4$ and $(\text{BH})_2\text{PdCl}_4(\text{BHCl})_2$ are formed. Water dissolved in the organic solution was confirmed not to take part in the formation of the complexes. The equilibrium constants for reactions (1) and (2) were determined as 1.0×10^2 and $2.6 \times 10^4 \text{ m}^3/\text{kmol}$ respectively.

Introduction

Precious metals are now used in various ways such as industrial catalysts, electronic parts and pretreatment reagents in gilding. The amount of these metals scrapped is increasing year by year. It seems important to recover and reclaim them as raw materials. Solvent extraction has been studied as a method for recovering these metals.^{1,12,13)} Many quantitative and qualitative analyses have been made for extraction with hydroxyoximes,^{5,7,8)} organic phosphine^{3,8,12)} or sulfur-containing compounds⁹⁾ as the extractant. Few quantitative studies, however, have been made of the system of extraction with long-chain alkyl amine as the extractant. The distribution ratio of palladium between an aqueous hydrochloric acid solution and an organic solution of tri-*n*-octylamine was reported to vary from 2×10^3 to 10 with change in concentration of hydrochloric acid in the aqueous solution.⁶⁾ The extraction capacities of precious metals increase in the order, primary < secondary < tertiary < quaternary amine.⁶⁾ No studies of the extracted species formed by the reaction or quantitative analyses of the extraction equilibrium and kinetics have yet been made. Quantitative information about the extraction equilibrium is important to the design of the extraction process.

In the present study, the extracted species formed by the reaction between chloro-palladium complex and the ammonium chloride salt of di(2-ethylhexyl) amine were estimated, and the formation constant of the species were determined by analysis of the extraction equilibrium results.

1. Experimental

1.1 Reagents

99.7% di(2-ethylhexyl) amine (hereafter called D2EHA) supplied by Koei Chemical Co. was used as the extractant without further purification. Toluene was used as the diluent. The aqueous solution was prepared by dissolving palladium chloride, lithium chloride and hydrochloric acid in deionized water. All reagents were GR grade Wako Purechemical Co..

1.2 Experimental procedure

1) Extraction of hydrochloric acid by toluene solution of D2EHA Equal volumes of aqueous hydrochloric acid and toluene solution of the amine at various concentrations were shaken in a flask and allowed to attain equilibrium in a water bath thermostated at 303 K. After that, the concentrations of the acid in both solutions were determined by neutralization titration with aqueous sodium hydroxide for the aqueous solution and methanol-butanol mixture solution of potassium hydroxide for the organic solution, using phenolphthalein as an

* Received July 27, 1989. Correspondence concerning this article should be addressed to Y. Kawano.

indicator. Infrared spectra of the organic solution after equilibration were observed to examine the species formed by the reaction between the acid and the amine. The water content of the organic solution was determined by the Karl Fischer method.

2) Extraction equilibrium of palladium by ammonium chloride salt of D2EHA Equal volumes of toluene solution of the amine equilibrated with 0.500 kmol/m³ hydrochloric acid* and the aqueous palladium solution were shaken in a flask at 303 K. After that, the concentration of palladium in the aqueous solution was determined by atomic absorption spectrophotometry. The water content of the organic solution was determined by the Karl Fischer method.

2. Experimental Results and Discussion

2.1 Extraction equilibrium of hydrochloric acid

The equilibrium concentration of the acid in the organic solution, $C_{A,org}$, is plotted against the concentration of the acid in the aqueous solution, $C_{A,aq}$ in Fig. 1. The values of $C_{A,org}$ increase and approach the respective initial concentrations of the amine in the organic solution, C_{B0} , with increasing $C_{A,aq}$. In low $C_{A,aq}$ ranges, the values of $C_{A,org}$ are clustered on a straight line having a slope of 4.0 independently of C_{B0} and are represented as the following equation.

$$C_{A,org} = 6.3 \times 10^5 (C_{A,aq})^4 \quad (1)$$

The extraction ratio of hydrochloric acid, Z , defined by $C_{A,org}/C_{B0}$ is plotted against $C_{A,aq}$ in Fig. 2. The value of Z increases and approaches 1.0 independently of C_{B0} with increasing $C_{A,aq}$. Furthermore, at still higher $C_{A,aq}$ the value of Z increases to more than 1.0. The plotted values cross each other at $C_{A,aq} = 0.02$ kmol/m³. It is not clear what species were formed in the range where Z is smaller than 1.0. In the range where Z is nearly 1.0, the acid is assumed to react with equal moles of the amine. The absorbance of IR spectra of the organic solution equilibrated with the aqueous acid solution are plotted against $C_{A,aq}$ in Fig. 3. The absorption due to $>N^+H_2$ and that due to water in toluene were observed at 2760 and 1600 cm⁻¹ and at 3680 and 3450 cm⁻¹,^{10,11} respectively. Absorbances at 2760 and 1600 cm⁻¹ increase with $C_{A,aq}$ and remain constant at $C_{A,aq}$ greater than 0.05 kmol/m³, at which the value of Z is constant at 1.0 in Fig. 2. The results indicate that the amine reacts with the acid to form an ion-paired species, $R_2N^+H_2Cl^-$ (hereafter called BHCl). However, the absorbances at 3680 and 3450 cm⁻¹ then decrease at $C_{A,aq}$ greater than 6 kmol/m³. In this concentration range the extraction ratio of the acid

* As shown in a later section, the amine was converted completely to alkyl ammonium chloride salt (BHCl)₂ under the experimental conditions.

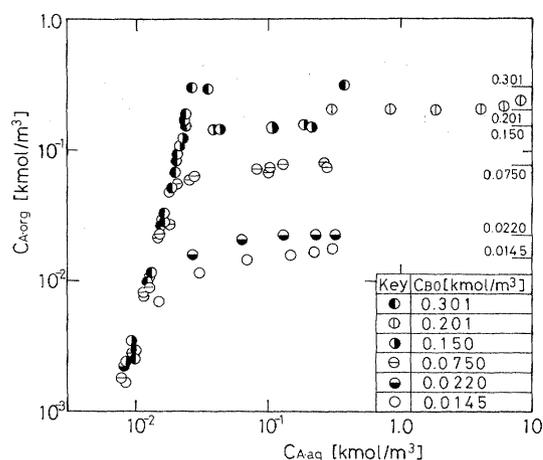


Fig. 1. Relation between $C_{A,org}$ and $C_{A,aq}$ in extraction of hydrochloric acid by the amine

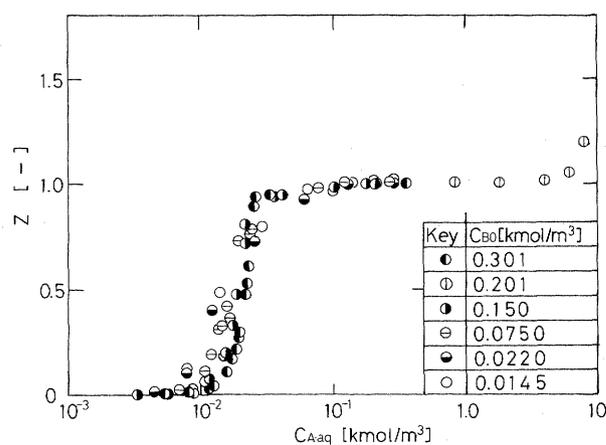


Fig. 2. Relation between distribution ratio of hydrochloric acid and acid concentration in the aqueous solution

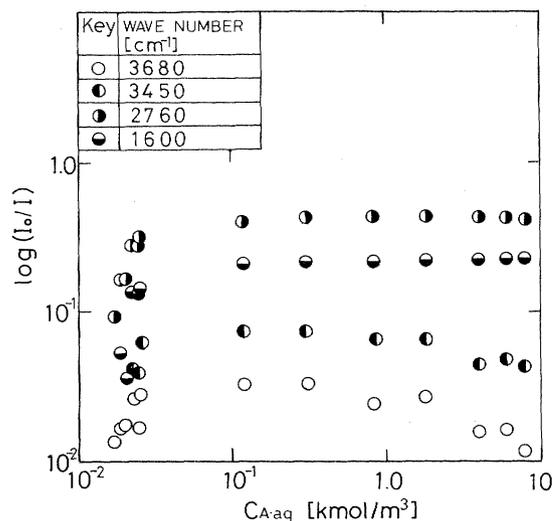


Fig. 3. Absorbances of IR spectra in the organic solution after equilibration for various acid concentrations

increases to more than 1.0, as shown in Fig. 2. The water content of the organic solution, $C_{W,org}$, after equilibration under various conditions is plotted

against $C_{A,org}$ in Fig. 4. The values of $C_{W,org}$ increase linearly with a slope of 1/3 from 0.035*, shown by the triangle in Fig. 4. Excess water, beyond the concentration of the amine does not dissolve in the organic solution. The results suggest that one mole of the acid reacts with one mole of the amine and with 1/3 mole of water to form the species $(BHCl)(1/3)H_2O$. Total concentration of the species formed in the organic solution equilibrated with aqueous hydrochloric acid solution, C_{pt} , was measured by vapor-phase osmometry at low C_{B0} . The average aggregation number of the species, \bar{n} was calculated by the following equation:

$$\bar{n} = (C_{B0}/C_{pt}) \quad (2)$$

The value of \bar{n} is plotted against equilibrium concentration of the acid $C_{A,eq}$ by circles in Fig. 5. The values of \bar{n} increase rapidly to a maximum value with increasing $C_{A,eq}$, and then immediately decrease to about 2.0. At $C_{A,eq}$ above 0.05 kmol/m³, the value of \bar{n} remained constant at 2.0. At high C_{B0} the total concentration of the species formed in the organic solution equilibrated with 1 kmol/m³ of hydrochloric acid was measured by ebullioscopy. The values of \bar{n} calculated by Eq. (2) are plotted against the concentration of the amine by triangles in Fig. 5. The values of \bar{n} remain constant at 2.0 independently of C_{B0} under this condition. The ion-paired species was assumed to exist as its dimer $(BHCl)_2(2/3)H_2O$ in excess acid concentration.

2.2 Distribution of palladium between aqueous hydrochloric acid and toluene solution

The distribution ratio of palladium between the aqueous and the organic solution, D , ($= C_{Pd,org}/C_{Pd,aq}$) is plotted against chloride-ion concentration, C_{Cl} , for various hydrogen ion concentrations, C_H in the aqueous solution in Fig. 6. The chloride ion concentration was adjusted by dissolving lithium chloride at a constant concentration of hydrochloric acid solution. In the range of C_H greater than 0.1 kmol/m³, all experimental values of D cluster on a curve where hydrochloric acid solution was used as the aqueous solution. The distribution ratios of palladium were measured for various concentrations of the ammonium chloride salt of the amine at C_H greater than 0.2 kmol/m³, and are plotted against C_{B0} in Fig. 7. In the range of C_{HCl} above 0.2 kmol/m³, palladium ion in the aqueous solution exists as a complex of $PdCl_4^{2-}$,⁹⁾ and the ammonium chloride salt of the amine in the organic solution exists as the dimer of the ion-pair, $(BHCl)_2$. The ammonium chloride salt of the amine was assumed to react with $PdCl_4^{2-}$ to form palladium-amine complexes by the following reactions:

* The value of 0.035 is the solubility of water in toluene.

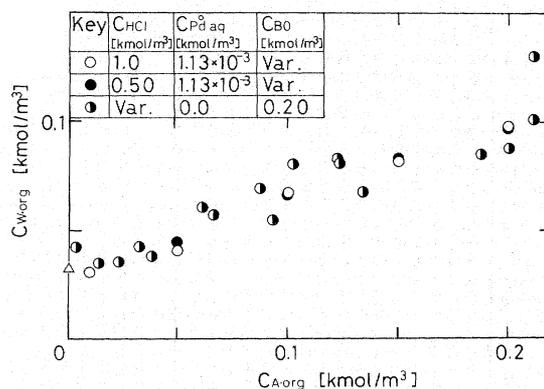


Fig. 4. Water content in the organic solution after equilibration for various acid concentrations

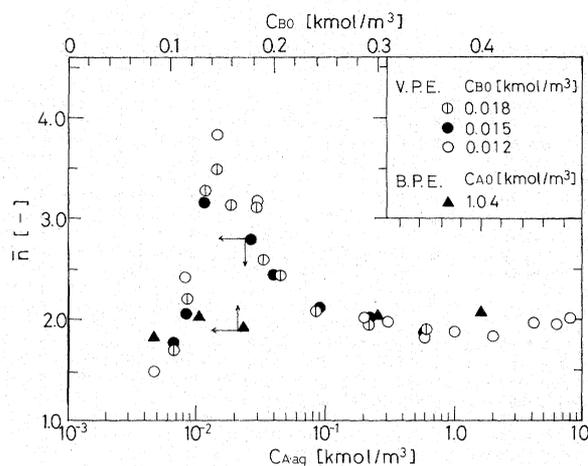


Fig. 5. Relation between average aggregation number of the species formed in the organic solution and equilibrium concentrations

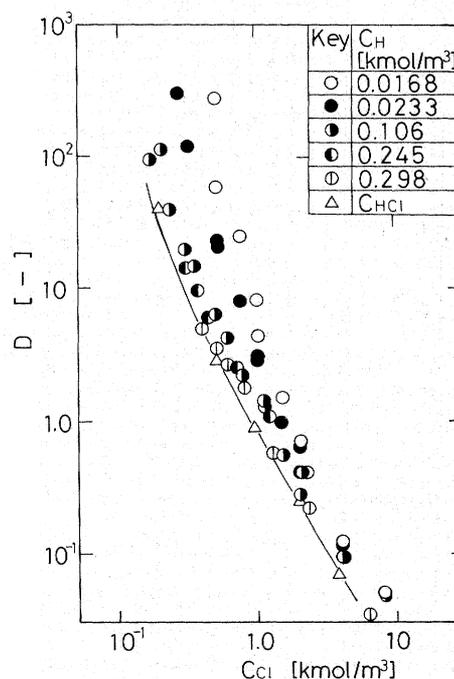


Fig. 6. Distribution ratio of palladium between the organic solution of the amine and the aqueous acid solution for various hydrogen ion concentrations

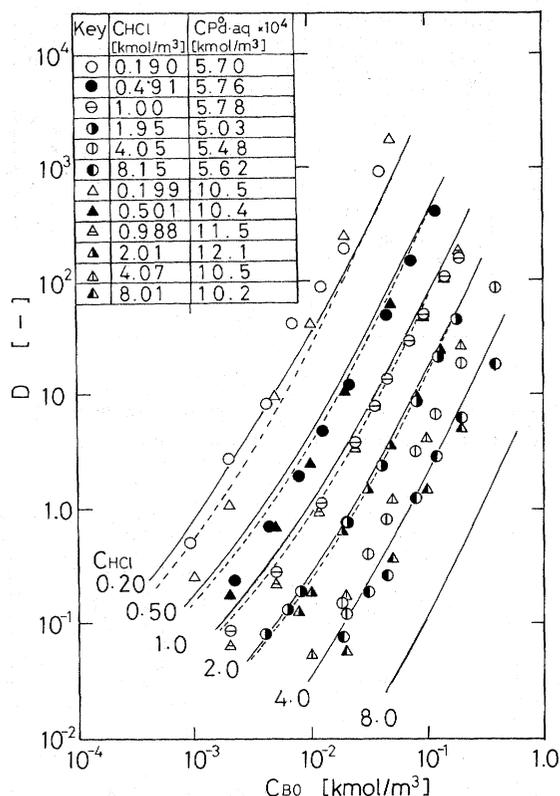
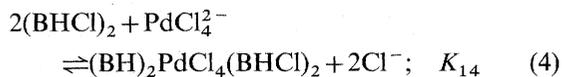
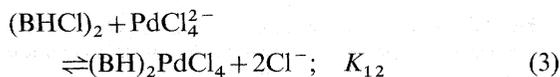


Fig. 7. Distribution ratio of palladium between the organic solution of the amine and aqueous acid solution for various concentrations of the amine



The equilibrium constants K_{12} and K_{14} are defined by the following equations:

$$K_{12} = \frac{[(\text{BH})_2\text{PdCl}_4] a_{\text{Cl}^-}^2}{[(\text{BHCl})_2] a_{\text{PdCl}_4^{2-}}} \quad (5)$$

$$K_{14} = \frac{[(\text{BH})_2\text{PdCl}_4(\text{BHCl})_2] a_{\text{Cl}^-}^2}{[(\text{BHCl})_2]^2 a_{\text{PdCl}_4^{2-}}} \quad (6)$$

where a_{Cl^-} and $a_{\text{PdCl}_4^{2-}}$ are the activities of chloride and PdCl_4^{2-} ions in the aqueous solution. Assuming that both species $(\text{BH})_2\text{PdCl}_4$ and $(\text{BH})_2\text{PdCl}_4(\text{BHCl})_2$ are formed by the reactions of Eqs. (3) and (4), the following equation is obtained from the mass balance of palladium:

$$\frac{D}{[(\text{BHCl})_2]} = K_{12} \gamma_{\text{PdCl}_4} / a_{\text{Cl}^-}^2 + K_{14} [(\text{BHCl})_2] \gamma_{\text{PdCl}_4} / a_{\text{Cl}^-}^2 \quad (7)$$

The value of γ_{PdCl_4} is expressed by $(\gamma_{\text{Pd}}^{1/5} \cdot \gamma_{\text{Cl}}^{4/5})$. The value of $\gamma_{\text{Pd}}^{1/5}$ was approximated as unity by the Debye-Huckel limiting law in low hydro-chloric acid concentration. ($C_{\text{HCl}} < 2.0 \text{ kmol/m}^3$)*. Considering the

* The value of γ_{Pd} is approximated by $\exp\{-0.509 \times (C_{\text{HCl}}/2)^{0.9}\}$.

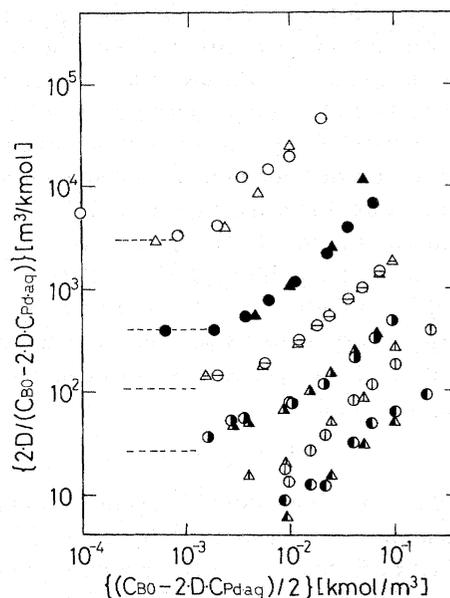


Fig. 8. Relation between the values of $\{D/(\text{BHCl})_2\}$ and $[(\text{BHCl})_2]$. Keys are the same as those in Fig. 7

mean activity coefficient of hydrochloric acid, γ_{HCl} . Eq. (7) can be rearranged as the following equation**:

$$\frac{D}{[(\text{BHCl})_2]} = K_{12} \{\gamma_{\text{HCl}}^{0.6} C_{\text{HCl}}\}^2 + K_{14} [(\text{BHCl})_2] / \{\gamma_{\text{HCl}}^{0.6} C_{\text{HCl}}\}^2 \quad (8)$$

In the range where the concentration of amine, $C_{\text{B}0}$, is much greater than $C_{\text{Pd}, \text{aq}}$, the value of $[(\text{BHCl})_2]$ is approximated by $C_{\text{B}0}/2$. In a low-concentration range of $C_{\text{B}0}$, the formation of $(\text{BH})_2\text{PdCl}_4(\text{BHCl})_2$ species is assumed to be negligibly small compared with that of $(\text{BH})_2\text{PdCl}_4$. Then $[(\text{BHCl})_2]$ is approximated by the following equation:

$$[(\text{BHCl})_2] = \{C_{\text{B}0} - 2DC_{\text{Pd}, \text{aq}}\} / 2 \quad (9)$$

The values of $D/[(\text{BHCl})_2]$ were calculated by these approximated values for $[(\text{BHCl})_2]$ and are plotted against $[(\text{BHCl})_2]$ for various concentration of C_{HCl} in Fig. 8. Since the difference between $C_{\text{Pd}, \text{aq}}$ and $C_{\text{Pd}, \text{aq}}^0$ was very small in the range of high C_{HCl} and low $C_{\text{B}0}$, and the value of $C_{\text{Pd}, \text{aq}}$ was too small to measure in the range of low C_{HCl} and high $C_{\text{B}0}$, a reliable value of D was not obtained experimentally in these ranges. The values of $D/[(\text{BHCl})_2]$ were plotted on straight lines having a slope of 1.0 for each C_{HCl} at a higher concentration of $[(\text{BHCl})_2]$. With decreasing $[(\text{BHCl})_2]$, the value of $D/[(\text{BHCl})_2]$ approaches each constant value depending on C_{HCl} . These profiles indicate that the experimental result is interpreted by Eq. (7). The intercepts and values of constants of the straight lines are plotted against $[\gamma_{\text{HCl}}^{0.6} C_{\text{HCl}}]$ in Fig. 9. The experimental results are plotted on each straight line having a slope of -1.9 except C_{HCl} values greater than

** The value of γ_{H} was assumed to be equal to that of γ_{Cl} .

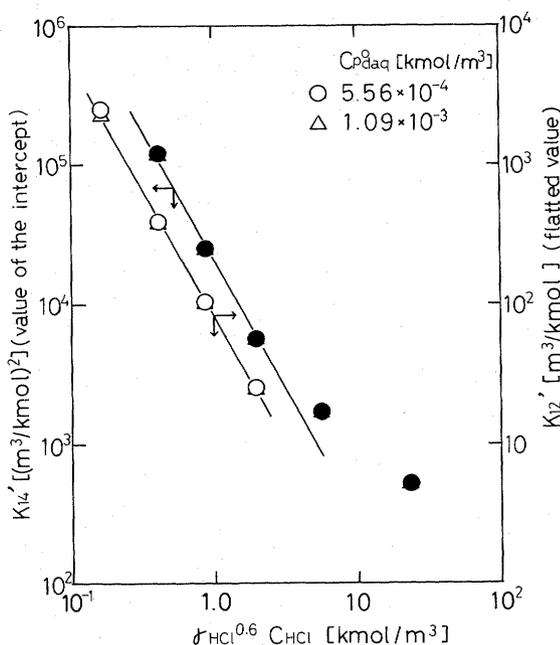


Fig. 9. Relation between constant values in Fig. 8 and C_{HCl}

4.0 kmol/m³. The results agree approximately with Eq. (8) at low concentrations of hydrochloric acid. The following values of K_{12} and K_{14} were obtained from the straight lines.

$$K_{12} = 1.0 \times 10^2 \quad (10)$$

$$K_{14} = 2.6 \times 10^4 \text{ m}^3/\text{kmol} \quad (11)$$

The results calculated with the above equilibrium constants are shown by the solid line and the dotted one for $C_{Pd, aq}^0 = 0.504 \times 10^{-4}$ and 1.08×10^{-3} kmol/m³ respectively in Figs. 6 and 7. Both lines, except for C_{HCl} values higher than 4.0 kmol/m³, agreed well with the experimental results. The difference from the experimental results at high C_{HCl} may be due to the assumptions of activity of palladium and chloride ions and/or the kind of ammonium chloride salt formed in the organic solution in the concentration ranges. When species $(BH)_2PdCl_4$ and $((BH)_2PdCl_4)_2$ were assumed to form, the experimental results could not be explained by the model.

Conclusion

The extraction equilibrium of palladium by di(2-ethylhexyl) amine in toluene was measured for various concentrations of the ammonium chloride salt of the amine, chloro-palladium complex and hydrochloric acid. The results were analyzed by a model in which the chloro-palladium complex reacts with the ammonium chloride salt of the amine to form complexes. The extracted species formed by the reactions was examined by the results of infrared spectrophotometry and water content in the organic

solution. The following results were obtained.

- (1) The distribution ratio of palladium increases with increasing C_{B0} and with decreasing C_{Cl} .
- (2) The ammonium chloride salt of the amine, $(BHCl)_2$, in the organic solution reacts with chloro-palladium complex, $PdCl_4^{2-}$, in the aqueous solution to form two kinds of complexes, $(BH)_2PdCl_4$ and $(BH)_2PdCl_4(BHCl)_2$.
- (3) The formation constants for these complexes were evaluated as 1.0×10^2 and 2.6×10^4 m³/kmol, respectively in the range of C_{HCl} smaller than 1.0 kmol/m³.

Nomenclature

a	= activity	[—]
C	= concentration	[kmol/m ³]
D	= distribution coefficient	[—]
K_{12}	= equilibrium constant for Eq. (3)	[—]
K_{14}	= equilibrium constant for Eq. (4)	[m ³ /kmol]
\bar{n}	= average aggregation number	[—]
Z	= extraction ratio for the equilibrium	[—]
γ	= activity coefficient	[—]

<Subscript>

A	= acid
aq	= aqueous solution
B	= amine
Cl	= chloride ion
H	= hydrogen ion
HCl	= hydrochloric acid
org	= organic solution
Pd	= palladium
$PdCl_4$	= palladium chloride
W	= water
0	= initial

<Superscript>

o	= initial
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