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Solvent Extraction of Palladium(II) from Aqueous Chloride Media with 1,2-Bis(*tert*-hexylthio)ethane

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The extraction equilibrium and kinetics of palladium(II) extraction from an aqueous chloride media with 1,2-bis(*tert*-hexylthio)ethane (mixture), abbreviated as *t*-BHTE and denoted by B, in toluene were studied at 303 K. Palladium(II) was extracted as a 1 : 1 Pd : extractant complex, $[PdCl_2B]$. The partition coefficient of this extractant was evaluated as $K_d=5.5\times10^4$ for hydrochloric acid and $K_d=2.5\times10^4$ for an aqueous ammonium chloride solution. The results of kinetic experiments were quantitatively explained in terms of a reaction scheme in which parallel reactions of *t*-BHTE with $[PdCl_3]^-$ and $[PdCl_4]^{2-}$ in an aqueous phase were the rate-determining steps:

$$[PdCl_3]^-_{aq.} + B_{aq.} \xrightarrow{k_1} [PdCl_2B]_{aq.} + Cl^-_{aq.}$$

$$[PdCl_4]^{2-}_{aq.} + B_{aq.} \xrightarrow{k_2} [PdCl_2B]_{aq.} + 2Cl^-_{aq.}$$

The reaction rate constants for the above were evaluated as $k_1=6.4\times10^4$ dm^3 mol^{-1} s^{-1} and $k_2=2.6\times10^2$ dm^3 mol^{-1} s^{-1} for extraction from an aqueous ammonium chloride solution, and $k_1=6.7\times10^4$ dm^3 mol^{-1} s^{-1} and $k_2=3.2\times10^2$ dm^3 mol^{-1} s^{-1} from a hydrochloric acid solution.

Precious metals such as gold, silver, and platinum group metals are the most important rare metals indispensable in the high-technology industries as raw materials of catalysts, electronic materials and so on. Therefore, it is very important to develop effective techniques to recover these metals from spent catalysts or various kinds of scrap. However, the current refining processes involving these metals are based on highly complicated selective-precipitation techniques which consume great amounts of energy and labour. Also, these are often insufficient in terms of the achieved separation efficiency.

A solvent-extraction process is a potential alternative refining technology as well as an ion-exchange process. The most important factor in the solvent extraction of metals is extractant selectivity to the specified metal ions to be recovered. Precious metals such as gold, silver, platinum, and palladium belong to the soft metals which possess a strong affinity to ligands containing donating-type sulfur atoms which act as soft bases.[1] Consequently, neutral organic compounds containing sulfur atoms are very selective and effective extractants for precious metals.[2–6]

In a previous paper,[7] the authors discussed the extraction equilibrium of mercury(II) from hydrochloric acids with 1,2-bis(hexylthio)ethane in 1,2-dichloroethane and found that it is extracted as a 1 : 1 metal : extractant complex. In the present study, the extraction of palladium(II) with 1,2-bis(*tert*-hexylthio)ethane[†] was investigated from a chloride media while stressing its kinetic aspect since the extraction rate of palladium(II) is very slow compared to that of mercury(II). Toluene was used instead of 1,2-dichloroethane as a diluent from the standpoint of practical application.

Experimental

Reagents. 1,2-Bis(*tert*-hexylthio)ethane(mixture), abbreviated as *t*-BHTE and denoted by B hereafter, was synthesized by a method similar to that of 1,2-bis(hexylthio)ethane described in a previous paper.[7] The product was purified by vacuum distillation(156—159 °C/6 mmHg(1 mmHg=133.322 Pa)) and identified using IR and NMR spectra and element analysis. The results of element analyses are as follows. Found: C, 63.9; H, 11.3 %. Calcd for $C_{14}H_{30}S_2$: C, 64.1; H, 11.5%. The product was a transparent liquid with a confirmed purity of about 97 % by gas chromatography. Analytical-grade toluene was used without further purification. Organic solutions of *t*-BHTE were prepared on a gravimetric basis by diluting *t*-BHTE with toluene. Aqueous solutions of palladium(II) were prepared by dissolving palladium(II) chloride in hydrochloric acid or aqueous ammonium chloride solutions containing a small amount of hydrochloric acid(0.01 mol dm^{-3}).

Procedure for the Measurement of Extraction Equilibrium. Under an excess concentration of *t*-BHTE over the palladium(II) concentration in the aqueous phase, palladium(II) was almost completely extracted over the whole concentration region of hydrochloric acid. The remaining amount of palladium(II) was too small to make a precise quantitative analysis. Therefore, only a loading test was carried out to determine the molar ratio of palladium(II) extracted into the organic phase to *t*-BHTE by varying the concentration ratio of *t*-BHTE in the organic phase to that of palladium(II) in the aqueous phase under the conditions

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[†] It was impossible to carry out the experiment of the extraction of palladium(II) with 1,2-bis(hexylthio)ethane in toluene because of the formation of a precipitate at the interface during extraction.

of a large excess of the palladium(II) concentration.

Equal volumes (0.02 dm^3) of the organic and aqueous phases taken in a 0.1 dm^3 stoppered glass flask were shaken for 5 d in a water bath maintained at 303 K. The concentration of *t*-BHTE in the organic phase was varied from 1×10^{-3} to 1×10^{-2} mol dm^{-3} and that of palladium(II) was varied about from 1.5 to 10 times of the *t*-BHTE concentration. After separating the two phases, the palladium(II) concentration in the aqueous phase was determined using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer and that in the organic phase was calculated from the mass balance of the palladium(II) concentration in the aqueous phase before and after equilibration.

Procedure for the Measurement of Aqueous Solubility of *t*-BHTE. The aqueous solubility of *t*-BHTE was measured spectrophotometrically at 303 K according to the following method. A toluene solution of *t*-BHTE and hydrochloric acid or an aqueous ammonium chloride solution of known concentrations was shaken vigorously for 24 h with a volume ratio of aqueous phase to organic phase 10:1 using Iwaki's mechanical shaker type V-VD. After phase separation, a sample of aqueous phase (0.19 dm^3) was transferred to a separatory funnel, to which 0.05 dm^3 of 2×10^{-3} mol dm^{-3} aqueous palladium(II) solution containing 0.01 mol dm^{-3} hydrochloric acid was added and shaken for 24 h by a mechanical shaker in order to completely convert any *t*-BHTE dissolved in the aqueous phase to its palladium(II) complex. A small amount of toluene (0.005 dm^3) was added and shaken vigorously for 24 h to transfer the palladium(II) complex into toluene. The absorbance of the palladium(II) complex was measured at 403 nm against a toluene blank using a Shimadzu UV 140 spectrophotometer. Then, the extractant concentration dissolved in the aqueous phase was calculated from the molar absorptivity and volume ratios.

Procedure for the Measurement of Extraction Rate. The experimental apparatus used was a batch-type stirred glass cell with a 10-cm inner diameter and a 15-cm depth as shown in Fig.1. The vessel was fitted with four baffles, each of which was 1-cm wide and 14-cm long. Stirring was carried out using a impeller with six flat blades connected to a speed controller. The baffles and impellers made of stainless steel or Teflon were used in the extraction from aqueous ammonium chloride solution and hydrochloric acid, respectively.

Equal volumes (0.3 dm^3) of aqueous ammonium chloride solution or hydrochloric acid solution containing palladium(II) and *t*-BHTE solution of toluene were carefully introduced into the vessel. After that, stirring was initiated at a constant speed and samples were taken at definite time intervals. After phase separation, the palladium(II) concentration in the aqueous phase was determined using the atomic absorption spectrophotometer. The initial palladium(II) concentration was 5×10^{-4} mol dm^{-3} in all kinetic runs. The concentrations of the extractant and chloride ions were varied in the range of 5×10^{-3} to 0.1 mol dm^{-3} and of 0.1 to 6 mol dm^{-3}, respectively. Since the extraction rate was found to be independent of the stirring speed in a range greater than 1500 rpm, subsequent experiments were carried out at a constant stirring speed of 1500 rpm.

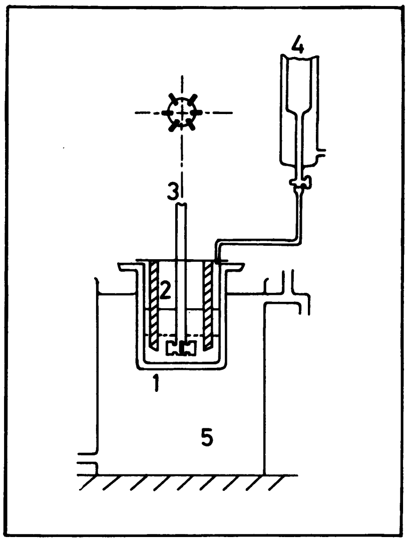

Fig. 1. Experimental apparatus.
1: Stirred glass cell, 2: baffle, 3: impeller, 4: reservoir with jacket, 5: thermostated bath.

Results and Discussion

Equilibrium. The result of the loading test is shown in Fig.2. It indicates that the molar ratio of *t*-BHTE to palladium(II) in the organic phase asymptotically approaches unity. From this, the stoichiometric relation of this extraction reaction is considered to be generally expressed by

$$[\mathrm{PdCl}_i]^{(i-2)-}{}_{\mathrm{aq.}} + \mathrm{B}_{\mathrm{org.}} \rightleftharpoons [\mathrm{PdCl}_2\mathrm{B}]_{\mathrm{org.}} + (i-2)\mathrm{Cl}^-.$$

Aqueous Solubility of *t*-BHTE. The equilibrium distribution of *t*-BHTE between the aqueous phase and the organic phase is expressed by its physical partition to the aqueous phase as

$$\mathrm{B}_{\mathrm{aq.}} \rightleftharpoons \mathrm{B}_{\mathrm{org.}} \quad K_{\mathrm{d}}' \tag{1}$$

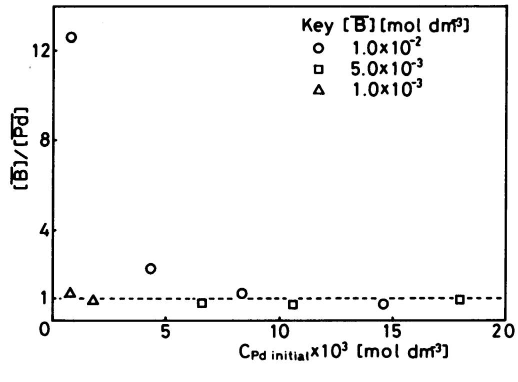

Fig. 2. Experimental results of the loading test at constant HCl concentration (1.0 mol dm^{-3}).

where K_d is the partition coefficient of *t*-BHTE and is expressed as

$$K_d = \frac{[\overline{B}]}{[B]}. \tag{2}$$

Here, the concentration of *t*-BHTE in the organic phase, $[\overline{B}]$, is nearly equal to its initial concentration since the partition coefficient is very large. The logarithm of Eq. 2 gives

$$\log [B] = \log [\overline{B}] - \log K_d. \tag{3}$$

Figure 3 shows the relation between the concentration of *t*-BHTE in the aqueous and organic phases based on Eq.3. The plotted points in this figure lie on a straight line with a slope of 1, regardless of the chloride ion concentration. There is, though, some scattering. From the intercept of the straight line with the ordinate, the partition coefficients, K_d, were evaluated as $K_d=5.5\times10^4$ and $K_d=2.5\times10^4$ for hydrochloric acid and aqueous ammonium chloride solution, respectively.

Kinetics. If it is assumed that the reaction rates in the forward and reverse directions are of pseudo-first-order with respect to the palladium(II) concentrations in the aqueous and organic phases, respectively. The relation between the palladium(II) concentration(a) in the aqueous phase and the contact time(t) is described as

$$\frac{a_i - a_e}{a_i} \ln \frac{a_i - a_e}{a_t - a_e} = k_f t, \tag{4}$$

where k_f denotes the observed reaction rate constant for the forward reaction and the subscripts i and e represent the initial and equilibrium states, respectively.

A typical experimental result is shown in Fig. 4. Here, the straight lines pass through the origin. The reaction-rate constants were obtained from the slopes of these straight lines.

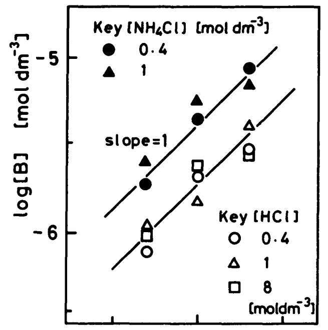

Fig. 3. Aqueous solubility of *t*-BHTE.

Figure 5 shows the effect of the *t*-BHTE concentration on the observed extraction rate constant. In Fig. 5, the plots cluster along straight lines with slopes of 1; consequently, it can be concluded that the extraction rate is first order with respect to *t*-BHTE under these concentration regions.

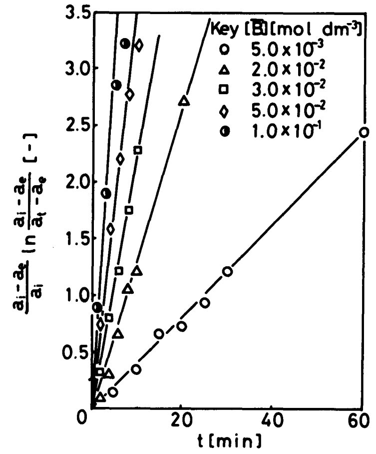

Fig. 4. Typical plot of the experimental results based on the pseudo-first-order rate expression at constant NH_4Cl concentration (0.5 mol dm^{-3}).

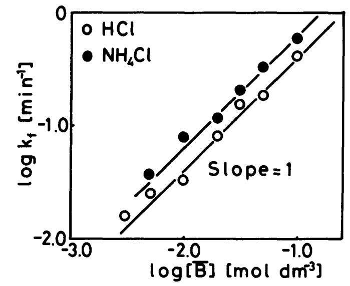

Fig. 5. Effect of *t*-BHTE concentration, at constant chloride ion concentration (0.5 mol dm^{-3}), on the observed extraction rate constant.

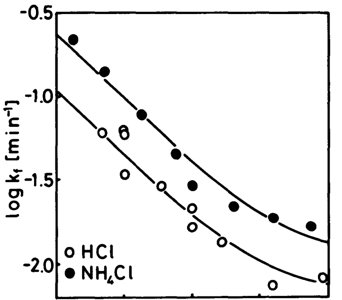

Fig. 6. Effect of chloride ion concentration, at constant *t*-BHTE concentration (1.0×10^{-2} mol dm^{-3}), on the observed extraction rate constant.

Similarly, the effect of chloride-ion concentration on the observed rate constants is shown in Fig. 6. For both aqueous media of hydrochloric acid and ammonium chloride, the plotted points lie on straight lines with slopes of −1 in the low-concentration range of chloride ions and approach constant values in the high-concentration range. Hence, it can be concluded that the extraction rate is inverse first order with respect to chloride ions in its low-concentration range and of zeroth order in its higher-concentration range.

In the concentration region of the chloride ions of the present study, the majority of palladium(II) exists as, tetrachloro complex, $[PdCl_4]^{2-}$, and a small amount of aquatrichloro complex, $[PdCl_3(H_2O)]^-$, coexists while the concentrations of the species, Pd^{2+}, $[PdCl(H_2O)_3]^+$, $[PdCl_2(H_2O)_2]$ can be negligible compared with those of the species, $[PdCl_3(H_2O)]^-$ or $[PdCl_4]^{2-}$. Among these, chloro complexes of palladium(II), the aquatrichloro complex, $[PdCl_3(H_2O)]^-$, is considered to be much more labile than other complexes as Rund[8] pointed out in their studies on the mechanism of substitution reactions of chloro complexes of palladium(II) with 1,10-phenanthroline and 2,2′-bipyridyl. Further, since *t*-BHTE has no interfacial activity, complexation with palladium(II) is not considered to take place at the interface between two phases but in the aqueous phase. Taking account of these facts, the following reaction scheme was put forward in order to explain the results of the extraction kinetics of palladium(II) mentioned above.

$$B_{org.} \rightleftharpoons B_{aq.} \qquad K_d^{-1} \tag{5}$$

$$[PdCl_3(H_2O)]^-_{aq.} + B_{aq.} \xrightarrow{k_1} [PdCl_2B]_{aq.} + Cl^-_{aq.} + H_2O \tag{6}$$

$$[PdCl_4]^{2-}_{aq.} + B_{aq.} \xrightarrow{k_2} [PdCl_2B]_{aq.} + 2Cl^-_{aq.} \tag{7}$$

$$[PdCl_2B]_{aq.} \rightleftharpoons [PdCl_2B]_{org.} \tag{8}$$

Assuming that the parallel reactions of $[PdCl_3(H_2O)]^-$ and $[PdCl_4]^{2-}$ with *t*-BHTE are the rate-determining steps, the rate expression can be described as follows:

$$\begin{aligned} -\frac{dC_{Pd}}{dt} &= k_1[[PdCl_3(H_2O)]^-][B] + k_2[[PdCl_4]^{2-}][B] \\ &= (k_1\beta_3[Cl^-]^3/\alpha + k_2\beta_4[Cl^-]^4/\alpha)C_{Pd}[B]. \end{aligned} \tag{9}$$

In the above equation, β_i is the stability constant of the *i*-th chloro complex of palladium(II) defined as follows.

$$\begin{aligned} &Pd^{2+} + iCl^- \rightleftharpoons [PdCl_i]^{(i-2)-} \qquad \beta_i \\ &\beta_i = [[PdCl_i]^{(i-2)-}]/[Pd^{2+}][Cl^-]^i. \end{aligned} \tag{10}$$

In the present study, the following values[9] were used as the stability constants of the chloro complex of palladium(II): $\beta_1=10^{4.7}$, $\beta_2=10^{7.7}$, $\beta_3=10^{10.3}$, $\beta_4=10^{11.9}$. In Eq. 9, α is defined by

$$\alpha = 1 + \sum_{i=1}^{4}\beta_i[Cl^-]^i. \tag{11}$$

Under the present experimental conditions, Eq. 11 may be approximated by Eq. 12:

$$\alpha \simeq \beta_3[Cl^-]^3 + \beta_4[Cl^-]^4. \tag{12}$$

Eq. 9 is consequently approximated as

$$-\frac{dC_{Pd}}{dt} = \left\{\frac{k_1\beta_3[Cl^-]^3 + k_2\beta_4[Cl^-]^4}{\beta_3[Cl^-]^3 + \beta_4[Cl^-]^4}\right\} K_d^{-1}C_{Pd}[\overline{B}]. \tag{13}$$

In an even higher concentration range of chloride ions, it is further approximated by

$$-\frac{dC_{Pd}}{dt} = \{k_1(\beta_3/\beta_4)[Cl^-]^{-1} + k_2\}K_d^{-1}C_{Pd}[\overline{B}]. \tag{14}$$

C_{Pd} and $[\overline{B}]$ denote the total concentration of palladium(II) in the aqueous phase and that of *t*-BHTE in the organic phase, respectively.

Consequently, the proposed rate expression, Eq. 14, suggests that the extraction rate is first order with respect to *t*-BHTE in the organic phase and palladium(II) in the aqueous phase, respectively, and that it is of the inverse first order with respect to chloride ion in its low concentration region and of zeroth order in its high concentration region.

From the experimental results shown in Fig. 6, the reaction rate constants, k_1 and k_2, were evaluated by the least-square method according to Eq. 13 as $k_1=6.4\times10^4\ dm^3\ mol^{-1}s^{-1}$ and $k_2=2.6\times10^2\ dm^3\ mol^{-1}s^{-1}$ for the extraction from aqueous ammonium chloride solution, and as $k_1=6.7\times10^4\ dm^3mol^{-1}s^{-1}$ and $k_2=3.2\times10^2\ dm^3\ mol^{-1}\ s^{-1}$ for that from hydrochloric acid using the distribution constants evaluated earlier. The values evaluated from two aqueous chloride media are in good agreement either for k_1 or for k_2. The large difference between k_1 and k_2 indicates that the aquatrichloro complex, $[PdCl_3(H_2O)]^-$, is much more labile than the tetrachloro complex, $[PdCl_4]^{2-}$, as mentioned earlier. However, these values are about two or three orders in magnitude greater than those obtained by Rund[8] in the complexation with 1,10-phenanthroline ($k_1=7.1\times10\ dm^3\ mol^{-1}s^{-1}$ and $k_2=2.2\ dm^3\ mol^{-1}s^{-1}$). This might suggest the possibility of an interfacial reaction mechanism between two phases rather than the homogeneous reaction mechanism discussed above. More information regarding this system seems to be required.

The solid lines in Fig. 6 are the calculated results from Eq. 13 using the evaluated values of k_1 and k_2, and the stability constants of the chloro complexes of palladium(II) and the partition coefficient of *t*-BHTE evaluated earlier. These lines are in fairly good agreement with the experimental results for both media. The difference between the rate of extraction from hydrochloric acid and that from aqueous ammonium chloride solution is attributable to that of the solubility of *t*-BHTE to both media.

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