

EXTRACTION CHARACTERISTICS OF PALLADIUM IN AQUEOUS HYDROCHLORIC ACID WITH TRI-n-OCTYLAMINE IN TOLUENE USING A VIBRO-MIXER

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The extraction of palladium in aqueous hydrochloric acid solution by toluene solution of tri-n-octylammonium chloride salt was investigated using vibro-mixer type extractors under various operating conditions. In the extractors, continuously fed heterogeneous solutions were mixed by the vibration of spiral circular plates installed in the extractor. The overall extraction rates were interpreted by (1,1) orders of reaction rate of the ammonium chloride salt of tri-n-octylamine in toluene and palladium chloride in aqueous solution for a residence time of 24 sec and 0 to 300 strokes per minute (spm) of the vibration frequencies. The overall reaction rate constants increased with the vibration frequencies and the feed velocities in the extractor. Equilibrium in the system investigated was attained at over 400 spm of the vibration for 24 sec of residence time. The mixed effluent phases from the extractor were separated easily into their aqueous and organic components in less than one minute.

1. Introduction

Solvent extraction is generally carried out using heterogeneous systems. It is important to increase the contact surface area to achieve high extraction efficiency. Forced mixing type extractors, centrifugal or mixer/settler extractors have been used generally as high efficiency contactors. Recently, various liquid membrane type extractor systems have been examined by many investigators on account of their extremely large interfacial area per unit volume or their simplicity^{1,5,7,8,9}). However, there are some difficulties in keeping operations stable at high efficiency for a long time in such apparatus⁶). In the previous paper, vibro-mixer type extractors were shown to be able to produce small droplets continuously and steadily and to cause high surface renewal by the vibration of the disks in the extractors. Furthermore, fast separation of both phases was obtained in the reactor in the biological hydrolysis of olive oil³). Furthermore, extraction equilibria for the extraction of Pd(II) with tri-n-octylamine in toluene were elucidated, and the separation of Pd(II) in the aqueous solution was shown to be depend on the pH value⁴). In order to further examine the performance of the vibro-mixer reactor, the extraction of palladium from aqueous acid solution with a toluene solution of the ammonium chloride salt of tri-n-octylamine was investigated using the vibro-mixer extractor. The effects of flow rate of the phases, vibration frequency of the disk, concentration of the ammonium chloride salt in toluene and palladium chloride salt in the aqueous solution on the extraction rates of palladium were examined.

2. Experimental

2.1 Reagents

Tri-n-octylamine (purity 99.7%) supplied from Koei Chemical Co. was used without further purification as the extractant. Toluene, hydrochloric acid and palladium chloride salt were supplied as guaranteed grade reagents by Wako Chemical Co. All other analytical reagents used were of guaranteed grades as described in the previous paper⁴). A toluene solution of the ammonium chloride salt of tri-n-octylamine (hereafter written ammonium chloride) was prepared by equilibrating a tri-n-octylamine solution in toluene with 0.1 M hydrochloric acid in aqueous solution. At equilibrium, all of the amine was shown to be converted to the ammonium chloride salt²).

1.2 Experimental apparatus and methods

To elucidate the effect of mixing on the extraction rate, two types of vibro-mixer extractors shown in Figure 1 were used in this work. In the first type of extractor (hereafter called reactor A), a set of spiral circular plates (hereafter written as spiral plate) of 16.0 mm D, 1.2 mm thick, 6.0 mm pitch were put into a cylindrical tube of 18.0 mm I. D. and 97.0 mm H with a volume of $3.27 \times 10^{-5} \text{ m}^3$. The spiral disk was vibrated up and down with 3 mm vertical vibration movement. In the second type of reactor (hereafter written reactor B), the cylindrical tube having a volume of $1.45 \times 10^{-5} \text{ m}^3$ contained five baffle disks. A toluene solution of ammonium chloride and an aqueous hydrochloric acid solution of the palladium chloride salt were pumped separately at equal flow rates into the bottom of the vibro-mixer extractor. Flow rates of both phases were varied from 1.7×10^{-7} to $1.0 \times 10^{-6} \text{ m}^3/\text{sec}$. Both solutions were prewarmed in a water bath at 303 K. The mixed effluent solution from the top of the vibro-mixer was allowed to settle and separated quickly into the component aqueous and toluene phases within one minute.

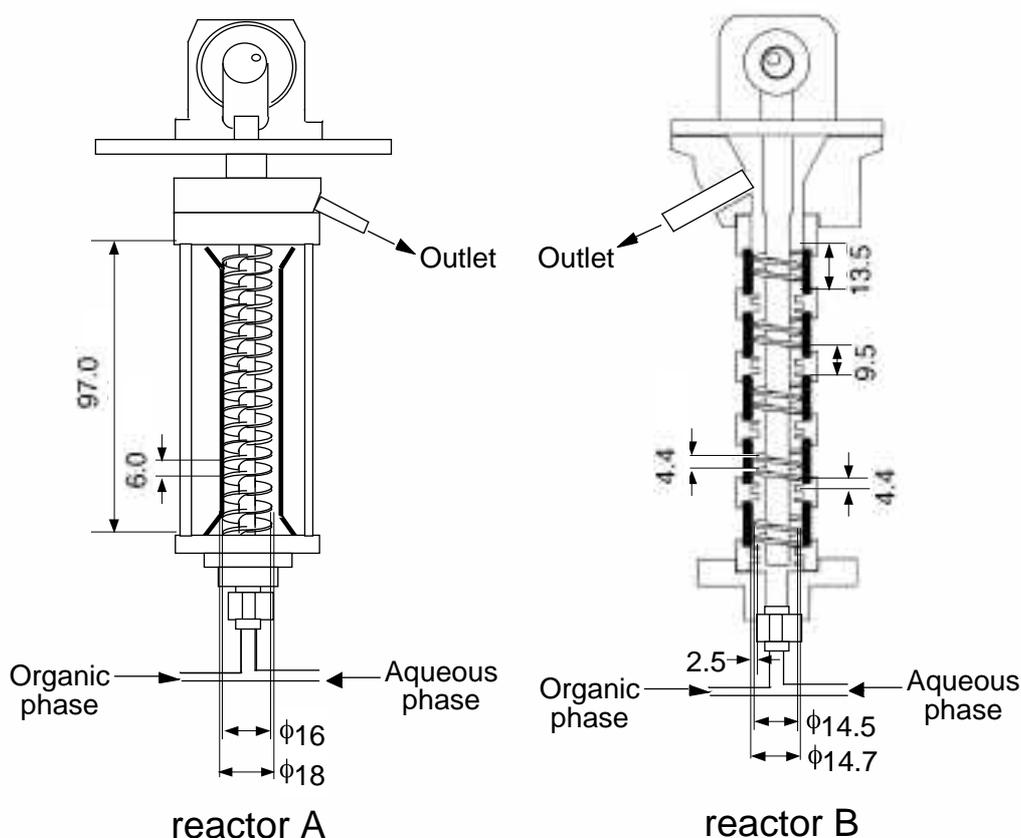


Fig. 1 Experimental apparatus

Complete separation was confirmed in advance. The concentrations of palladium in the aqueous solutions were measured by atomic absorption spectrophotometry. The initial concentrations of tri-n-octylamine in toluene were analyzed by titration with a butanol-methanol mixed solution of hydrochloric acid using phenolphthalein as an indicator.

3. Results and discussion

3.1 Extraction in Reactor A

A toluene solution of the ammonium chloride salt and aqueous palladium chloride solution were pumped continuously into reactor A. The concentrations of palladium in the effluent aqueous solution, C_{Pd} , were plotted in Figure 2 against the circulation time, t , which is the operation time after the phases were pumped into the reactor. C_{Pd} was found to be essentially constant within the experimental error for all circulation times greater than 2.5 minutes. Steady state operation of the extractor for palladium extraction was found to be attained in that time.

The values of C_{Pd} were plotted against the average residence time of the phases in the extractor, τ at constant $C_{B,0}$ and $C_{Pd,0}$ for each f in Figure 3. Without vibration of the spiral plate, the values of C_{Pd} were not influenced by the residence time in the extractor. At greater than 300 spm, reaction equilibrium was attained in the reactor. The values of C_{Pd} in the effluent solutions at 300 spm were not influenced by τ . C_{Pd} was plotted against the initial concentrations of ammonium chloride, $C_{B,0}$ for constant $C_{Pd,0}$ and a residence time, τ of 24 sec in Figure 4. C_{Pd} decreased with increasing $C_{B,0}$. Reaction between palladium and ammonium chloride appeared to affect the extraction rate of palladium. C_{Pd} was plotted against f in Figure 5. C_{Pd} decreased with increasing f and approached a constant value dependent on the value of $C_{B,0}$

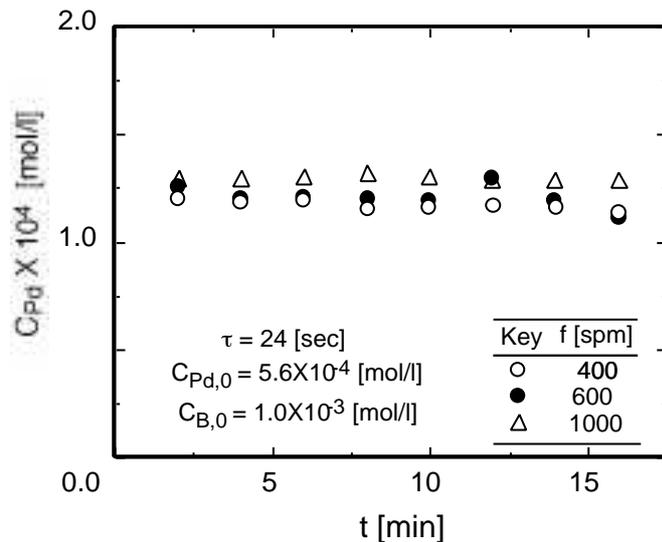


Fig. 2 Effect of the circulation time on the concentrations of palladium in the effluent aqueous solution in reactor A

calculated using the equilibrium constant for the reaction⁴). As the droplet size of the dispersed phase in the extractor decreased with vibration frequency, overall reaction rates in the extractor increased with increasing vibration frequency of the spiral plate. At greater than 400 spm, the reaction between palladium and ammonium chlorides is considered to attain equilibrium. The flow velocities of the phases in the extractor and the vibration frequencies of the disks affect the extraction rate of palladium. The mixing of both phases is dependent on the fluid dynamic properties in the extractor.

The fractional extraction of

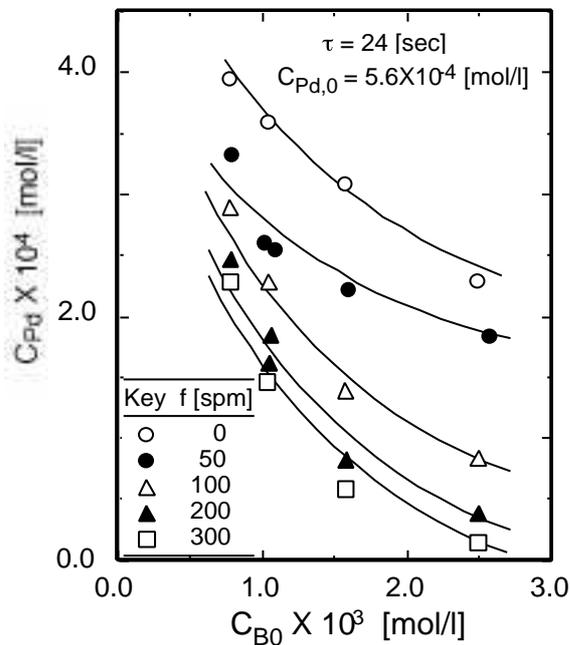


Fig. 4 Effect of the concentration of tri-n-octylamine on the values of C_{Pd} at constant $C_{Pd,0}$ for each f in reactor A

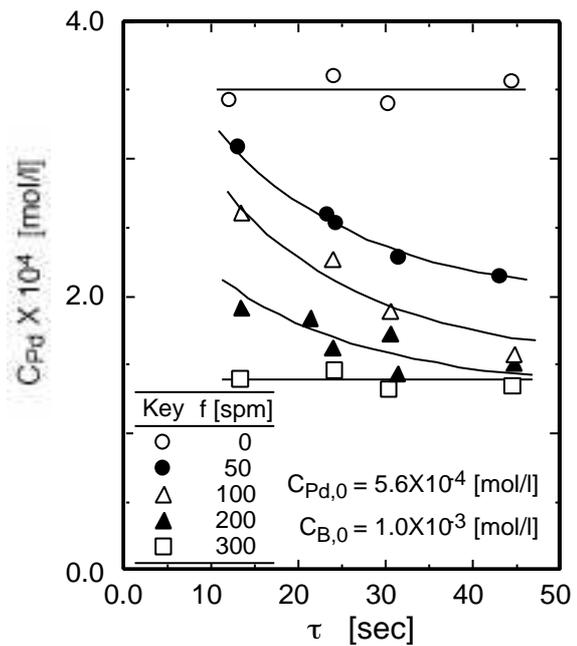


Fig. 3 Effect of the average residence time of the phases in the extractor, τ , on the values of C_{Pd} at constant $C_{B,0}$ and $C_{Pd,0}$ for each f in reactor A

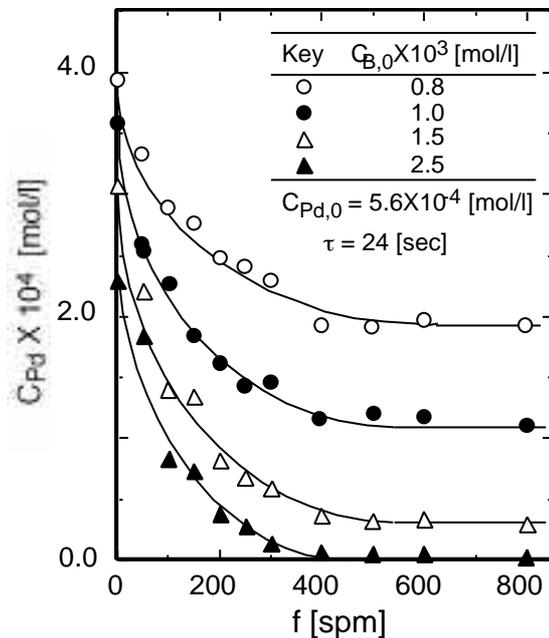


Fig. 5 Effect of the vibration frequency, f , on the values of C_{Pd} at constant $C_{Pd,0}$ and $C_{B,0}$ in reactor A

palladium, E_A was calculated by the following equation;

$$E_A = (C_{Pd,0} - C_{Pd}) / C_{Pd,0} \quad (1)$$

The overall extraction rate, r_{Pd} , was calculated by the following equation;

$$r_{Pd} = (C_{Pd,0} - C_{Pd}) / \tau \quad (2)$$

Considering Eq.(1), Eq.(2) can be transformed as follows,

$$r_{Pd} = C_{Pd,0} \cdot E_A / \tau \quad (3)$$

As shown in the previous paper⁴), palladium chloride reacted with tri-n-octylamine ammonium chloride to form a palladium-amminochloride complex by the following equation,



Considering this equation and assuming that the overall reaction rate equation for the extraction of palladium is first order for palladium and n-th order for ammonium chloride, the following equation was obtained.

$$r_{Pd} = k_r \cdot C_{Pd} \cdot C_B^n \quad (5)$$

Combining Eqs.(3) and (5), the following equation was obtained,

$$\ln\{C_{Pd,0} \cdot E_A / (\tau \cdot C_{Pd})\} = \ln(k_r) + n \cdot \ln(C_B) \quad (6)$$

The values of $\ln\{C_{Pd,0} \cdot E_A / (\tau \cdot C_{Pd})\}$ were plotted against $\ln(C_B)$ at various f in Figure 6. Straight lines of slope of 1.0 were obtained for each f except that at greater than 300 spm. Then, the reaction rate for the ammonium salt and palladium was interpreted as being first order for both the concentration of palladium and ammonium chloride. The following equation was obtained by combining Eqs.(1), (3) and (5) at $n=1.0$.

$$1/E_A = 1/\{k_r \cdot \tau \cdot C_B\} + 1.0 \quad (7)$$

The values of $1/E_A$ for reactor A were plotted against $1/(\tau \cdot C_B)$ for each f in Figure 7. Experimental values of $1/E_A$ were plotted as straight lines having a slope dependent on f . The slopes of the straight lines in Figure 7 show the values of $(1/k_T)$ for each f . The reciprocal values of the slopes of the straight lines, k_T , were plotted (symbol) against f in Figure 8. The overall reaction rate constant k_T increased with increasing vibration frequency of the spiral plate in the extractor.

3.2 Results in Reactor B

The fraction of extraction, E_A in reactor B was plotted against the vibration frequencies of the disk in Figures 9 and 10 for residence times of 13 and 24 sec, respectively. E_A attained equilibrium values at 200 spm for a residence time of 24 sec. As in

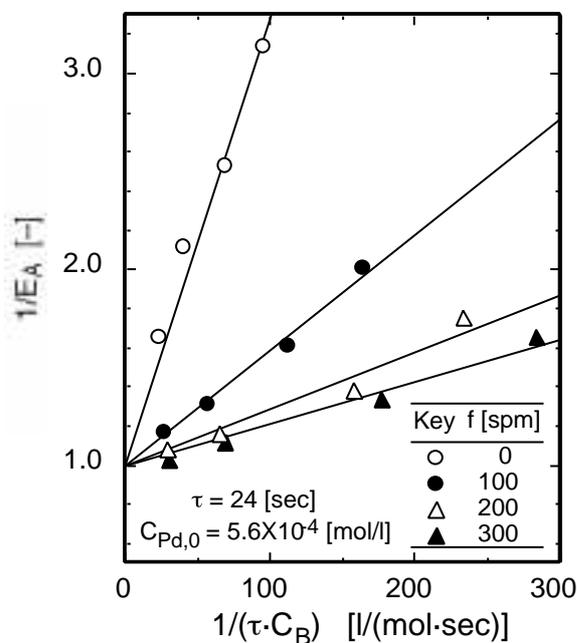


Fig. 7 Relationship between $1/E_A$ and $1/(\tau \cdot C_B)$ in reactor A

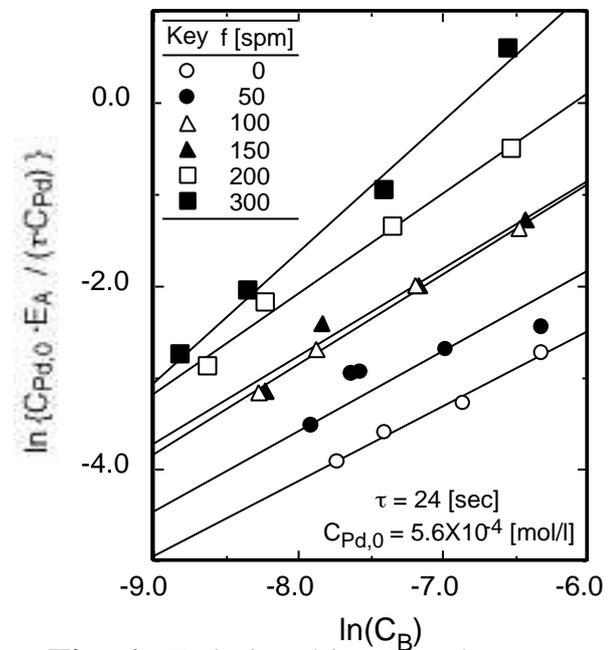


Fig. 6 Relationship between $\ln\{C_{Pd,0} \cdot E_A / (\tau \cdot C_{Pd})\}$ and $\ln(C_B)$ in reactor A

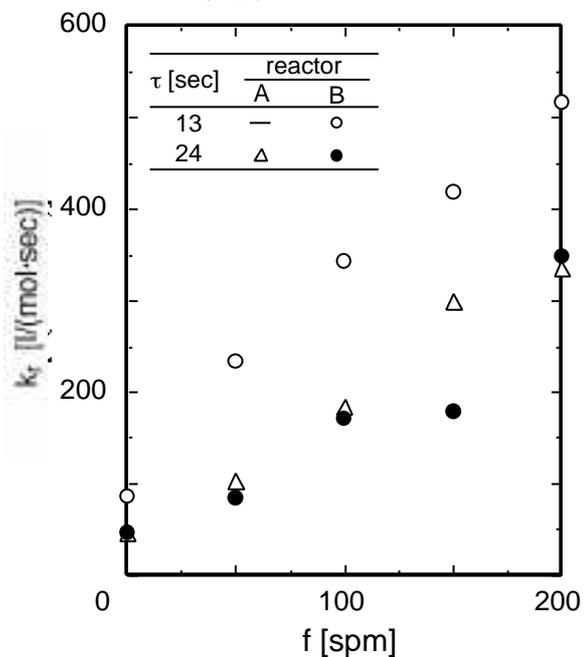


Fig. 8 Effect of vibration frequency, f , on the value of k_T

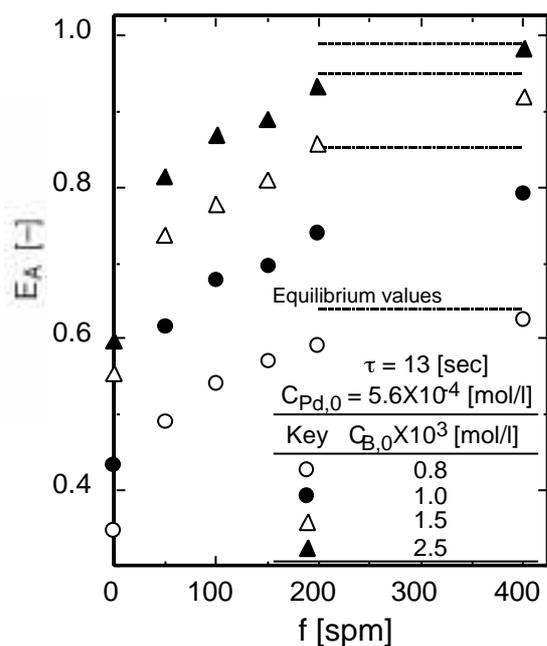


Fig. 9 Effect of the vibration frequency, f , on the values of E_A at constant $C_{Pd,0}$ and $C_{B,0}$ and $\tau=13$ sec in reactor B

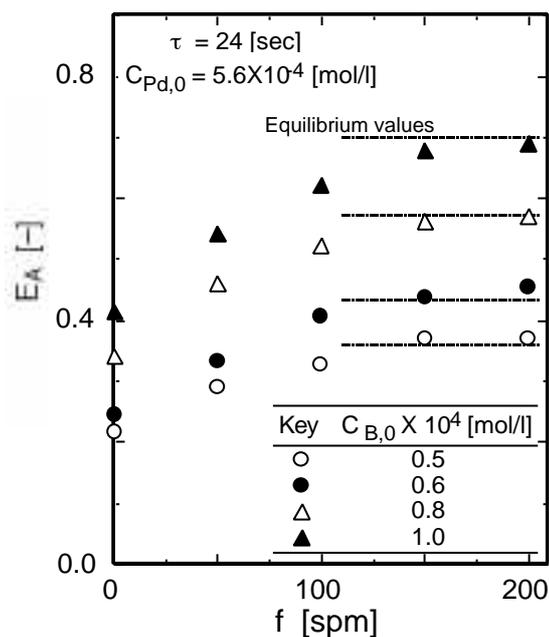


Fig. 10 Effect of the vibration frequency, f , on the values of E_A at constant $C_{Pd,0}$ and $C_{B,0}$ and $\tau=24$ sec in reactor B

the previous analysis, $1/E_A$ was plotted against $1/(\tau \cdot C_B)$ for $\tau = 13$ sec in Figure 11. The results were plotted as straight lines having slopes dependent on the value of f . The results were similar to those shown in Figure 7 for reactor A. For the experimental results at $\tau = 24$ sec, $1/E_A$ was plotted against $1/\tau \cdot C_B$. Similar straight line profiles were obtained for each value of f .

The values of k_r calculated from the slopes of these straight lines in reactor B were plotted (symbols and) to compare with that of reactor A in Figure 8. The values of k_r increased with increasing f . As τ decreases the linear velocity of the phases in the reactor

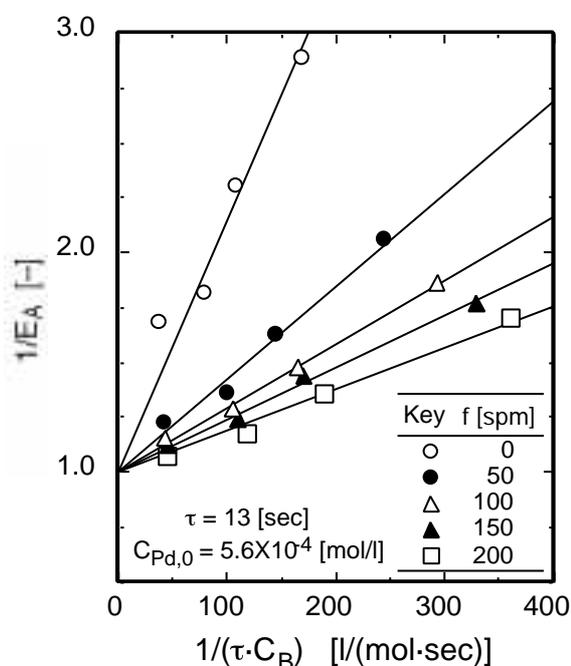


Fig. 11 Relationship between $1/E_A$ $1/(\tau \cdot C_B)$ in reactor B

increase. The phase mixing in the reactor becomes vigorous. Hence, the overall reaction rate constant increased with increasing phase velocity in reactor B. As the net volume of reactor B is smaller than that of reactor A, the linear velocity in reactor B is smaller than that in reactor A for the same residence time. Thus the mixing efficiency of the phases in reactor B is considered to have been increased by introducing the baffles. Further analysis of the mixing characteristic of the phases in the vibro-mixer is necessary in future work.

By using the vibro-mixer type extractor in the separation of palladium from aqueous solution with a toluene solution of tri-n-octylamine, 13 sec was required to bring $0.73 \times 10^{-5} \text{ m}^3$ of the aqueous solution containing the metal to the equilibrium state at 400 spm of vibration. Effluent liquids from the extractor was found to be separated into two phases within 1.0 minute.

4. Conclusion

The extraction rate of palladium in aqueous hydrochloric acid with tri-n-octylammonium chloride in toluene was investigated by using vibro-mixer extractors under various operating conditions. Two types of extractors, with baffles and without baffles were used in this study. The extraction rates for the system were found to be affected by the concentrations of palladium chloride and tri-n-octylammonium chloride, the vibration frequency of the spiral plate, and the velocity of the phases in the extractor. The following results for the extraction rate of palladium in the aqueous solution with tri-n-octylammonium chloride in toluene in the vibro-mixer were obtained;

- (1) The extraction rate was influenced by the overall interfacial reaction rate of palladium in the aqueous solution and the ammonium salt in toluene in the range of vibration frequencies of less than 300 spm, in which the rate showed a first order dependence on each of the concentrations of palladium and the ammonium salt.
- (2) Overall rate constants for the second order reaction were affected by the interfacial surface area and the surface renewal rates, and increased with increasing vibration frequency of the spiral plate, the linear velocity of the mixed phases in the extractor, due to the increase of intensity of mixing of the phases and the setting of the baffles.
- (3) At vibration frequencies greater than 400 spm, extraction equilibrium was attained in the extractor in 13 sec of residence time.

Nomenclature

C	= concentration	[mol/]
E	= fraction of extraction	[-]
f	= frequency numbers	[1/min]
k	= reaction rate constant	[/ (mol·sec)]
r	= reaction rate	[mol/(·sec)]
t	= circulation time	[min]
τ	= average residence time	[sec]
<Subscript>		
A	= palladium	
B	= ammonium chloride salt	
Pd	= palladium	
0	= initial state	

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