CHEMISTRY LETTERS, pp. 1297-1300, 1988.

Solvent Extraction of Palladium(II) with N,N-Dioctylglycine from Chloride Media

Katsutoshi INOUE, Yoshinari BABA, Kazuharu YOSHIZUKA, and Youichirou NIHEDA
Department of Applied Chemistry, Fuculty of Science and Technology,
Saga University, Honjo-machi, Saga 840

Distribution equilibrium was investigated in the solvent extraction of palladium(II) from aqueous mixture of hydrochloric acid and sodium chloride with the title extractant in toluene at 303 K. Palladium(II) was found to be extracted as a chelate with the composition of 1:2 metal:reagent and the equilibrium constant of the extraction reaction was evaluated.

In early 1970s, the National Institute for Metallurgy (NIM) of South Africa developed a novel separation process for refining precious metals by using solvent extraction and ion exchange techniques which has many economic advantages over conventional selective precipitation processes on a commercial scale.1) In this process, palladium and platinum are coextracted from acidic chloride media with a novel extracting reagent of an amino-acid derivative which is synthesized from monochloroacetic acid and Amberlite LA-2, a commercial long-chain secondary alkylamine. With this extractant, both metals can be effectively extracted from dilute hydrochloric acid solution and easily stripped with concentrated hydrochloric acid solution from the solvent. Contrarily, primary, secondary, and tertiary amines, which are the conventional metal extractants, so strongly extract these metals that stripping is very difficult even with very concentrated hydrochloric acid solutions. This makes it difficult to use the amines for extraction of these metals as the commercial base. The difference of the extraction mechanism with these two types of extracting reagents is responsible for that of the extraction behaviors, while only a few works have been conducted on the solvent extraction of metals with amino-acid type extracting reagents. Recently, Zhang et al. investigated the solvent extraction of platinum(II), palladium(II) and gold(III) from hydrochloric acid solutions with N,N-di(sec-octyl)glycine in kerosene.2,3) They concluded that palladium(II) is extracted as an ion pair of the type, $(R_2NHCH_2COOH)^+[PdCl_3(R_2NCH_2COOH)]^-$. However, since these types of reagents have the similar structure with complexones such as EDTA, these reagents may form metal-chelates with five-membered rings. In the present paper, the authors synthesized N,N-dioctylglycine to investigate the extraction mechanism of palladium(II) from acidic chloride media.

The reagent was synthesized from dioctylamine and monochloroacetic acid by using a conventional method according to the following reaction:

$$(C_8H_{19})_2NH + ClCH_2COOH \longrightarrow (C_8H_{19})_2NCH_2COOH + HCl$$

The product was shaken with 30% sodium hydroxide aqueous solution to precipitate the sodium salt of the reagent, which was washed several times with acetone. The precipitate was dissolved in benzene and transferred to a separatory funnel to be washed with 2 mol/dm^3 sulfuric acid solution and subsequently with water. After phase separation, benzene was removed by distillation under reduced pressure after drying. Identification of the purified product was carried out by using NMR spectra and elemental analysis. The yield was 56% and the purity was 93%. Analytical grade of toluene was used as a diluent.

Prior to the experiment of solvent extraction, the apparent molecular weight of the reagent was measured by means of vapor-phase osmometry using a Hitachi model 117 osmometer to examine the degree of aggregation of the reagent in the organic solution. It was found that the great majority of the reagent exists as a dimeric species just as carboxylic acid extractants.

Equal volumes of aqueous and organic phases were shaken in a flask immersed in a thermostated water bath maintained at 30±0.1 °C overnight to attain equilibrium. The equilibration had been confirmed to be attained within one hour in a preliminary experiment. The initial palladium concentration was about 1 mmol/dm^3 for all experiments. The initial and equilibrium concentrations of palladium(II) in the aqueous phase were determined by using a Nippon Jarrell-Ash model AA-782 atomic absorption spectrophotometer. The palladium concentration in the organic phase was calculated from the mass balance of the metal contents in the aqueous phase before and after the equilibria.

Figure 1 shows the effect of pH on the distribution ratio in the extraction from aqueous mixture of hydrochloric acid and sodium chloride in which total chloride ion concentration was maintained at 1.0 mol/dm^3. In this experiment, pH was calculated from the hydrogen ion concentration determined by means of titration and the activity coefficient of hydrogen ion in the aqueous mixture of hydrochloric acid and sodium chloride.4) The plots cluster on a straight line with the slope of 2, which suggests that two hydrogen ions are released by substitution with one metal ion during extraction.

Figure 2 shows the effect of the concentration of the dimeric species of the reagent on the distribution ratio in the extraction from 1.0 mol/dm^3 hydrochloric acid solution, where the concentration was calculated as the half of the total or analytical reagent concentration. The plots are lying on a straight line with the slope of unity. This fact suggests that palladium(II) is extracted as a 1:2 metal:reagent complex since the majority of the reagent exists as a dimeric species in the organic phase as mentioned earlier.

Figure 3 shows the effect of the activity of chloride ion on the distribution ratio in the extraction from the aqueous chloride media in which hydrogen ion concentration is maintained at 1.0 mol/dm^3. Here, the activity of chloride ion was calculated from the chloride ion concentration and the activity coefficient of chloride ion.5) The plots are lying on a straight line with the slope of -4 except for the high concentration region. This indicates that four chloride ions are released per unit metal ion during extraction. On the other hand, the plots deviate upward from the straight line in the higher concentration region, which may be attributed to the salting out effect by the chloride ion.

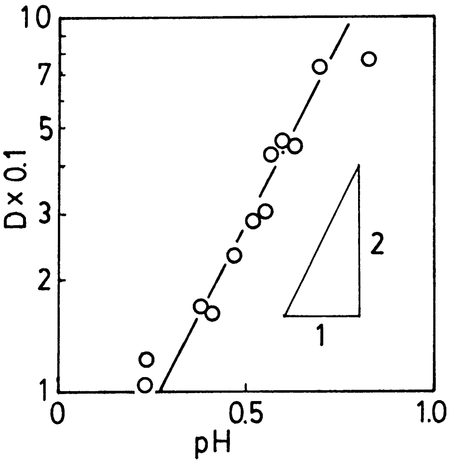

Fig. 1. Effect of pH on the distribution ratio (D) (reagent concentration = 10 mmol/dm^3, total chloride ion concentration = 1.0 mol/dm^3).

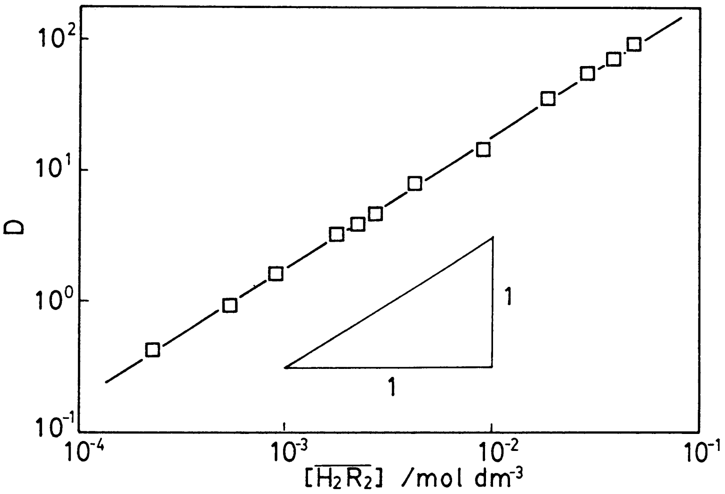

Fig. 2. Effect of the concentration of the dimeric reagents on the distribution ratio (D) in the extraction from 1.0 mol/dm^3 hydrochloric acid solution.

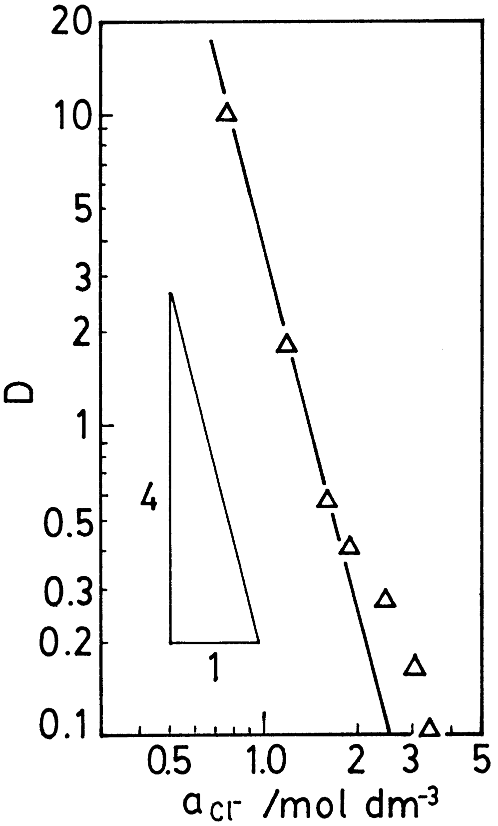

Fig. 3. Effect of the activity of chloride ion on the distribution ratio (D) (reagent concentration = 10 mmol/dm^3).

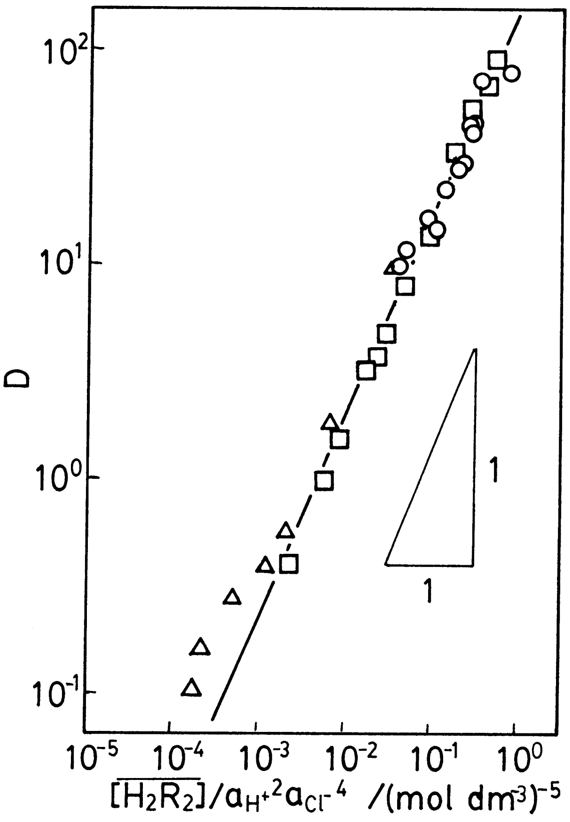

Fig. 4. Relationship between the distribution ratio (D) and $[\overline{H_2R_2}]/a_{H^+}{}^2 a_{Cl^-}{}^{4}$. Keys are the same with those in Figs. 1-3.

From the above-mentioned concentration dependences of the reactant species on the distribution ratio and by taking into consideration that the majority of palladium(II) exists as the tetrachloro complex in the aqueous solutions with high concentration of chloride ion under the present experimental conditions, it can be concluded that palladium(II) is extracted as a metal-chelate complex shown as in the following extraction reaction:

$$PdCl_4^{2-} + \overline{H_2R_2} \rightleftharpoons \overline{PdR_2} + 2\ H^+ + 4\ Cl^- \qquad (1)$$

Based on the above-described extraction reaction, the distribution ratio (D) is expressed as

$$D = K_e\beta_4[\overline{H_2R_2}]/a_{H^+}^{2}(\ 1 + \sum_{i=1}^{4}\beta_i a_{Cl^-}^{i}\ ) \qquad (2)$$

where K_e and β_i denote the equilibrium constant of the extraction reaction and the stability constant of the i-th chloro complex of palladium(II), respectively. The above equation is approximated so as to be Eq. 3 in the high concentration of chloride ion, when the tetrachloro complex of palladium(II) is predominant under the present experimental condition.

$$D \simeq K_e[\overline{H_2R_2}]/a_{H^+}^{2}a_{Cl^-}^{4} \qquad (3)$$

Figure 4 shows the plot of the all data for those in Figs. 1-3, which were calculated based on Eq. 3. The plots are lying on a straight line with the slope of unity as expected from Eq. 3. The equilibrium constant of the present extraction reaction was evaluated as $K_e = 2.2\text{x}10^2\ (\text{mol/dm}^3)^5$ from the intercept of the straight line with the ordinate in this figure.

The authors are deeply indebted to Mr. Y. Hori of Department of Applied Chemistry of Saga University for his instruction of the synthesis of the N,N-dioctylglycine.

References

1) R.I. Edwards, "Proc. Int. Solv. Extr. Conf. (ISEC) '77," ed by B.H. Lucas, G.M. Ritcey, and H.W. Smith, Can. Inst. Min. Metall., Montreal (1979), p.24.
2) Zhang Jianmin, Zhang Aiyou, He Zhenyu, Ma Guangjia, Yuan Chengye, Zhou Liying, and Tu Tongyuan, Jinshu Xuebao, 21, B241 (1985).
3) Zhang Jianmin, Zhang Aiyou, He Zhenyu, Yuan Chengye, Zhou Liying, and Tu Tongyuan, Kexue Tangbao, 32, 839 (1987).
4) H. Ohtaki and M. Tanaka, Jpn. Analyst, 18, 280 (1969).
5) H.S. Harned, J. Phys. Chem., 63, 1299 (1959).

(Received May 9, 1988)