DAEHAN HWAHAK HWOEJEE
(*Journal of the Korean Chemical Society*)
Vol. 27, No. 4, 1983
Printed in the Republic of Korea

# β-디페닐글리옥심으로 침윤시킨 폴리우레탄 포움에 의한 팔라듐의 추출

姜三祐† · 李承錫
한남대학 이공학부 화학과

(1983. 1. 19 접수)

# The Extraction of Palladium by Polyurethane Foam impregnated with β-Diphenylglyoxime

**Sam Woo Kang**† and **Seung Seok Lee**
*Department of Chemistry, Han Nam College, Taejon 300, Korea*

(Received January 19, 1983)

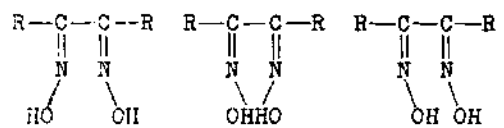
**요 약.** β-디페닐글리옥심으로 침윤시킨 폴리우레탄 포움을 사용하여 수용액에서 Pt(IV) 및 Ni(II) 이온으로부터 Pd(II) 이온의 추출을 시도하였다. Pd(II) 이온은 0.01~0.05 *M* HCl 농도범위에서 정량적으로 추출이 되였으며 반면 같은 농도 범위에서 Pt(IV) 이온은 단지 미량 추출이 되었으나 Ni(II) 이온은 전혀 추출되지 않았다. 따라서 뱃치법에 의하여 0.01~0.05*M* HCl 용액에서 Pd(II) 이온을 Pt(IV) 및 Ni(II) 이온으로부터 선택적으로 분리가 가능하였으며 또한 용리법으로 Pd(II)의 제거 및 회수도 가능하였다.

**ABSTRACT.** Polyurethane foam impregnated with β-diphenylglyoxime has been applied to the extraction of palladium(II) from platinum(IV) and nickel(II) in aqueous solution. Palladium(II) is quantitatively extracted from 0.01~0.05*M* HCl. On the other hand, platinum(IV) was slightly extracted and nickel(II) was not found to be extracted in the same experimental condition. Based on the results obtained, the selecetive separation, removal and recovery of Pd(II) from Pt(IV) or Ni(II) was possible by batch or elution method.

## INTRODUCTION

The use of open-pore polyurethane foam as a separation medium was first reported by Bowen[1], who used polyurethane foam as selective absorbent for a number of metal ions from aqueous solution. Braun and Farag[2~4] have made extensive studies on the use of open-pore polyurethane foam as a solid support for reversed-phase partition chromatography. Foam that is specially treated with hydrophobic chelating agent has been used in the extraction and separation of metal ions in aquous solution[5~9].

It is well known that glyoximes form complexes with several transition metals, including nickel, platinum, and palladium. However, of the three possible isomer forms (anti, syn, amphi), only the anti isomer (or α-form) is capable of forming complexes easily, whereas,



the syn (β-form) and amphi (γ-form) isomers form few or no complexes. This is explained by the fact that the syn and amphi isomers form strong intramolecular hydrogen bonds in addition to possible steric hindrance. In spite of this general behavior of the β and γ isomers of dioximes, it was found by Dwyer and Mellor[10] that β-diphenylglyoxime forms complexes with palladium. The use of dimethylglyoxime and α-diphenylglyoxime treated polyurethane foam was recently reported for the selective extraction of nickel from aqueous solution.[11~12],

In this paper, β-diphenylglyoxime (β-DGO) impregnated open-pore polyurethane foam has been applied to the selective adsorption of palladium from platinum and nickel in aqueous solution.

## EXPERIMENTAL

### Reagents and Materials

β-Diphenylglyoxime was prepared according to Brady.[13] α-Diphenylglyoxime (10g) was dissolved in the minimum of freshly distilled and boiling aniline and cooled. The precipitated crystals were sucked as dry as possible and after being washed with dilute hydrochloric acid and with water the crystals were recrystallized twice using alcohol : mp 204~206°C.

Open-pore polyurethane foam was supplied by the Ziklag Chemicals Ltd., Haifa, Israel.

All chemicals used were of analytical reagent grade. Palladium, platinum and nickel solutions were prepared by dissolving the chloride salts in 0.25*M* hydrochloric acid solution. Water purified by distillation and ion exchange resin (Dowex 1-X8, $OH^-$ and Dowex 50-X8, $H^+$ form) was used throughout the work.

### Instruments

Pye-Unicam sp-8-100 spectrophotometer and IL-251 atomic absorption spectrophometer were empolyed.

### Preparation of β-Diphenylglyoxime (β-DGO)-Foam

The polyurethane foam (cubes of about 5mm edge) was washed by 1*M* hydrochloric acid solution, followed by distilled water until the washing were free from chloride ion. Then, the foam material was washed with acetone and dried at 80°C. The dried foam cubes were impregnated with the appropriate solution of β-DGO-acetone for about 2 hours to ensure complete saturation. The impregnated foam was dried between two sheets of filter paper to remove the excess of β-DGO-acetone solution and dried at room temperature in a vaccum desiccator.

### Measurement of the amount of β-DGO impregnated Foam.

An exact amount of dried β-DGO impregnated foam was transferred to a glass column with a sintered glass disk at its bottom, and then β-DGO adsorbed on the foam was eluted through the column with methanol. The collected effluent was analyzed by the U.V. spectrophotometer at 250 nm. The amount of β-DGO was calculated in units of mmol/g foam.

### Procedure for the adsorption of palladium, platinum and nickel.

**Batch Method.** The adsorption of the metal ions from solutions of tetrachloropalladate(II), hexachloroplatinate (IV), and hexaaquonickel chloride in dilute hydrochloric acid solutions of various strengths was tested. Aliquot (25m*l*) of hydrochloric acid solutions containing Pd (II), Pt(IV) or Ni(II) ions were shaken with 0.1gr of β-DGO impregnated foam for 3h in a mechanical shaker. The uncollected metal ion was determined by atomic absorption spectrophotometer at 247.6 nm for Pd(II), 265.9nm for Pt(IV) and 232nm for Ni (II) and then the extracted metal ion was calculated by differen-

ce. In some experiments, the amount of palladium retained on the foam was determined directly by shaking the foam with 20m*l* of 2.0*M* HCl-20% MeOH solution for about 1h and measuring the absorbance of the leached palladium in the aqueous solution.

*Elution method*: Glass columns of 2.0 cm diameter and 20 cm length were used. About 5 gr of cylindrical plugs of the dried impregnated foam was packed into the column by vacuum method[3] to produce a 10cm bed height. Aliquot (10m*l*) of palladium solution containing Pt (IV) or Ni(II) was allowed to pass through the foam column at a flow-rate of 0.6~0.8m*l*/min and then eluted with 0.01*M* HCl. The collected palladium on the foam was eluted from the foam by elution with 2.0*M* HCl-20% MeOH solution and effluent was analyzed by atomic absorption spectrophotmeter at 247.6nm.

## RESULTS AND DISCUSSION

**Amount of β-DGO on the Foam.** To investigate amount of β-DGO impregnated on the foam, amount of β-DGO adsorbed after impregnation with various concentration of β-DGO-acetone was eluted with methanol and the determined by UV spectrophotometer. As shown in *Fig.* 1, the total amount of β-DGO adsorbed on the foam is, within experi mental error linearly related to concentration of β-DGO-acetone applied. The main process of the adsorption is probably due to physical wetting on the foam matrix and some of it is due to some type of chemical bonding, such as molecular sorption between β-DGO molecule and the foam matrix. Therefore, the impregnation β-DGO can be stripped by a simple wash with a suitable organic solvent. To obtain the fixed amount of β-DGO ($4.7\times10^{-1}$mmol/g), the foam was impregnated with $5.0\times10^{-2}M$ β-DGO-acetone solution.

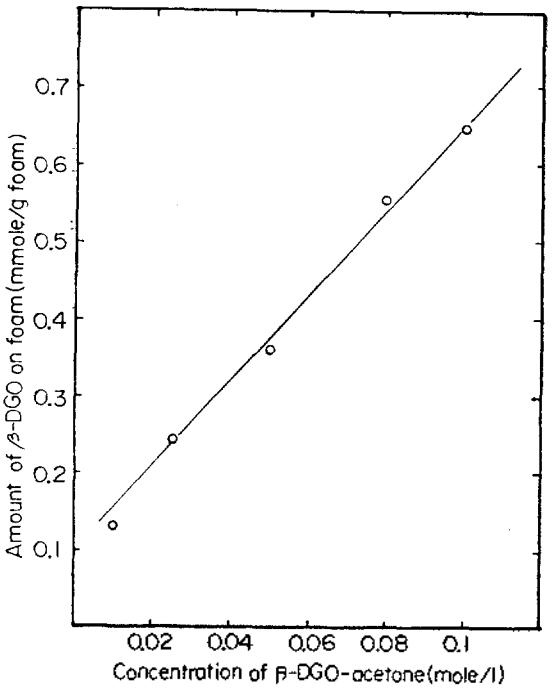



*Fig.* 1. Amount of of β-DGO on Foam *vs.* concentration of β-DGO-acetone solution.

**Extraction of Pd(II), Pt(IV) and Ni(II)** The effect of hydrochloric acid concentration on extraction of Pd(II), Pt(IV) and Ni(II) was investigated by batch method. The concentration of the metal ions was made excess compared to the capacity of β-DGO on the foam, so as to observe the difference in the amount of metal ions adsorbed. The results are shown in *Fig.* 2. The extraction of Pd(II) is maximum in the range over 0.01~0.05*M* HCl, but falls off gradually with increasing hydrochloric acid concentration. At higher hydrochloric acid concentration than 1 *M*, Pd(II) was not extracted apparently. The extraction of Pd(II) may be attributed to the formation of hydrophobic complex between Pd(II) and β-DGO impregnated on the foam in the range from 0.01 to 0.5 *M* hydrochloric acid solution. Pd (II) reacts with β-DGO impregnated on the foam immediately to form the yellow colored

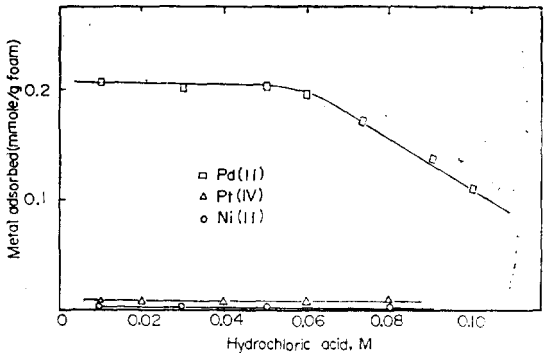



*Fig.* 2. Extraction of Pd (II), Pt(IV) and Ni(II) from Hydrochloric Acid media. β-DGO-Foam taken : 100mg ($4.7\times10^{-1}$mmol β-DGO/g foam), volume of solution: 25m*l*, shaking time : 180min.

complex and Pd(II)-β-DGO complex is firmly retained in the foam. This phenomena could be comfirmed by an observation during experiment. On the other hand, Pt(IV) was slightly extracted and Ni(II) was not found to be extracted at all. In this case, Pt(IV) and Ni(II) do not form complex with β-DGO on the foam in the same experimental condition. According to the data in *Fig.* 2, the extraction of Pd(II) from the various synthetic sample solution is possible by batch method. As can be seen from *Table* 1, the extraction of Pd(II) from aqueous solution is quantitative down to such low concentration as 1ppm, at which conventional procipitation methods fail.

*Table* 1. Extraction of Pd(II) by the Batch method at optimum condition.

| Concentration of Pd(II), ppm | Amount of Pd(II), μg | Found μg | Adsorbed μg | Extracted % |
|---|---|---|---|---|
| 10 | 250 | 3.2 | 246.8 | 98.7 |
| 6 | 150 | 2.2 | 147.8 | 98.5 |
| 4 | 100 | 2.2 | 97.8 | 97.8 |
| 2 | 50 | 2.0 | 48.0 | 96.0 |
| 1 | 25 | 1.9 | 23.1 | 92.4 |

β-DGO on the foam : $4.7\times10^{-1}$ mmol/g foam; foam taken, *ca* ; 90 mg; Medium : 0.03 *M* HCl; 25m*l*; shaking time : 180min.

**Seperation of Pd(II) from Pt(IV) or Ni(II) by Batch Method and Elution Method.**

Seperation of Pd(II) from a wide range concentration of Pt (IV) and Ni (II) was carried out in batch experiments under optimum condition. As shown in *Table* 2, the quantitative separation of Pd(II) could be obtained in the presence of high excess of Ni (II) (the ratio 1:10) but the separation of Pd(II) was decreased with increase of concentration of Pt(IV). Accordingly, Ni(II) dose not interfere, while

*Table* 2. Effect of Ni(II) and Pt(IV) on the extraction of Pd(II) from mixture solution.

| Ions present | | Ratio of | Pd(II) | | |
|---|---|---|---|---|---|
| Pd(II) (μg) | Ni(II) or Pt(IV) (μg) | Pd(II)/Ni(II), Pd(II)/Pt(IV) | Found (μg) | Adsorbed (%) | Extracted (%) |
| 200 | 200 | 1 : 1 | 2.8 | 197.2 | 98.6 |
| 200 | 400 | 1 : 2 | 3.4 | 196.6 | 98.3 |
| 200 | 600 | 1 : 3 | 3.8 | 196.2 | 98.1 |
| 200 | 800 | 1 : 4 | 4.6 | 195.4 | 97.7 |
| 200 | 1000 | 1 : 5 | 6.3 | 193.7 | 96.9 |
| 200 | 2000 | 1 : 10 | 9.7 | 190.3 | 95.2 |
| 200 | 100 | 1 : 0.5 | 2.8 | 197.2 | 98.6 |
| 200 | 200 | 1 : 1 | 5.2 | 194.8 | 97.4 |
| 200 | 400 | 1 : 2 | 12.8 | 187.2 | 93.6 |
| 200 | 1000 | 1 : 5 | 36.7 | 163.3 | 81.7 |

β-DGO on the foam : $4.7\times10^{-1}$mmol/g foam; Foam taken : *ca.* 100mg; Shaking time : 180min; Volume of solution: 20.0 ml.

Pd(II) was relatively unaffected by the small amount of Pd(IV) present but affected by the large concentration of Pt(IV).

Some examples by the elution method are also presented in *Table* 3. The removal and recovery of Pd (II) was examined by elution method from mixture solution containing Ni(II).

Aliquot (10m*l*) of mixture sample soluion was loaded on the β-DGO-foam in column and then eluted with 20 m*l* of 0.01 *M* HCl. As shown in *Table* 3, all of the effluents contained Pd(II) less than about 4%. Therefore, Pd(II) over than 96% could be removed from mixture solution of Ni(II). The collected Pd(II) was then washed slowly with distilled water followed by a solution of 2*M* HCl-20 % MeOH by which Pd(II)-β-DGO complex can be easily decomposed. *Table* 3 shows that the mean recoveries for Pd (II) at concentration levels of 8 and 10ppm are about 92 and 95%, respectively. The *Table* 3 shows also that at the lower concentration level(4ppm), the mean recovery for Pd(II) is approximately 88%.

As a result, the present method may be applied to the separation of palladium from natural polluted water and the recovery of palladium from industrial waste.

*Table* 3. Removal and recovery of Pd(II) from Ni(II) solution by elution Method.

| Sample solution | | | Pd(II) | | |
|---|---|---|---|---|---|
| Concentration Ni(II) | Pd(II) ppm | Taken, m*l* | Found in effluent, ppm | Removal % | recovery % |
| 200 | 10 | 10 | 0.23 | 97.7 | 94.5 |
| 100 | 10 | 10 | 0.28 | 97.2 | 95.3 |
| 200 | 8 | 10 | 0.21 | 97.4 | 92.7 |
| 100 | 8 | 10 | 0.18 | 97.8 | 91.5 |
| 200 | 4 | 10 | 0.15 | 96.3 | 88.6 |
| 100 | 4 | 10 | 0.13 | 96.8 | 88.0 |

Foam bed : ca, 2.0×10cm. β-DGO on the foam : $4.7 \times 10^{-1}$ mmol/g foam. Flow rate : 0.6~0.8ml/min.

## REFERENCES


1. H. J. M. Bowen, *J. Chem. Soc.* (*a*)., 1082 (1970).
2. T. Braun and A. B. Farag. *Talanta.*, **19**, 828 (1972).
3. T. Braun and A. B. Farag. *Anal. Chim. Acta.*, **61**, 265 (1972).
4. T. Braun, E. Huszar and L. Bakos, *Anal. Chim. Acta.*, **64**, 77 (1973).
5. S. Sukiman, *Radiochem. Radioanal. Letter.*, **18**, 129 (1974).
6. J. F. Uthe, J. Reinke and H. D. Gesser., *Envioronmental Letters.*, **3**, 117 (1972).
7. T. Braun, A. B. Farag and A. Klimers-Szmik., *Anal. Chim. Acta.*, **64**, 71 (1973).
8. T. Braun and A. B. Farag. *Anal. Chim. Acta.*, **71**, 133 (1974)
9. A. Chow and D. Buksak, *Can. J. Chem.*, **53**, 1373 (1974).
10. F. P. Dwyer and D. P. Mellor, *J. Proc. Roy. N. S. Wales.*, **68**, 107(1935). *Chem. Abstr.*, **29**, 4690 (1935).
11. D. W. Lee and M. Halman, *Anal. Chem.*, **48**, 2214(1976).
12. M. Halmann and D. W. Lee., *Anal. Chim. Acta.*, **113**, 383 (1980).
13. O. L. Brady and H. M. Perry, *J. Chem. Soc.*, 2874 (1925).