Extraction Equilibria of Palladium(II) and Platinum(IV) with *N,N*-Di(2-ethylhexyl)aminomethylquinoline from Hydrochloric Acid

Yoshinari BABA¹, Akemi ARIMA¹, Shintaro KANEMARU¹,
Minako IWAKUMA² and Tatsuya OSHIMA¹

¹Department of Applied Chemistry, Faculty of Engineering,
University of Miyazaki,

1-1 Gakuen-Kibanadai Nishi, Miyazaki-shi, Miyazaki 889-2192, Japan

²Department of Chemical Science and Engineering,

Miyakonojo National College of Technology,

473-1 Yoshio-cho, Miyakonojo-shi, Miyazaki 885-8567, Japan

Keywords: Selective Extraction, Palladium, Platinum, Extraction Equilibrium, Quinoline

N,N-Di(2-ethylhexyl)aminomethylquinoline (DEQ) has been newly synthesized to develop selective extractants for precious metals. DEQ is designed so as to exhibit high selectivity for precious metals through the electrostatic force and coordination ability of the tertiary amine and quinoline moieties, respectively. DEQ in toluene exhibits a high selectivity for gold(III), palladium(II) and platinum(IV) over base metals such as copper(II), nickel(II) and cobalt(II) from hydrochloric acid. This is attributed to the strong basicity of the tertiary amine and high coordination ability of quinoline for precious metals. Palladium(II) and platinum(IV) extraction is significantly dependent on the concentration of hydrochloric acid, while gold(III) is quantitatively extracted over the whole concentration region of hydrochloric acid examined. We have quantitatively discussed the extraction equilibria of palladium(II) and platinum(IV) with DEQ in toluene from hydrochloric acid. It is observed that palladium(II) was extracted by the anion exchange mechanism, while platinum(IV) was extracted through the anion exchange and solvation mechanisms. Palladium(II) was extracted as a 1 : 1 complex formed by ion pair formation and coordination bonding, and its extraction equilibrium constant was determined as 1.28×10^7 [—]. Platinum(IV) was extracted as a 1 : 1 complex and a 1 : 2 complex at low and high concentrations of hydrochloric acid, respectively. These extraction equilibrium constants were determined as 4.15×10^2 [mol dm⁻³] and 3.46×10^4 [—], respectively.

Introduction

The platinum group metals (PGMs: Pd, Pt, Rh, Ir, Ru and Os) are more commonly used in industry for a variety of purposes, such as dental applications, electronic and electrical devices, and as automobile exhaust emission control catalysts (Kim *et al.*, 2000). Much attention has been focused on the recovery and recycling of PGMs from not only ore process streams (primary metals), but also secondary metals due to the importance of PGMs related to the fact that they are rarely found in nature, which has caused the prices to be very high (Shibata and Okuda, 2002). The selective extraction of these precious metals from mainly acidic chloride solutions, which also often contain large amounts of other transition metals (e.g. copper, nickel and ferric iron), is a very difficult technique (Benguerel *et al.*, 1996). The separation of platinum group metals by means of solvent

extraction technology has attracted much attention for the recovery of these metals from a variety of wastes such as spent catalysts and scrap from electronic and electric industries (Mhaske and Dhadke, 2001). A large number of extractants have been developed, and some of them are commercially available. High molecular amines (Iqbal *et al.*, 1978; Jiang and Su, 1991; Belova *et al.*, 1997; Lokhande *et al.*, 1998) and quaternary ammonium salts (Inoue *et al.*, 1988; Belova *et al.*, 1995; Guo *et al.*, 2003) have been commercially used to recover and purify various metals from hydrochloric acid. These extractants can extract PGMs as ion pair complexes through the electrostatic force between a cation group of the amines and anionic metals in hydrochloric acid. However, these extractants do not show high extraction selectivity to precious metals because most of them exist as anions in the hydrochloric acid.

When anionic metal complexes are extracted in industrial processes, the complexing anions present in the bulk solution are normally limited to one or more of the following: sulfate, chloride and nitrate, because of their availability and relatively low cost. Therefore, it would

Received on November 12, 2010; accepted on July 13, 2011

Correspondence concerning this article should be addressed to
Y. Baba (E-mail address: t0g202u@cc.miyazaki-u.ac.jp).

be advantageous to refine these processes by improving the efficiency and action of the cationic site of an extractant, as little can be done to improve the complexing ability of the anions described above.

Exhaustive studies have been directed towards improving the commercially available tertiary and quaternary ammonium extractants. These studies have concentrated on varying the nature and length of the alkyl groups attached to ammonium extractants by experimenting with their stereochemistry and their compatibility with the diluents. Ion pairing, however, can be regarded as fundamental to the mechanism of solvent extraction where bulky cations are used to stabilize anionic metal complexes. An enhancement in this ion pairing remains a potential area of improvement in the functioning of these extractants.

As is well known, platinum group metals form stable complexes with heterocyclic nitrogen compounds such as pyridine owing to the “soft” character of the π -type nitrogen atom of pyridine (Szczepańska *et al.*, 2003). The aim of this work was to clarify the extraction equilibria of PGMs from hydrochloric acid media with an alkylquinoline derivative as an extraction reagent by solvent extraction method.

1. Experimental

1.1 Materials and analysis

Analytical-grade palladium(II), copper(II), nickel(II), cobalt(II), iron(III), gold(III) and platinum(IV) chlorides (Wako Pure Chemical Industries, Ltd.) were used to prepare test solutions containing each metal. 2-Chloromethylquinoline (Tokyo Kasei Kogyo Co., Ltd.) was used as a raw material for the synthesis of the extractant. Other chemicals were analytical reagent grade and used as received. Nuclear magnetic resonance spectra were recorded on a Bruker AV400M for ^1H NMR (400 MHz) and for ^{13}C NMR (100 MHz) in CDCl_3 with TMS as the internal standard for the identification of products. Initial and equilibrium concentrations of metal ions in the aqueous solution were determined by an atomic absorption spectrometer (AAS, AAnalyst 100, Perkin-Elmer Co., Ltd.) and an inductively coupled plasma spectrometer (ICPS, ICPS-7000, Shimadzu Corp.).

1.2 Synthesis of di(2-ethylhexyl)aminomethylquinoline (DEQ)

We have designed a new extractant composed of a tertiary amine moiety with anion exchange ability and a quinoline ring with coordination ability. *N,N*-Di(2-ethylhexyl)aminomethylquinoline, DEQ, was synthesized by alkylation of di(2-ethylhexyl)amine with 2-chloromethylquinoline as shown in **Figure 1**. 2-Chloromethylquinoline and di(2-ethylhexyl)amine were dissolved in DMF containing NaH as a catalyst. The mixture was stirred at room temperature for 2 d. The reaction mixture was evaporated. Ethyl acetate and a

Fig. 1 Synthesis route of di(2-ethylhexyl)aminomethylquinoline (DEQ)

1.0 mol dm^{-3} HCl solution were added to the residue, and then the two phases were separated with a separatory funnel. Ethyl acetate phase was successively washed using a 1.0 M NaOH solution and distilled water, and then dried over anhydrous Na_2SO_4 . The product was obtained with 75% yield and the purity of the product measured by gas chromatography was 97%. ^1H NMR (400 MHz, CDCl_3) δ 7.98 (d, 2H), 7.70 (d, 1H), 7.60 (t, 2H), 7.40 (d, 1H), 3.75 (s, 2H), 2.25 (d, 4H), 1.40 (m, 2H), 1.25 (m, 16H), 0.85 (t, 12H). ^{13}C NMR (100 MHz, CDCl_3) δ 160.4, 145.8, 136.1, 128.2, 126.8, 124.7, 120.5, 62.5, 60.1, 38.5, 31.2, 28.8, 23.9, 23.1, 14.1, 10.9.

1.3 Extraction selectivity for metal ions with DEQ

The aqueous phase was prepared by dissolving metal chloride into hydrochloric acid. The initial concentration of each metal was about $1.0 \times 10^{-3} \text{ mol dm}^{-3}$. The organic phase was prepared by diluting with toluene gravimetrically. The initial concentration of DEQ was $1.0 \times 10^{-2} \text{ mol dm}^{-3}$. All experiments concerning the extraction equilibria for metal ions were performed by a batchwise method at 303 K for 24 h. Equal volumes (10 cm^3) of both phases were mixed in a conical flask and vigorously shaken mechanically. After phase separation, the concentrations of hydrochloric acid and metal ion in the aqueous phase were determined by acid-base titration and AAS, respectively. The extraction percentage ($E\%$) of metal ion was calculated from the concentration change in the aqueous solution before and after equilibrium using Eq. (1). The distribution ratio (D) was defined as the ratio of the metal ion concentration extracted into the organic phase to its equilibrium concentration in an aqueous phase using Eq. (2).

$$E\% = \frac{[\text{M}]_0 - [\text{M}]_{\text{eq}}}{[\text{M}]_0} \times 100 \quad (1)$$

$$D[-] = \frac{[\text{M}]_{\text{org}}}{[\text{M}]_{\text{w}}} = \frac{[\text{M}]_0 - [\text{M}]_{\text{eq}}}{[\text{M}]_{\text{eq}}} \quad (2)$$

Here, $[\text{M}]_0$ and $[\text{M}]_{\text{eq}}$ represent the concentrations of metal ions in the aqueous phase before and after equilibrium, respectively.

Stripping of palladium(II), platinum(IV) and

Fig. 2 Effect of concentration of hydrochloric acid on the extraction percentage of metal ions with 0.01 mol dm⁻³ DEQ

gold(III) was performed by a single contact batch method using a 1.0 mol dm⁻³ aqueous thiourea solution containing 1.0 mol dm⁻³ hydrochloric acid. Stripping percentages over 95% were obtained for all metals.

2. Results and Discussion

2.1 Extraction selectivity for metal ion with DEQ

First, the extraction selectivity for metal ions in hydrochloric acid with DEQ in toluene was examined. Figure 2 shows the effect of the hydrochloric acid concentration on the extraction percentage of metal ions with DEQ. DEQ exhibited high selectivity for only gold(III), palladium(II) and platinum(IV) over copper(II), nickel(II), cobalt(II) and iron(III) over the whole concentration region of hydrochloric acid.

As observed in this figure, the extraction selectivity for metal ions is different from that with commercial long-chain amine extractants such as triisooctylamine (Tanaka and Akaiwa, 2000). This is probably attributable to the introduction of a quinoline group. At lower concentrations of hydrochloric acid, DEQ can be utilized in the selective separation of gold(III) and palladium(II) from copper(II), nickel(II), cobalt(II) and iron(III) in hydrochloric acid leach liquors.

2.2 Extraction equilibrium of palladium(II)

The effects of the various chemical species on the distribution ratio of palladium(II) from hydrochloric acid were examined in order to investigate the chemical species of palladium(II) existing in both phases.

2.2.1 Effect of concentration of hydrochloric acid on the distribution of palladium(II) To elucidate the extraction equilibrium of palladium(II), we examined the effects of the concentrations of hydrogen ion, chloride ion and extractant on the distribution ratio of palladium(II) at 303 K. Figure 3 shows the effect of hydrochloric acid concentration on the distribution ratio of palladium(II) with DEQ. The distribution ratio increased with an increase in hydrochloric acid concentration in its

Fig. 3 Effect of concentration of hydrochloric acid on the distribution ratio of palladium(II) with 0.01 mol dm⁻³ DEQ; solid line is the theoretical curve based on Eq. (6)

lower concentration region. The maximum value of the distribution ratio was obtained at around 0.5 mol dm⁻³ hydrochloric acid, and then the distribution ratio decreased with an increase in the hydrochloric acid concentration in the range of hydrochloric acid concentration more than 0.5 mol dm⁻³. This indicates that the extraction of palladium(II) is prevented by neutralization of DEQ with large excess of hydrogen ion.

2.2.2 Effect of hydrogen ion and chloride ion concentrations on the distribution of palladium(II) In order to separately evaluate the effects of hydrogen ion and chloride ion concentrations on the distribution ratio of palladium(II), the effect of hydrogen ion was examined at a constant chloride ion concentration ($[Cl^-] = 3.0$ mol dm⁻³), while the effect of chloride ion was examined at a constant hydrogen ion concentration ($[H^+] = 0.01$ mol dm⁻³). Here, the chloride concentration was changed using LiCl.

Figure 4 shows the effects of hydrogen ion and chloride ion concentrations on the distribution ratio of palladium(II). In the low concentration region of hydrogen ion, the distribution ratio increased with an increase in the hydrogen ion concentration. The distribution ratio appeared to lie on a straight line with a slope of 1. However, in the higher concentration region, the distribution ratio approaches a constant value, suggesting that free extractant molecules were saturated with hydrochloric acid.

On the other hand, for the effect of the chloride ion concentration, the distribution ratio decreased with an increase in chloride ion concentration. The plotted points lie on a straight line with a slope of -1. As is clear from a comparison of Figures 3 and 4, the dependence of the hydrochloric acid concentration on the distribution ratio of palladium(II) indicates the effect of hydrogen ion in the lower concentration region of hydrochloric acid, and

Fig. 4 Effect of concentrations of hydrogen ion and chloride ion on the distribution ratio of palladium(II) with 0.01 mol dm⁻³ DEQ: filled circle: [H⁺] = 0.01 mol dm⁻³, [Cl⁻] = 0.1–4.0 mol dm⁻³, open circle: [Cl⁻] = 3.0 mol dm⁻³, [H⁺] = 0.01–1.0 mol dm⁻³; solid lines are the theoretical curves based on Eq. (6), respectively

Fig. 5 Effect of concentration of DEQ on the distribution ratio of palladium(II). [HCl] = 1.5 mol dm⁻³; solid line is the theoretical curve based on Eq. (6)

the effect of chloride ion on the distribution ratio of palladium(II) in higher concentration of hydrochloric acid.

2.2.3 Effect of DEQ concentration on the distribution of palladium(II) Figure 5 shows the effect of DEQ concentration on the distribution ratio of palladium(II). As can be seen from this figure, the distribution ratio increased with an increase in the extractant concentration. The plotted points lie on a straight line with a slope of 1, indicating that one molecule of DEQ participates in the extraction reaction of palladium(II) from hydrochloric acid.

From these experimental results, it may be concluded that palladium(II) is extracted according to the

following Eqs. (3) and (4).

Here, RNN stands for the extractant (DEQ), and the upper-bar indicates the organic phase.

First, the hydrochloric acid salt of DEQ is formed with the hydrochloric acid, and then PdCl₃⁻ is extracted with this hydrochloric acid salt through the anion exchange mechanism as shown by Eq. (4).

From the mass balance of the extractant, we obtain the following equation since the palladium(II) concentration is very small compared with the concentration of DEQ.

$$[\overline{\text{RNN}}]_0 \cong [\overline{\text{RNN}}] + [\overline{\text{RNNHCl}}] \quad (5)$$

From Eqs. (3) to (5), the distribution ratio is shown as follows:

$$\log D = \log \left(\frac{K_1 K_2 [\text{H}^+] [\overline{\text{RNN}}]_0 \alpha_{\text{Pd}_3}}{1 + K_1 [\text{H}^+] [\text{Cl}^-]} \right) \quad (6)$$

$$\alpha_{\text{Pd}_3} = \frac{\beta_3 [\text{Cl}^-]^3}{1 + \sum_{n=1}^4 \beta_n [\text{Cl}^-]^n}$$

Equation (6) can be approximated by Eq. (7) at a high-concentration region of the chloride ion.

$$\log D \cong -\log [\text{Cl}^-] + \log K_2 + \log [\overline{\text{RNN}}]_0 + \log \alpha_{\text{Pd}_3} \quad (7)$$

The overall stability constants of the chloro complexes of palladium(II) are known to be $\beta_1 = 10^{4.7}$ [mol dm⁻³]⁻¹, $\beta_2 = 10^{7.7}$ [mol dm⁻³]⁻², $\beta_3 = 10^{10.3}$ [mol dm⁻³]⁻³ and $\beta_4 = 10^{11.9}$ [mol dm⁻³]⁻⁴ (Gel'fman and Kiseleva, 1969). The equilibrium constant (K_2) was obtained using values of β_n ($n = 1-4$) based on Eq. (7) from the distribution ratio in the high concentration region of chloride ion. The equilibrium constant (K_1) was obtained using values of K_2 based on Eq. (6). The values of the equilibrium constants were $K_1 = 4.65$ [mol dm⁻³]⁻² and $K_2 = 1.28 \times 10^7$ [—]. The solid curves in Figures 3 to 5 are theoretical ones based on Eq. (6). The theoretical curves are in good agreement with the experimental results, indicating that the extraction equilibrium of palladium(II) with DEQ are expressed by Eqs. (3) and (4).

2.3 Extraction equilibrium of platinum(IV)

2.3.1 Effect of concentration of hydrochloric acid on the distribution of platinum(IV) In order to elucidate the extraction equilibrium of platinum(IV), the effects of the concentrations of hydrogen ion, chloride ion and extractant on the distribution ratio of platinum(IV) were examined at 303 K. Figure 6 shows the effect of hydrochloric acid concentration on the distribution ratio of platinum(IV) with DEQ. The distribution ratio increased with an increase in the hydrochloric acid concentration.

2.3.2 Effect of hydrogen ion and chloride ion concentra-

Fig. 6 Effect of concentration of hydrochloric acid on the distribution ratio of platinum(IV) with 0.01 mol dm^{-3} DEQ

Fig. 7 Effect of concentrations of hydrogen ion and chloride ion on the distribution ratio of platinum(IV) with 0.01 mol dm^{-3} DEQ. Filled circle: $[\text{H}^+] = 0.01 \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 0.01\text{--}3.0 \text{ mol dm}^{-3}$, open circle: $[\text{Cl}^-] = 1.0 \text{ mol dm}^{-3}$, $[\text{H}^+] = 0.001\text{--}1.0 \text{ mol dm}^{-3}$; solid lines are the theoretical curves based on Eq. (11), respectively

tions on the distribution of platinum(IV) In a similar manner to the extraction equilibrium of palladium(II), the concentration dependencies of hydrogen ion and chloride ion were examined in order to separately evaluate their effects on the distribution ratio of platinum(IV). The effect of hydrogen ion was examined at a constant chloride ion concentration, while the effect of chloride ion was examined at a constant hydrogen ion concentration.

Figure 7 shows the effects of hydrogen ion and chloride ion concentration on the distribution ratio of platinum(IV). As can be seen from Figure 7, in the case of the chloride ion, the distribution ratio was constant value over the whole concentration region of the chlo-

Fig. 8 Effect of concentration of DEQ on the distribution ratio of platinum(IV): Filled circle: $[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.0 \text{ mol dm}^{-3}$, open circle: $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$, $[\text{Cl}^-] = 1.0 \text{ mol dm}^{-3}$; solid lines are the theoretical curves based on Eq. (11)

ride ion. On the other hand, in the case of the hydrogen ion, the distribution ratio was constant in the low concentration region of the hydrogen ion, and then the plotted points asymptotically approach a straight line with a slope of 2 in the high concentration region of chloride ion. Therefore, we examined the effect of the extractant concentration in two regions of hydrogen ion with a constant ionic strength of 1 mol dm^{-3} in the subsequent experiments.

2.3.3 Effect of DEQ concentration on the distribution of platinum(IV) The effect of extractant was examined at constant values of hydrogen ion concentration, i.e. 0.1 mol dm^{-3} and 1 mol dm^{-3} . The experimental results are shown in Figure 8. As can be seen from Figure 8, the distribution ratio increased with an increase in the extractant concentration. The plotted points appear to lie on a straight line with a slope of 2, indicating that two extractants participate in the extraction of platinum(IV) at high hydrogen ion concentration ($[\text{H}^+] = 1.0 \text{ mol dm}^{-3}$). While, at low hydrogen ion concentration ($[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$), it is clear from Figure 8 that the plotted points seem to lie on a straight line with a slope of 1.

From these experimental results, it may be concluded that platinum(IV) is extracted according to Eqs. (8) to (10).

First, platinum(IV) is extracted as a complex with a free molecule of DEQ through the coordination bonds by two kinds of nitrogen atom on DEQ. Furthermore, a hydrochloric acid salt of DEQ is formed as expressed by

Eq. (8), and then PtCl_6^{2-} is extracted with this hydrochloric acid salt through an anion exchange mechanism as shown by Eq. (10).

From the mass balance of the extractant, we obtain the following equation as the theoretical distribution ratio of platinum(IV) in a similar manner to palladium(II).

$$\log D = \log \left\{ \frac{[\overline{\text{RNN}}]_0 \alpha_{\text{Pt}_6}}{[\text{Cl}^-]^2} \left(K_1^2 K_4 [\text{H}^+]^2 [\text{Cl}^-]^2 + \frac{K_3}{[\overline{\text{RNN}}]_0^2} \right) \right\}$$

$$\alpha_{\text{Pt}_6} = \frac{\beta_6 [\text{Cl}^-]^6}{1 + \sum_{n=1}^6 \beta_n [\text{Cl}^-]^n} \quad (11)$$

Equation (11) can be approximated by the following equations at low and high-concentration regions of hydrogen ion, respectively:

$$\log D \cong -2 \log [\text{Cl}^-] + \log K_3 + \log [\overline{\text{RNN}}]_0 + \log \alpha_{\text{Pt}_6} \quad (12)$$

$$\log D \cong 2 \log K_1 + \log K_4 + 2 \log [\overline{\text{RNN}}]_0 + 2 \log [\text{H}^+] + \log \alpha_{\text{Pt}_6} \quad (13)$$

The over-all stability constants of the chloro complexes of platinum(IV) are known to be $\beta_1 = 10^{4.8} [\text{mol dm}^{-3}]^{-1}$, $\beta_2 = 10^{8.6} [\text{mol dm}^{-3}]^{-2}$, $\beta_3 = 10^{11.3} [\text{mol dm}^{-3}]^{-3}$, $\beta_4 = 10^{13} [\text{mol dm}^{-3}]^{-4}$, $\beta_5 = 10^{16.7} [\text{mol dm}^{-3}]^{-5}$ and $\beta_6 = 10^{19} [\text{mol dm}^{-3}]^{-6}$ (Nikolaeva *et al.*, 1965a, 1965b). The equilibrium constant (K_3) was obtained using values of β_n ($n = 1-6$) based on Eq. (12) from the value of the distribution ratio in the low-concentration region of the hydrogen ion. The equilibrium constant (K_4) was obtained using values of β_n ($n = 1-6$) based on Eq. (13) from the value of the distribution ratio in the high-concentration region of the hydrogen ion. The values of the equilibrium constants were as follows: $K_3 = 4.15 \times 10^2 [\text{mol dm}^{-3}]$ and $K_4 = 3.46 \times 10^4$ [—]. These suggest that the extracted species of platinum(IV) are almost ion pair type because the extraction equilibrium constant of the ion pair type of complex ($K_4 = 3.46 \times 10^4$ [—]) is greater than that of the coordination type of complex ($K_3 = 4.15 \times 10^2 [\text{mol dm}^{-3}]$). The solid curves in Figures 7 and 8 are theoretical ones based on Eq. (11) with these constants. The theoretical curves are in good agreement with the experimental results, indicating that the extraction equilibrium of platinum(IV) with DEQ are expressed by Eqs. (8) to (10).

Conclusions

N,N-Di(2-ethylhexyl)aminomethylquinoline (DEQ) with two kinds of nitrogen atom as ligands was newly synthesized to develop selective extractants for precious metals. DEQ is designed so as to exhibit high selectivity for precious metals through an electrostatic force by protonated tertiary amine and the coordination ability of quinoline base. As expected, DEQ in toluene exhibited

high selectivity for gold(III), palladium(II) and platinum(IV) over base metals such as copper(II), nickel(II) and cobalt(II) from hydrochloric acid. Gold(III) was quantitatively extracted over the tested concentration region of hydrochloric acid, while the extraction of palladium(II) and platinum(IV) significantly depends on the concentration of hydrochloric acid. Palladium(II) was extracted as a 1 : 1 complex through the ion pair formation and coordination bond as was expected, while platinum(IV) was extracted as a 1 : 1 complex and a 1 : 2 complex at low and high concentrations of hydrochloric acid, respectively.

Literature Cited

- Belova, V. V., A. I. Kholkin, T. I. Jidkova, T. P. Sidorova and N. G. Aleksandrova; "Use of Binary Extractants for Extraction and Separation of Noble Metals," *Miner. Process. Extr. Metall. Rev.*, **15**, 165 (1995)
- Belova, V. V., T. I. Jidkova, S. A. Vasilevich and A. I. Kholkin; "Influence of the Amine Nature on the Composition of Palladium Complexes in Solvent Extraction Systems," *Solvent Extr. Ion Exch.*, **15**, 1023-1042 (1997)
- Benguerel, E., G. P. Demopoulos and G. B. Harris; "Speciation and Separation of Rhodium(III) from Chloride Solutions: A Critical Review," *Hydrometallurgy*, **40**, 135-152 (1996)
- Gel'fman, M. I. and N. V. Kiseleva; "Stability Constants of Palladium Chloride Complexes," *Zh. Neorg. Khim.*, **14**, 502-504 (1969)
- Guo, J.-X., X. Sun, Z.-L. Yin, X.-M. Li, H.-Y. Yu, Y.-Z. Yang and S.-X. Sun; "Solvent Extraction of Gold(III) by Octadecyldimethylbenzylammonium Chloride (ODMBAC) from Chloride Solution," *J. Radioanal. Nucl. Chem.*, **256**, 595-598 (2003)
- Inoue, K., T. Furusawa, I. Nagamatsu, Y. Baba and K. Yoshizuka; "Solvent Extraction of Palladium(II) with Trioctylmethylammonium Chloride," *Solvent Extr. Ion Exch.*, **6**, 755-769 (1988)
- Iqbal, M., M. Ejaz, S. A. Chaudhri and Zamiruddin; "The Extraction of Trace Amounts of Gold from Different Aqueous Mineral Acid Solutions by Diphenyl-2-pyridylmethane Dissolved in Chloroform—Determination of Gold by Neutron Activation Analysis," *J. Radioanal. Nucl. Chem.*, **42**, 335-348 (1978)
- Jiang, T. and Y. Su; "Extracting Valuable Metals from Chloride Leaching Solutions of Smithsonite II. Extraction of Cadmium Chlorocomplexes by High Molecular Weight Amines," *Huadong Huagong Xueyuan Xuebao*, **17**, 15-20 (1991)
- Kim, C.-H., S. I. Woo and S. H. Jeon; "Recovery of Platinum-Group Metals from Recycled Automotive Catalytic Converters by Carbochlorination," *Ind. Eng. Chem. Res.*, **39**, 1185-1192 (2000)
- Lokhande, T. N., M. A. Anuse and M. B. Chavan; "Liquid-Liquid Extraction of Palladium(II) with *N*-*n*-Octylaniline from Hydrochloric Acid Media," *Talanta*, **46**, 163-169 (1998)
- Mhaske, A. A. and P. M. Dhadke; "Extraction Separation Studies of Rh, Pt and Pd Using Cyanex 921 in Toluene—A Possible Application to Recovery from Spent Catalysts," *Hydrometallurgy*, **61**, 143-150 (2001)
- Nikolaeva, N. M., B. V. Ptitsyn and E. D. Pastukhova; "In Stability Constant," *Zh. Neorg. Khim.*, **10**, 1058 (1965a)
- Nikolaeva, N. M., B. V. Ptitsyn and I. I. Gorbacheva; "In Stability Constant," *Zh. Neorg. Khim.*, **10**, 1051 (1965b)
- Shibata, J. and A. Okuda; "Recycling Technology of Precious Metals," *Shigen-to-Sozai*, **118**, 1-3 (2002)
- Szczepańska, I., A. Borowiak-Resterna and M. Wiśniewski; "New Pyridinecarboxamides for Rapid Extraction of Palladium from Acidic Chloride Media," *Hydrometallurgy*, **68**, 159-170 (2003)
- Tanaka, M. and H. Akaiwa; *Handbook of Solvent Extraction Chemistry* (Yubai-Chushutsu-Kagaku), p. 239, Shokabo, Tokyo, Japan (2000)