The first effective extractant for trivalent rhodium in hydrochloric acid solution

Hirokazu Narita,* Kazuko Morisaku and Mikiya Tanaka

Received (in Cambridge, UK) 6th August 2008, Accepted 9th September 2008
First published as an Advance Article on the web 8th October 2008
DOI: 10.1039/b813593b

The first effective extractant capable of the selective recovery of rhodium^{3+} from hydrochloric acid solution, *N*-*n*-hexyl-bis(*N*-methyl-*N*-*n*-octylethylamide)amine (HBMOEAA), has been developed.

Rhodium^{3+} extraction from acidic chloride solution to an organic solvent is one of the most difficult reactions.[1] To date, there has been no effective Rh extractant developed for industrial use, and in most of the separation and purification processes of platinum group metals (PGMs), rhodium remains in the raffinate.[2] Since Rh is primarily used in automobile catalysts, along with palladium and platinum, and is the most expensive of the PGMs (*e.g.* Rh $\approx$ Pt $\times$ 5),[3] recovery of Rh prior to the other PGMs seems to be desirable from an economic standpoint. Development of a useful Rh extractant is sorely needed.

In commercial processes, PGMs are dissolved using concentrated chloride media.[2] Rhodium forms octahedral aquo-chloro complexes of the general formula $[\mathrm{RhCl}_x(\mathrm{H_2O})_{6-x}]$ ($x \geqslant 5$) in those solutions, which are nearly impossible to extract. It has been explained that the poor Rh extraction would be based on steric hindrance of the highly charged octahedral complexes and the difficulty of packing two or three cationic organic molecules around a single ion.[1] Furthermore, the Rh^{3+} aquo-chloro complexes are kinetically inert;[2a,4] therefore, replacement of $\mathrm{Cl^-/H_2O}$ in the inner coordination sphere by extractants is generally unsuccessful. Although the addition of stannous chloride to Rh^{3+} in HCl solution drastically improves Rh extraction,[5] there are two problems: the use of a large amount of stannous chloride, and the difficulty of back-extraction. The capacity to both extract and back-extract Rh^{3+} from the chloride media without additives is preferable for a new extractant.

An ion-pair extraction using protonated extractants is considered for the Rh aquo-chloro anion complex because of their inert properties, although such a simple mechanism is insufficient to achieve high extraction efficiency. Hence, additional effects to the ion-pair reaction seem to be required. Recently, we demonstrated excellent extractions of PGMs using *N*-disubstituted amide compounds.[6] In addition, tertiary amine compounds can easily be protonated,[2b] and therefore, it is anticipated that tertiary amine compounds containing *N*-disubstituted amide groups will generate some synergistic effects relating to the Rh extraction. We report herein PGM extraction using a tertiary amine compound containing two *N*-disubstituted amide groups, *N*-*n*-hexyl-bis(*N*-methyl-*N*-*n*-octyl-ethylamide)amine (HBMOEAA) (Fig. 1), and compare it with that using tri-*n*-octylamine (TOA), *N*,*N*′-dimethyl-*N*,*N*′-di-*n*-octyldiglycolamide $\{n\text{-}\mathrm{C_8H_{17}(CH_3)NC(O)CH_2}\}_2\mathrm{O}$ (MODGA) and -thiodiglycolamide $\{n\text{-}\mathrm{C_8H_{17}(CH_3)NC(O)CH_2}\}_2\mathrm{S}$ (MOTDGA).

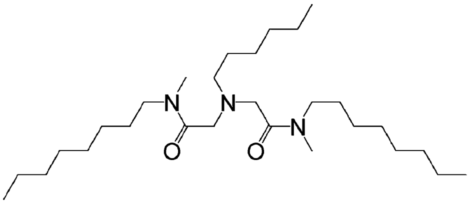

Fig. 1 Structure of HBMOEAA.

HBMOEAA was synthesized *via* two paths from commercially available materials.† MOTDGA and MODGA were synthesized according to literature methods.[6] TOA, purchased from Wako Pure Chemical Industries, Ltd., was used without further purification. All the other chemicals used in this study were of reagent grade. The extraction of metal ions was carried out batchwise at 23 ± 1 °C.‡

Fig. 2 shows the extraction percentages (*E*%) of Rh^{3+}, Pd^{2+} and Pt^{4+} with 0.50 M HBMOEAA, and Rh^{3+} with 0.50 M TOA, MOTDGA and MODGA as a function of HCl concentration. The Rh extraction with TOA, MODGA and MOTDGA is very poor, except that the *E*% of Rh with MOTDGA increases to approx. 50% at higher HCl concentration. In contrast, HBMOEAA extracts over 80% of Rh at 1.0–2.0 M HCl. This *E*% value is the highest ever obtained in Rh^{3+} extraction from highly concentrated HCl solution ($>$1 M). The *E*% of Rh drastically decreases past 3 M HCl. At 10 M HCl, Rh is hardly extracted. As for Pd and Pt extraction, the *E*% with HBMOEAA is almost 100% over the entire range of HCl concentration studied. This extraction pattern is similar to that in the MOTDGA–Pd and the TOA–Pd and –Pt systems, while the *E*% values in the MOTDGA–Pt and the MODGA–Pd and –Pt systems sharply increase with an increase in the HCl concentration (Fig. 3).

The drastic decrease in the *E*% of Rh in the HBMOEAA system provides for good selectivity during the back-extraction. As seen in Fig. 2, Pd and Pt are highly extracted at 10 M HCl, while Rh is hardly extracted. Therefore, the HBMOEAA

Research Institute for Environmental Management Technology, National Institute of Advanced Industrial Science and Technology (AIST), 16-1 Onogawa, Tsukuba, Ibaraki 305-8569, Japan. E-mail: hirokazu-narita@aist.go.jp; Fax: +81-29-861-8458; Tel: +81-29-861-8486

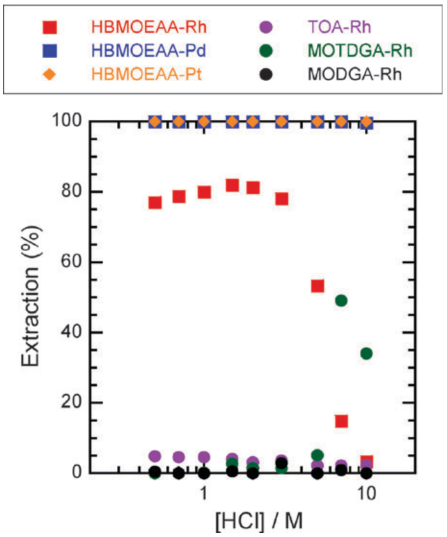

Fig. 2 Extraction percentages of Rh^{3+}, Pd^{2+} and Pt^{4+} with HBMOEAA, and Rh^{3+} with TOA, MOTDGA and MODGA as a function of HCl concentration. [Extractants]: 0.50 M.

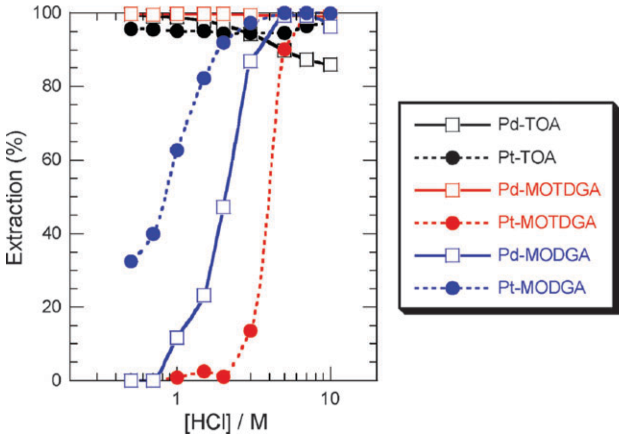

Fig. 3 Extraction percentages of Pd^{2+} and Pt^{4+} with TOA, MOTDGA and MODGA as a function of HCl concentration. [Extractants]: 0.50 M.

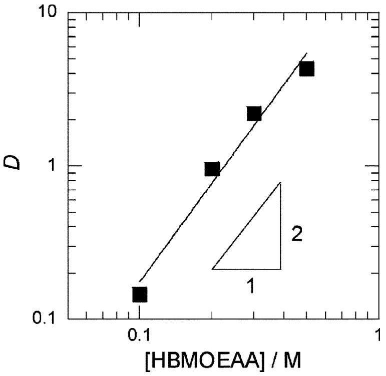

Fig. 4 Dependence of D_{Rh} on the HBMOEAA concentration. [HCl]: 2.0 M.

solution, after extracting Pd, Pt and Rh from 2.0 M HCl, was contacted with a 10 M HCl solution; as a result, the back-extraction percentage was approx. 90% for Rh and about 0% for Pd and Pt. This is a breakthrough because Rh can be recovered prior to Pd and Pt. Using a 10 M HNO_3 solution as a back-extraction reagent, the Pd and Pt are back-extracted with efficiency of approx. 80 and 40%, respectively. On the other hand, the Rh extracted in the MOTDGA is not back-extracted using a dilute HCl solution.

Plots of the logarithm of the distribution ratio of Rh (D_{Rh}) *vs.* log [HBMOEAA] at 2.0 M HCl lie on a straight line with a slope of 2 (Fig. 4); that is, two HBMOEAA molecules are involved in the extracted complex. The Rh loading capacity of the 0.50 M HBMOEAA–2.0 M HCl system was estimated from plots of the Rh concentrations in the organic *vs.* aqueous phases at the extraction equilibrium. As the initial Rh concentration in the aqueous phase increases, the Rh concentration in the organic phase is first enhanced, and then saturates at *ca.* 0.26 M (Fig. 5). This suggests that two moles of HBMOEAA extract one mole of Rh, which is consistent with the result from Fig. 4.

To gain an understanding of the extraction mechanism of the HBMOEAA–Rh system, we examined the dominant Rh species in HCl solution and compared the extraction behavior with that in the other systems studied (Fig. 2 and Fig. 3). The kinetic-based Rh–Cl speciation diagram in HCl solution using the activities of H_2O and Cl^{-} [1] shows that the abundance of $[RhCl_5(H_2O)]^{2-}$ is approx. 80% in 0.5–2 M HCl solution, and that it decreases with an increase in HCl concentration. $[RhCl_6]^{3-}$ becomes dominant (*ca.* 50%) at 5 M HCl, and *ca.* 90% at 10 M HCl. The variation in the abundance of $[RhCl_5(H_2O)]^{2-}$ with HCl concentration is nearly coincident with the change in the *E*% of Rh, suggesting that HBMOEAA cannot extract $[RhCl_6]^{3-}$, but rather, extracts $[RhCl_5(H_2O)]^{2-}$. As for the PGM extraction behavior, a drastic increase in the *E*% with an increase in HCl concentration is shown in the MODGA–Pd and –Pt, and MOTDGA–Pt and –Rh systems. Since Pd, Pt and Rh predominantly exist as anion complexes (*e.g.* $[PdCl_4]^{2-}$, $[PtCl_6]^{2-}$ and $[RhCl_6]^{3-}$) at the HCl concentration studied,[1,7] an ion-pair reaction between the protonated extractants and the anion complexes likely occurs. In contrast, MOTDGA efficiently extracts Pd at lower HCl concentration because the S atom of the MOTDGA molecule can directly

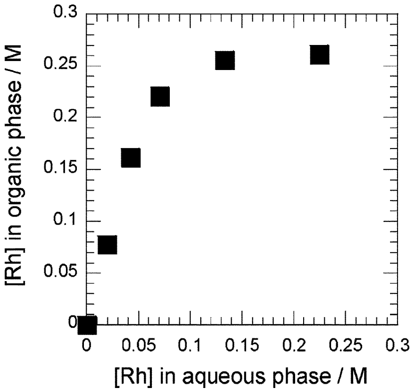

Fig. 5 Relationship between the Rh concentrations in the organic and aqueous phases at the extraction equilibrium with 0.50 M HBMOEAA as a function of the concentration of Rh in the initial aqueous phase. [HCl]: 2.0 M.

coordinate to the Pd; that is, the coordinative mechanism is dominant. In the TOA system, Pd and Pt are extracted well below 1.0 M HCl. TOA is a strong base extractant which is readily protonated at relatively low acid concentrations.[2b] For HBMOEAA, the extraction behavior of the PGMs is similar to that using TOA. This means that HBMOEAA primarily displays the properties of a tertiary amine rather than those of an *N*-disubstituted amide with regard to PGM extraction. Considering the dominant species at approximately 2.0 M HCl ($[RhCl_5(H_2O)]^{2-}$) as well as the 2 : 1 HBMOEAA–Rh stoichiometry obtained in this study, it could be concluded that two protonated HBMOEAA molecules extract Rh mainly by an ion-pair reaction. However, the much greater Rh extraction with HBMOEAA than with TOA must be attributable to some additional effects of the amide groups. In general, more stable complexes are presumably formed by hydrogen-bonding interactions between atoms/molecules in the inner coordination sphere and donor atoms of ligands (especially multidentate ligands).[8] The carbonyl O atom of the HBMOEAA molecule can be hydrogen bonded to the H atom of the coordinated water in the $[RhCl_5(H_2O)]^{2-}$ complex, as seen in the carbamylmethylenephosphonate erbium complex.[9] It is possible that such an interaction is conducive toward the good extraction of Rh in the HBMOEAA system. We are now performing a further structural study, in order to elucidate the detailed coordination mode in this extraction system.

In summary, we have found a new effective extractant, HBMOEAA, for trivalent Rh in HCl solution, which is promising for practical use in the future.

The authors wish to thank Dr Tsuyoshi Yaita, Japan Atomic Energy Agency, for many discussions, and Ms Kaeko Takada for technical assistance. This work was financially supported in part by a Grant-in-Aid for Scientific Research (20686060).

Notes and references

† The synthesis of HBMOEAA was performed according to the literature.[10] Chloroacetyl chloride (29.11 g, 0.25 mol) in diethyl ether (25 mL) was added dropwise to *N*-methyl-*N*-*n*-octylamine (73.10 g, 0.50 mol) in diethyl ether (175 mL) at −2 °C. The organic solution was stirred for 24 h at room temperature. The resulting solution was filtered and evaporated. After removal of the solvent under vacuum, the residue was purified by column chromatography (silica gel; hexane–ethyl acetate 19 : 1) to give 34.89 g (0.16 mol, yield 63.5%) of *N*-methyl-*N*-*n*-octylchloroacetamide. Found: C, 59.99; H, 9.99; N, 6.34%. Calcd for $C_{11}H_{22}NOCl$: C, 60.12; H, 10.09; N, 6.37%. ^1H NMR ($CDCl_3$): δ 0.88 (t, 3H), 1.2–1.4 (m, 10H), 1.5–1.7 (m, 2H), 2.96 and 3.07 (2s, 3H), 3.25–3.40 (t, 2H), 4.09 (s, 2H). The *N*-methyl-*N*-*n*-octylchloroacetamide (34.89 g, 0.16 mol) obtained was dissolved in chloroform (80 mL) which was added dropwise to a mixed solution of *n*-hexylamine (8.20 g, 0.08 mol) and triethylamine (17.68 g, 0.18 mol) in chloroform (120 mL). The mixture was stirred for 120 h at room temperature and 15 h at 50 °C. The organic solution was successively washed with 0.5 M HCl, 2.5 wt% Na_2CO_3 solution and water, and then dried over anhydrous Na_2SO_4. After the solvent was removed under vacuum, the residue was purified by column chromatography (silica gel; hexane–ethyl acetate 4 : 1) to give 21.97 g (0.05 mol, yield 59.1%) of *N*-*n*-hexyl-bis(*N*-methyl-*N*-*n*-octylethylamide)amine. Found: C, 70.55; H, 11.99; N, 8.72%. Calcd for $C_{28}H_{57}N_3O_2 \cdot 0.5H_2O$: C, 70.54; H, 12.26; N, 8.81%. ^1H NMR ($CDCl_3$): δ 0.88 (t, 9H), 1.2–1.4 (m, 26H), 1.4–1.6 (m, 6H), 2.69 (t, 2H), 2.90 and 3.04 (2s, 6H), 3.33 (t, 4H), 3.51 (s, 4H).

‡ In practical diluents like *n*-dodecane–2-ethylhexanol, HBMOEAA showed a good extraction property, while the other extractants tend to form a third phase during the metal extraction from highly concentrated HCl solution. Thus, chloroform is used as a diluent. The extractant diluted in chloroform was pre-equilibrated with the same volume of HCl solution in the absence of metal ions. After that, 1 mL of the pre-equilibrated organic phase and the same volume of the HCl solution containing 10^{-3} M metal ions (Pd, Pt and Rh) were poured into a 10 mL glass tube, vertically shaken for 30 min at an amplitude of 100 mm and a frequency of 200 spm, and then centrifuged. The Rh loading capacity was determined by the saturated concentration of Rh in the organic phase (0.50 M HBMOEAA) in a single extraction from a 2.0 M HCl solution, which was evaluated by increasing the initial Rh concentration from 0.10 to 0.50 M. The back-extraction of the extracted PGMs in the 0.50 M HBMOEAA after extraction from a 2.0 M HCl solution was performed using the same volume of a 10 M HCl or HNO_3 solution. The metal concentrations in the aqueous phase were measured by ICP-AES (Horiba ULTIMA2). The concentrations in the organic phase were calculated by the mass balance of the metals before and after the extraction.

1 E. Benguerel, G. P. Demopoulos and G. B. Harris, *Hydrometallurgy*, 1996, **40**, 135.

2 (*a*) M. Cox, in *Principles and Practices of Solvent Extraction*, ed. J. Rydberg, M. Cox, C. Musikas and G. R. Choppin, Marcel Dekker, Inc., New York, 2004, 2nd edn, pp. 455–505; (*b*) F. L. Bernardis, R. A. Grant and D. C. Sherrington, *React. Funct. Polym.*, 2005, **65**, 205.

3 *Platinum Today*, Johnson Matthey, http://www.platinum.matthey.com/ (accessed July 2008).

4 (*a*) S. A. Cotton, *Chemistry of Precious Metals*, Chapman & Hall, London, 1997, ch. 2; (*b*) L. Spiccia, *Inorg. Chim. Acta*, 2004, **357**, 2799.

5 (*a*) E. Benguerel, G. Cote, A. Lautie, G. P. Demopoulos and D. Bauer, *J. Chem. Technol. Biotechnol.*, 1995, **62**, 380; (*b*) E. Benguerl and G. P. Demopoulos, *J. Chem. Technol. Biotechnol.*, 1998, **72**, 183.

6 (*a*) H. Narita, M. Tanaka, K. Morisaku and T. Abe, *Chem. Lett.*, 2004, **33**, 1144; (*b*) H. Narita, M. Tanaka, K. Morisaku and K. Tamura, *Solvent Extr. Res. Dev., Jpn.*, 2006, **13**, 101; (*c*) H. Narita, M. Tanaka and K. Morisaku, *Miner. Eng.*, 2008, **21**, 483; (*d*) H. Narita, M. Tanaka and K. Morisaku, in *General Abstracts: Extraction and Processing, Proceedings of TMS 2007*, ed. B. Davis and M. Free, The Minerals, Metals & Materials Society, Pennsylvania, 2007, pp. 101–106.

7 (*a*) S. A. Wood, B. W. Mountain and P. Pan, *Can. Mineral.*, 1992, **30**, 955; (*b*) W. A. Spieker, J. Liu, J. T. Miller, A. J. Kropf and J. R. Regalbuto, *Appl. Catal., A*, 2002, **232**, 219.

8 (*a*) T. S. Franczyk, K. R. Czerwinski and K. N. Raymond, *J. Am. Chem. Soc.*, 1992, **114**, 8138; (*b*) V. C. Pierre, M. Botta, S. Aime and K. N. Raymond, *J. Am. Chem. Soc.*, 2006, **128**, 5544; (*c*) K. J. Bell, A. N. Westra, R. J. Warr, J. Chartres, R. Ellis, C. C. Tong, A. J. Blake, P. A. Tasker and M. Schröder, *Angew. Chem., Int. Ed.*, 2008, **47**, 1745.

9 S. M. Bowen, E. N. Duesler and R. T. Paine, *Inorg. Chim. Acta*, 1982, **61**, 155.

10 D. Erne, N. Stojanac, D. Ammann, E. Pretsch and W. Simon, *Helv. Chim. Acta*, 1980, **63**, 2264.