

Short communication

Solid phase extraction of some precious metals from hydrochloric acid to polystyrene-divinylbenzene porous resin impregnated with polyoxyethylene-type nonionic surfactant

Tohru Saitoh*, Syuntaro Suzuki, Masataka Hiraide

Department of Molecular Design and Engineering, Graduate School of Engineering, Nagoya University, Chikusa, Nagoya 464-8603, Japan

Received 8 August 2005; received in revised form 29 September 2005; accepted 3 October 2005

Available online 2 November 2005

Abstract

The solid phase extraction of gold(III), platinum(II), and palladium(II) to surfactant-impregnated polystyrene-divinylbenzene porous resin (XAD-4) was studied. The extracting media could be prepared just by mixing the resin in aqueous surfactant solutions. XAD-4 impregnated with a nonionic surfactant, polyethylene glycol monooleyl ether, was useful for extracting gold(III) from hydrochloric acid. The extractions of platinum(II) and palladium(II) were improved in the use of XAD-4 impregnated with a nitrogen-containing nonionic surfactant, polyethylene glycol stearyl amine. On the other hand, base metals such as copper(II), cobalt(II), nickel(II) and zinc(II), were hardly extracted.

© 2005 Elsevier B.V. All rights reserved.

Keywords: Solid phase extraction; Precious metal; Gold; Platinum; Palladium; Nonionic surfactant; XAD-4; Polyethylene glycol stearyl amine

1. Introduction

Solvent extraction of gold and other precious metals has been extensively studied for analytical or industrial purposes. Diethyl ether and isobutylmethylketone were wellknown solvents for extracting gold from acidic media [1–4]. The extraction was explained by the interaction between gold(III) salt and protonated oxygen atom of these solvents. Such interaction is also successfully utilized in the solvent extraction of gold(III) from hydrochloride with the use of polyoxyethylene-type nonionic surfactants as the extracting agents [5]. Protonated oxyethylene-moieties of the surfactants seemed to act as a chelating agent for gold(III)tetrachloride anion.

On the other hand, separation methods using surfactant micelles as separation media have been extensively studied [6]. Aqueous solutions of a certain polyoxyethylene-type nonionic surfactant separate into two distinct phases above its critical temperature, termed by cloud point [7]. One is aqueous phase containing few amounts of micelles, other is surfactant-rich phase

composing of concentrated aqueous micellar solution. This phenomenon has been used as a kind of efficient solvent extraction (namely cloud point extraction) of hydrophobic compounds [8–10]. When hydrophobic chelating agents are introduced to the micellar solution, metal ions that can complex with the chelating agents are extracted into the surfactant-rich phase [11,12]. In gold extraction, nonionic surfactants can act as both of extracting solvent and chelating agent. Applications of cloud point extraction of gold(III) from hydrochloride have been successfully demonstrated [13,14]. Another micelle-mediated separation method is micellar-enhanced ultrafiltration. Since surfactant micelles can be separated by passing the solution through an ultrafilter, the ultrafiltration of micellar solution is an effective method for separating hydrophobic solutes [15,16]. A successful application has been also performed for gold separation in aqueous solution by the use of the interaction of gold(III) salt to polyoxyethylene-moieties of surfactant molecules [17]. Different from the conventional solvent extraction, micelle-mediated separation methods eliminated the use of volatile, toxic, and highly flammable organic solvents. However, difficulties lie in the use of these methods because of the requirement of heating, centrifuging, or compressing the solution. The handling of viscous solution containing highly concentrated surfactant is also troublesome.

* Corresponding author. Tel.: +81 52 789 3579; fax: +81 52 789 3241.
E-mail address: saitoh@numse.nagoya-u.ac.jp (T. Saitoh).

Recently, we have designed a simple and efficient method for collecting gold in water [18]. The method is based on the selective complexation with a polyoxyethylene-type nonionic surfactant, polyethylene glycol (10) mono-*p*-iso-nonylphenyl ether (PONPE), impregnating in porous polystyrene resins. Gold in water samples was efficiently extracted onto the surfactant-impregnated resin. In the present study, the extractabilities of other precious metals, platinum and palladium, were also studied. Since it is reported that PONPE possibly decomposed to phenolic compounds having estrogenic activity during sewage process [19,20], polyethylene glycol stearyl alcohol having no phenolic moieties was used. Polyethylene glycol stearylamine having nitrogen atom was also used for improving the extractabilities of precious metals.

2. Experimental

2.1. Materials

Fine particles (75–140 μm) of porous polystyrene-divinylbenzene resin (Amberlite XAD-4, pore diameter 5.5–8 nm, Rohm and Haas, Paris, France) were prepared by crushing the resin with an 18–34-type ball mill (Mitamura Riken, Tokyo, Japan) and fractionating with stainless sieves. The particles were washed with 99.5% (v/v) ethanol until negligible absorption (Abs. <0.001) at 254 nm was observed in the eluate and subsequently rinsed with water. Nonionic surfactants, polyethylene glycol (20) oleyl ether ($\text{C}_{18}\text{H}_{35}(\text{OCH}_2\text{CH}_2)_{20}\text{OH}$, $\text{C}_{18}\text{EO}_{20}$), polyethylene glycol (10) stearylamine ($\text{C}_{18}\text{H}_{37}\text{N}(\text{OCH}_2\text{CH}_2)_x(\text{OCH}_2\text{CH}_2)_y\text{OH}$ ($x+y=10$), $\text{C}_{18}\text{NEO}_{10}$), were obtained from Tokyo Kasei (Tokyo, Japan). *N*-(Dithiocarboxy)sarcosine ammonium salt (DTCS) was purchased from Dojindo Lab. (Kumamoto, Japan). Other reagents used were of analytical grade. Water was prepared with a Milli-Q reagent water system (Millipore, St. Louis, MO, USA).

2.2. Preparation of surfactant-impregnated XAD-4 resin

To 1.0 ml of aqueous suspension containing 100 mg of XAD-4 was added a prescribed amount of the aqueous solution of a nonionic surfactant. The mixture was gently shaken for 2 h. The amount of the surfactant sorption was estimated from the concentration of the surfactant remained in the bulk aqueous solution. The nonionic surfactants were determined on the basis of micellar enhanced fluorescence of 1,8-anilino-naphthalene sulfonate (excitation: 385 nm, emission: 475 nm), that was the minor modification of the method reported by Lucy and Tsang [21]. After the suspension was gently mixed for 2 h, the surfactant-coated polymer resins were washed with water at six times and equilibrated with acidic solution.

2.3. Extraction of metal ions

A 10-ml portion of 0–4 M hydrochloric acid containing $50\ \mu\text{g l}^{-1}$ each of gold(III), platinum(II), palladium(II), cobalt(II), nickel(II), and copper(II) was poured into a 15-ml glass tube in which surfactant-impregnated resin, composing

500 mg of XAD-4 and prescribed amounts of nonionic surfactant (520 mg or 0.45 mmol for $\text{C}_{18}\text{EO}_{20}$, 510 mg or 0.70 mmol for $\text{C}_{18}\text{NEO}_{10}$), were precedently placed. After the tube was gently mixed for 30 min, it was stood for sinking the resin. All procedures were performed at room temperature (ca. 25 °C). The extent of metal extraction was calculated based on the determination of the metal in the supernatant with a Perkin-Elmer AAnalyst 600 graphite furnace atomic absorption spectrometer. The wavelengths (nm) for the determination of the respective metals are 242.8 (gold), 265.8 (platinum), 267.6 (palladium), 242.5 (cobalt), 232.0 (nickel), and 324.8 (copper).

3. Results and discussion

3.1. Sorption of nonionic surfactant on XAD-4

Nonionic surfactants, $\text{C}_{18}\text{EO}_{20}$ and $\text{C}_{18}\text{NEO}_{10}$, were well sorbed on XAD-4 resin due to highly hydrophobic properties of their alkyl moieties. The strong sorption of polyoxyethylene-type nonionic surfactants onto polystyrene-type resins has been reported in the areas of colloid and surface sciences [22,23]. At room temperature, the time for their equilibrium sorption was within 2 h. The sorption of the respective surfactants to XAD-4 increased with increasing the amount of the surfactant added and, then, became constant in the further addition (Fig. 1). The maximum sorption of $\text{C}_{18}\text{EO}_{20}$ and $\text{C}_{18}\text{NEO}_{10}$ on 1 g of XAD-4 was 0.9 and 1.4 mmol, respectively. On the other hand, negligible ($<0.5\%$) surfactants were eluted by washing with 50 ml of water or acidic solutions.

3.2. Extraction of metals to surfactant-impregnated XAD-4

The extraction of gold, platinum, palladium, and some base metals from different concentrations of hydrochloric acid to $\text{C}_{18}\text{EO}_{20}$ -impregnated XAD-4 was shown in Fig. 2. The extraction of gold(III) increased with increasing the concentration of hydrochloric acid. This is explained by the interaction of increasing formation of anionic gold(III)tetrachloride and protonated

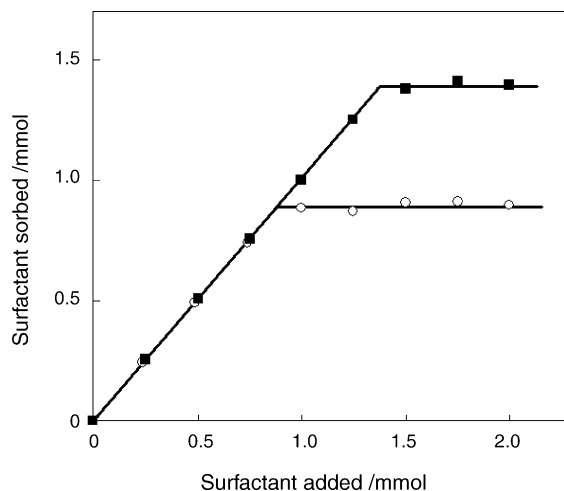


Fig. 1. Sorption of nonionic surfactant on 1 g of XAD-4. Surfactant: (○) $\text{C}_{18}\text{EO}_{20}$, (■) $\text{C}_{18}\text{NEO}_{10}$.

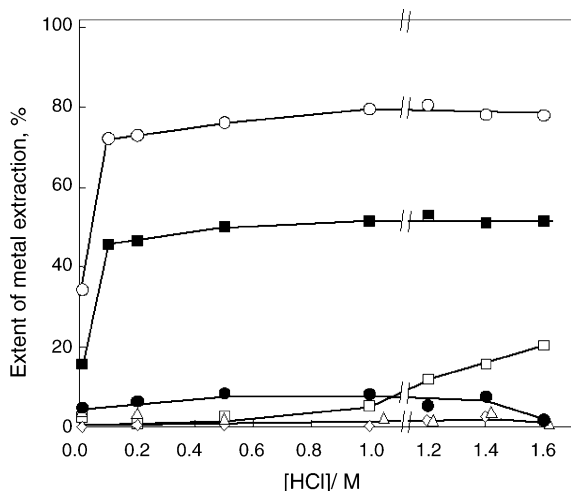


Fig. 2. The extraction of metal ions to $C_{18}EO_{20}$ -impregnated XAD-4 (500 mg) from 10 ml of hydrochloric acid as a function of HCl concentration. Metal ion ($50 \mu\text{g l}^{-1}$): (○) gold(III), (□) platinum(II), (■) palladium(II), (●) cobalt(II), (△) nickel(II), (◇) copper(II).

polyoxyethylene moiety of $C_{18}EO_{20}$. In contrast, the extractions of nickel(II) and cobalt(II), and copper(II) were negligible. In cloud point extraction, the extraction of these base metals could not completely be eliminated [14]. As previously reported, the concentration of surfactant in the surfactant-rich phase separated from the aqueous solution of PONPE-7.5 was ca. 18% [24]. This indicates that the surfactant-rich phase is normal micellar solution containing considerable amount of bulk aqueous solution. Metal ions can be distributed into the aqueous portion of surfactant-rich phase regardless of the interaction with the surfactant molecules. In the present study, because of the complete resolution of surfactant-impregnated resins from bulk aqueous solution, only the metals that can interact with surfactant molecules were extracted. However, recoveries of other precious metals, platinum(II) and palladium(II), were not satisfactory.

Alkyl amines have been successfully used as extracting agents for platinum(II) and palladium(II) from acidic solutions [25–28]. The extraction was attributed to the interaction of the metals to nitrogen atom of alkylamines. Thus, the surfactants possessing nitrogen atom are expected to have ability to bind with platinum(II) and palladium(II). The extents of the extraction of metal ions to $C_{18}NEO_{10}$ -impregnated XAD-4 are shown in Fig. 3. The extractions of platinum(II) and palladium(II) were remarkably improved. The capacities in the retentions of these metals to 1 g of the surfactant-impregnated resin were at least 50 mg for gold, 30 mg for platinum, and 20 mg for palladium.

Finally, elution of these precious metals from 500 mg of $C_{18}NEO_{10}$ -impregnated XAD-4 with 1 ml of eluting solvent was attempted. Thiosulfate or thiourea had often been employed for eluting gold from ion-exchange or chelating resins [29–31]. Aqueous solution of 0.5 M sodium thiosulfate was ineffective. Good elution ($67 \pm 3\%$, average of three experiments) of gold was achieved with the use of the aqueous solution containing 0.5 M thiourea and 0.02 M hydrochloride. On the other hand, the elution of platinum and palladium were not satisfac-

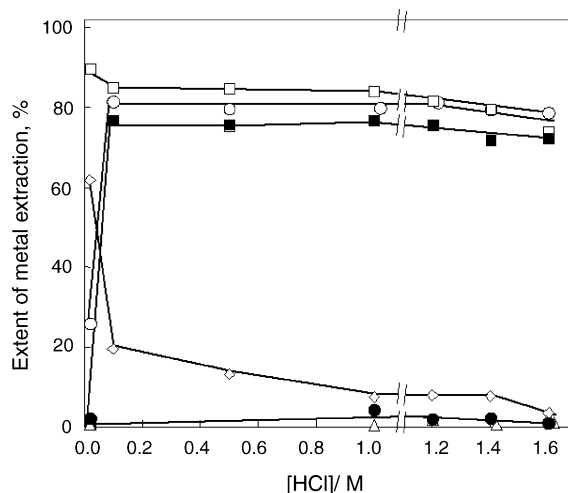


Fig. 3. The extraction of metal ions to $C_{18}NEO_{10}$ -impregnated XAD-4 (500 mg) from 10 ml of hydrochloric acid as a function of HCl concentration. Metal ion ($50 \mu\text{g l}^{-1}$): (○) gold(III), (□) platinum(II), (■) palladium(II), (●) cobalt(II), (△) nickel(II), (◇) copper(II).

tory ($10 \pm 2\%$ for platinum and $42 \pm 6\%$ for palladium). An aqueous solution of sulfur-containing chelating agent, DTCS (0.05 M), was effective for eluting gold ($96 \pm 1\%$) and palladium ($78 \pm 3\%$). However, the elution of platinum was still low ($15 \pm 2\%$). Platinum may form inert chelates with $C_{18}NEO_{10}$.

4. Conclusion

Surfactant-impregnated porous polystyrene-divinylbenzene resins were useful for extracting precious metals from hydrochloride. Separation media could be prepared just by mixing the resins in aqueous solution of nonionic surfactants. Without chemical synthesis, chelating functionality was easily introduced on solid surfaces. Easy introduction of specific functionalities would greatly extend the feasibilities of the preparation of separation media.

Acknowledgment

This work was supported by the 21st Century COE Program “Nature-Guided Materials Processing” of the Ministry of Education, Japan.

References

- [1] R. Bock, Z. Anorg. Allg. Chem. 263 (1950) 146.
- [2] H.M. Irving, Quart. Rev. 5 (1951) 200.
- [3] H. Goto, S. Suzuki, M. Saito, M. Kishimoto, Nippon Kagaku Zashi 85 (1978) 75.
- [4] N. Ichinose, Talanta 18 (1971) 105.
- [5] S. Akita, L. Yang, H. Takeuchi, Hydrometallurgy 43 (1996) 37.
- [6] W.L. Hinze, ACS Symp. Ser. 342 (1987) 2.
- [7] T. Nakagawa, in: M.J. Schick (Ed.), Nonionic Surfactant, Surfactant Science Series, vol. 1, Marcel Dekker, New York, 1967, pp. 481, 571, 843.
- [8] W.L. Hinze, E. Pramauro, CRC Crit. Rev. Anal. Chem. 24 (1993) 133.
- [9] B.M. Cordero, J.L.P. Pavón, C.G. Pinto, M.E.F. Laespada, Talanta 40 (1993) 1703.
- [10] F.H. Quina, W.L. Hinze, Ind. Eng. Chem. Res. 38 (1999) 4150.

- [11] H. Watanabe, H. Tanaka, *Talanta* 25 (1978) 585.
- [12] C.D. Stalikas, *Trends Anal. Chem.* 21 (2002) 343.
- [13] H. Koshima, H. Onishi, *Nippon Kagaku Kaishi* 1986 (1986) 889.
- [14] S. Akita, M. Rovira, A.M. Satre, H. Takeuchi, *Separ. Sci. Technol.* 33 (1997) 2159.
- [15] L.L. Gibbs, J.F. Scamehorn, S.D. Christian, *J. Membr. Sci.* 30 (1987) 67.
- [16] R.O. Dunn, J.F. Scamehorn, S.D. Christian, *Colloids Surf.* 35 (1989) 49.
- [17] S. Akita, L. Yang, H. Takeuchi, *J. Membr. Sci.* 133 (1997) 189.
- [18] T. Saitoh, S. Akita, T. Torii, M. Hiraide, *J. Chromatogr. A* 932 (2001) 159.
- [19] A.M. Soto, H. Justicia, J.W. Wray, C. Sonnenschein, *Environ. Health Perspect.* 92 (1991) 167.
- [20] J.J. Lech, S.K. Lewis, L. Ren, *Fundam. Appl. Toxicol.* 30 (1996) 229.
- [21] C.A. Lucy, J.S.W. Tsang, *Talanta* 50 (2000) 1283.
- [22] H. Carstensen, B.W. Müller, R.H. Müller, *Int. J. Pharm.* 67 (1991) 29.
- [23] M.S. Romero-Cano, A. Martín-Rodríguez, F.J. de las Nieves, *J. Colloid Interf. Sci.* 227 (2000) 322.
- [24] H. Hoshino, T. Saitoh, H. Taketomi, T. Yotsuyanagi, *Anal. Chim. Acta* 147 (1983) 339.
- [25] F.J. Alguasil, A. Cobo, A.G. Coedo, M.T. Dorado, A. Sastre, *Hydrometallurgy* 44 (1997) 203.
- [26] T.N. Lokhande, M.A. Anuse, M.B. Chavan, *Talanta* 46 (1998) 163.
- [27] T.N. Lokhande, M.A. Anuse, M.B. Chavan, *Talanta* 47 (1998) 823.
- [28] I.A. Kovalev, L.V. Bogacheva, G.I. Tsysin, A.A. Formanovsky, Y.A. Zolotov, *Talanta* 39 (2000) 52.
- [29] T. Braun, A.B. Farag, *Anal. Chim. Acta* 65 (1973) 115.
- [30] T. Groenewald, *Hydrometallurgy* 1 (1976) 277.
- [31] K. Terada, K. Morimoto, T. Kiba, *Anal. Chim. Acta* 116 (1980) 127.