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Extraction of Au(III) Using Aromatic Ketones in Acidic Chloride Media

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Recently, the extraction of Au(III) using the series of aliphatic ketones in hydrochloric acid media has been investigated in detail. The present study describes the extraction behaviors of Au(III) using a series of aromatic ketones, which has never been reported. Aromatic ketones with shorter alkyl side chains showed higher extractability. The rapid extraction and the extraction capacity using aromatic ketones were comparable to the industrial extractant dibutyl carbitol (DBC). Aromatic ketones, except acetophenone, are less soluble in water than DBC. The flash points of aromatic ketones are satisfactorily high for industrial operation, but their specific gravities comparable to that of water are unwelcome. Butyrophenone selectively extracted Au(III) from many other metals, except for high extraction of Fe(III) and Ga(III) at high concentrations. Au(III) extracted using butyrophenone recovered quantitatively as metallic gold by reduction using oxalic acid.

1. Introduction

Due to its excellent physical properties such as electrical conductivity and corrosion resistance, gold is used in electronic devices, resulting in price soaring. Solvent extraction is commonly used as a separation technique of gold due to the advantages such as high separation factors and large-scale processing [1-4]. Some oxygen-containing organic solvents can directly extract Au(III) as chloride complexes in hydrochloric acid media, which is classified as “ion solvation extraction”. Dibutyl carbitol (diethylene glycol dibutyl ether; DBC) is the most popular solvent for the extraction of Au(III) based on ion solvation [5-10]. Extraction of Au(III) using DBC from hydrochloric acid has various industrial advantages: rapid extraction, high extraction capacity, high selectivity for Au(III), and reductive recovery of gold under mild conditions. However, DBC gradually leaks into the aqueous phase in continuous operation due to its slight solubility in water (3 g/dm^3). Methyl isobutyl ketone (4-methyl-2-pentanone; MIBK) is also known to be a good solvent for the extraction of Au(III) [11,12]. The extractability of MIBK is higher than that of the most popular extractant DBC. However, MIBK is disadvantageous in industrial operation due to its safety risk based on the low flash point and the higher water solubility.

In recent years, the authors have investigated extraction behaviors of Au(III) using various organic solvents. Cyclopentyl methyl ether (CPME) was found to be available for the extraction of Au(III) [13,14]. However, CPME is disadvantageous for applying in industrial process due to the low flash point [15].

Aromatic diethers have also developed for the extraction of Au(III) [16]. 1,2-Dimethoxybenzene showed the highest extractability for Au(III) in the series of aromatic 1,2-diethers. Extraction behaviors using aliphatic ketones have also been studied [17]. All of the aliphatic ketones tested showed extractability for Au(III). Aliphatic ketones with shorter alkyl side chains showed higher extractability. However, lower molecular weight ketones have lower flash points and higher water solubility. Namely, there seems to be a trade-off relationship between extractability and the physical properties for industrial use. 2-nonanone (2-NON) has a good balance of extractability and physical properties.

As with the precedent for aliphatic ketones, aromatic ketones are also expected to extract Au(III). In the present study, extraction behaviors of Au(III) using several aromatic ketones were investigated. As physical properties of the solvent are important for industrial use, those of several aromatic ketones, DBC, MIBK were compared. Au(III) extractabilities using aromatic ketones with different alkyl side chain lengths were compared. As high extraction capacity is one of the key requirements in solvation extraction, concentration of Au(III) in aromatic ketones using an aqueous solution containing high concentration of Au(III) was demonstrated. Extraction selectivity for various metal ions was also studied. There have been no systematic reports of Au(III) extraction using aromatic ketones in the past.

2. Experimental

2.1 Reagents

The following organic solvents at analytical-grade were purchased and used without further purification; acetophenone (AcP), propiophenone (PrP), butyrophenone (BuP), valerophenone (VaP), octanophenone (OcP), MIBK, DBC (Fujifilm Wako Pure Chemical Industries, Ltd., Japan). The structures of the organic solvents are shown in Fig. 1. To determine the aqueous solubility of aromatic ketones, the aromatic ketone (AcP, PrP, BuP, VaP, or OcP) (1.0 cm^3) was contacted with distilled water (1.0 cm^3). After shaking the mixture at 30 °C for 24 h, the aqueous and organic phases were separated and the concentration of the aromatic ketone in the aqueous solution was determined using a UV-Vis spectrometer (Shimadzu UV-2450, Kyoto, Japan). The viscosity of the aromatic ketones at 25 °C was determined using a Cannon Fenske glass capillary viscometer. The logarithm of the partitioning coefficient between *n*-octanol and water (log*P*) is generally used as an index of their hydrophilic-lipophilic balance for organic molecules. The log*P* values were estimated using MarvinSketch 6.2.1 software (ChemAxon Ltd., Budapest, Hungary) and the KLOP (Klopman's) method [18].

Analytical-grade tetrachloroauric(III) acid tetrahydrate was purchased from Fujifilm Wako Pure Chemical Industries, Ltd., Japan, to prepare aqueous solutions for the extraction tests. Metal chlorides (Pd(II), Pt(IV), Fe(III), Al(III), Ga(III), In(III), La(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) (Wako Pure Chemical Ind. Ltd., Japan) were of analytical grade and were used as received.

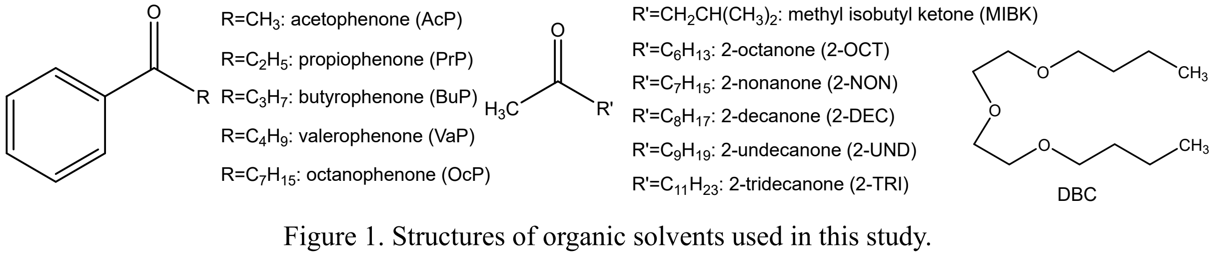

Figure 1. Structures of organic solvents used in this study.

2.2 Extraction of Au(III) and other metal ions

An aqueous solution was prepared by dissolving tetrachloroauric(III) acid (Au(III), 1.0×10^{-3} mol/dm^3) in 0.1 – 8.0 mol/dm^3 hydrochloric acid. The aqueous solution (5.0 cm^3) was contacted with an organic solvent (1.0 cm^3) in a glass sample bottle. Therefore, the volume ratio between organic and aqueous phases is 1:5 (O/A=0.2). The mixture was shaken (120 rpm) for 24 h in a thermostatted water bath at 30°C. After phase separation of the mixture, the concentration of Au(III) was determined using an atomic absorption spectrophotometer (AAS, Shimadzu AA-7000, Shimadzu Co., Kyoto, Japan). The extraction percentage of Au(III) was calculated based on the mass balance from the decrease of Au(III) concentration in the aqueous phase according to eq. (1):

$$\mathit{Extraction}\ [\%] = \frac{[\mathrm{M}]_{\mathrm{aq,init}} - [\mathrm{M}]_{\mathrm{aq,eq}}}{[\mathrm{M}]_{\mathrm{aq,init}}} \times 100 \qquad (1)$$

where $[\mathrm{M}]_{\mathrm{aq,init}}$ represents the initial concentration of Au(III) in the aqueous phase, and $[\mathrm{M}]_{\mathrm{aq,eq}}$ is the total concentrations of Au(III) in the aqueous phase at equilibrium.

Extraction of Au(III) using BuP as a function of initial Au(III) concentration was also carried out by contacting the aqueous solution (10.0 cm^3) containing $1.0 – 50 \times 10^{-3}$ mol/dm^3 Au(III) and BuP (1.0 cm^3) (O/A=0.1). Additionally, the extraction of various metal ions (Pd(II), Pt(IV), Fe(III), Al(III), Ga(III), In(III), La(III), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), or Pb(II)) using BuP was examined. The concentrations of metal ions were determined using AAS or an inductively coupled plasma atomic emission spectrometer (ICPS-8100, Shimadzu, Japan).

2.3 Reductive recovery of gold from BuP

Reductive recovery of Au(III) extracted in BuP using oxalic acid as a reductant was examined as follows. To extract Au(III) into BuP, an aqueous solution (20 cm^3) containing 1.0×10^{-3} mol/dm^3 Au(III) in 5.0 mol/dm^3 HCl and BuP (20 cm^3) (O/A=1.0) was contacted. After shaking the mixture at 30°C for 24 h, the phases were separated and the BuP solution (5.0 cm^3) into which Au(III) was extracted was contacted with a fresh aqueous solution (5.0 cm^3, O/A=1.0) that contained 0.10 mol/dm^3 oxalic acid in 0, 0.10 or 5.0 mol/dm^3 HCl. The aqueous solutions containing oxalic acid were not stock solutions and were used immediately after preparation. After shaking the mixture again at 30°C for 24 h, a solid substance with metallic luster, which would be metallic gold, was formed. After removal of the aqueous solution and the solid substance, the remaining BuP solution (3.0 cm^3) was contacted again with a fresh aqueous solution (3.0 cm^3, O/A=1.0) that contained 0.10 mol/dm^3 thiourea in 0.10 mol/dm^3 HCl at which Au(III) is quantitatively stripped [15-17]. After shaking the mixture at 30 °C for 24 h, the aqueous solution was separated. The concentration of Au(III) in the aqueous solutions was quantified to determine the recovery percentage (Recovery [%]) of gold as the solid substance according to eq. (2):

$$\mathit{Recovery}\ [\%] = \frac{[\mathrm{Au(III)}]_{\mathrm{org,init}} - [\mathrm{Au(III)}]_{\mathrm{oxa}} - [\mathrm{Au(III)}]_{\mathrm{thio}}}{[\mathrm{Au(III)}]_{\mathrm{org,init}}} \times 100 \qquad (2)$$

where $[\mathrm{Au(III)}]_{\mathrm{org,init}}$ represents the initial Au(III) concentration in the organic phase before reduction, $[\mathrm{Au(III)}]_{\mathrm{oxa}}$ is the concentration of Au(III) in the aqueous phase of oxalic acid, and $[\mathrm{Au(III)}]_{\mathrm{thio}}$ is the Au(III) concentration in thiourea solution. Additionally, a X-ray diffraction (XRD) pattern of gold recovered from

BuP was recorded using CuK$_\alpha$ radiation on a PANalytical X'Pert PRO MRD diffractometer (Malvern Ltd., UK).

3. Results and Discussion

3.1 Physical properties of aromatic ketones

Solvents for the extraction of Au(III) used in industrial processes must not only have a high extractability, but also satisfy various physical properties. Table 1 summarizes the physical properties of aromatic ketones and other solvents. The aqueous solubilities of aromatic ketones except for acetophenone have lower water solubility than DBC, which results in fewer leaks of the solvent into the aqueous phase. The flash points of aromatic ketones are reasonably high and industrially acceptable. Their viscosities are comparable to DBC. A disadvantage of aromatic ketones is their specific gravities close to that of the aqueous phase, which would result in phase inversion. In a recent study, 2-NON was suggested to have the optimal balance in aliphatic ketones [17]. As the physical properties of BuP are close to those of 2-NON and are acceptable as an extraction solvent, extraction behavior using BuP was especially focused in the following extraction tests.

Table 1. Properties of aromatic ketones and other solvents.

	AcP	PrP	BuP	VaP	OcP	2-NON	DBC	MIBK
Molar weight [g/mol]	120.15	134.18	148.21	163.23	204.31	142.2	218.33	100.16
Solubility in water [g/dm^3]	6.1	1.6	0.51	0.16	0.00085	0.5	3.0	19.1
Viscosity [mPa･s]	1.76	1.73	2.19	2.58	4.52	1.3	2.40	0.61
Boiling point [°C]	202	216	221	244	290	195	255	116
Specific gravity [g/cm^3]	1.01	0.998	0.979	0.963	0.934	0.82	0.88	0.80
Flash point [°C]	80	92	88	102	113	76	122	17
log*P*	1.63	2.41	2.88	3.35	4.76	3.13	3.11	1.52

3.2 Extraction behaviors of Au(III) using aromatic ketones

Figure 2 shows the time course of Au(III) extraction using BuP in 5.0 mol/dm^3 HCl. The extraction percentage increased within short shaking time and reached a plateau after 10 min. Rapid extraction is a typical behavior in solvation extraction, as shown in Au(III) extraction using other oxygen-containing organic solvents [13,14,16,17]. For operational convenience, the extraction experiments in the following sections were conducted by contacting the aqueous and organic phases for 24 h.

Figure 3 shows the extraction profiles of Au(III) using aromatic ketones, MIBK, DBC, and 2-NON as a function of hydrochloric acid concentration. In ion solvation extraction in hydrochloric acid media, ketones and ethers are considered to extract Au(III) as a monoanionic tetrachloride complex $AuCl_4^-$ [1,8]. The

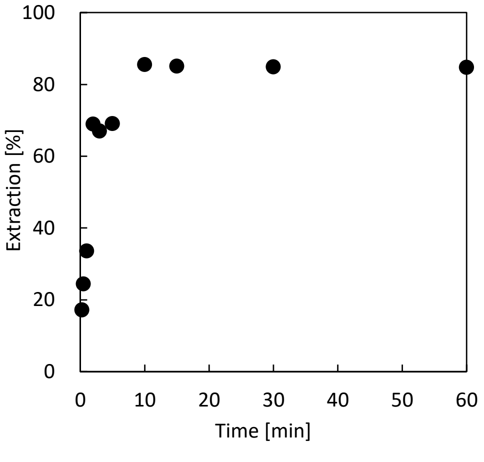

Figure 2. Rate of Au(III) extraction using BuP. [Au(III)]=1.0 × 10^{-3} mol/dm^3, [HCl]=5.0 mol/dm^3.

extraction percentage increases with the increase of hydrochloric acid, which is similar behavior to those using other solvents such as aliphatic ketones and aromatic diethers in recent studies [16,17]. The order of extractability of aromatic ketones in 0.1 – 1.0 mol/dm^3 HCl was AcP > PrP > BuP > VaP > OcP, which means that more polar solvents are better for extraction. In our recent study [17], more polar aliphatic ketones also showed higher extractability. As the polarity of the solvents seems to influence to the extraction, the relationship between the extraction percentage of Au(III) in 0.1 mol/dm^3 HCl and the log*P* of various ketones and DBC was investigated (Figure 4). The results using aliphatic ketones are cited from a previous paper [13]. The extraction decreased as the increase of log*P* value, suggesting a correlation between them. Recently, the relationship between the extractability for Au(III) and the Hansen solubility parameters (HSPs) was investigated [19]. As a correlation between the extractability and HSPs was also suggested, the extractability for Au(III) seems to be governed by solvent properties including polarity.

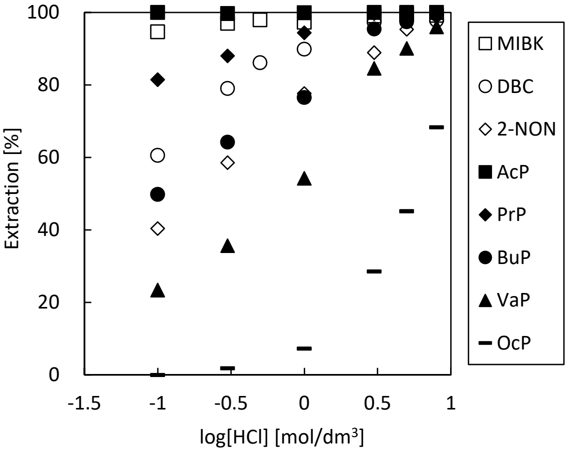

Figure 3. Extraction profiles of Au(III) using aromatic ketones, DBC, MIBK, and 2-NON as a function of HCl concentration: O/A = 0.2, [Au(III)] = 1.0 × 10^{-3} mol/dm^3.

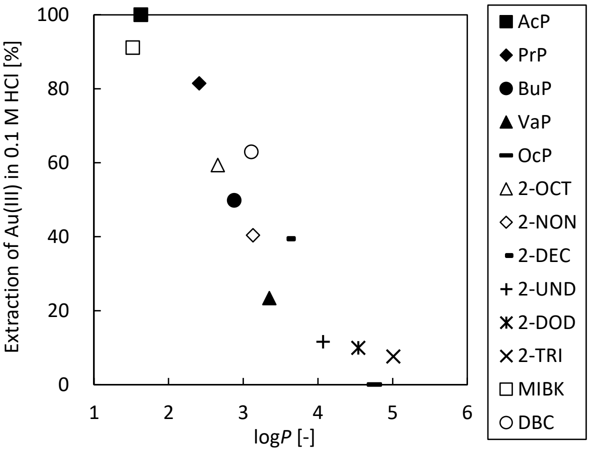

Figure 4. Relationship between log*P* of the solvents and the extraction percentage of Au(III) from 0.1 mol/dm^3 HCl.

In solvation extraction, large quantity of Au(III) is extracted into the extracting solvents [1,6,14]. Figure 5 shows the Au(III) concentration in the organic phase after extraction using MIBK, DBC, 2-NON and BuP as a function of the initial Au(III) concentration in the aqueous phase. As the extraction tests were performed at O/A = 0.1, Au(III) can be concentrated 10-fold in the organic phase. The concentration in the organic phase increased with the increase of the initial concentration of

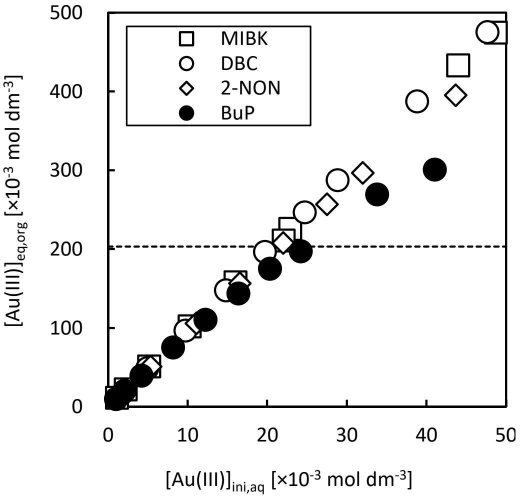

Figure 5. Effect of Au(III) concentration on Au(III) extraction using BuP, DBC, MIBK, and 2-NON [17] in HCl media: O/A = 0.1, [HCl] = 5.0 mol/dm^3. Broken line represents $[\mathrm{Au(III)}]_{\mathrm{eq,org}}$ = 40.0 g/dm^3 (0.203 mol/dm^3).

Au(III) in the aqueous phase. Industrially, the concentration of Au(III) in the extracting solvents should be above 40 g/dm^3 [1,14]. The concentration of Au(III) in any solvents examined exceeded the threshold. The extraction quantity of Au(III) into the extraction phase using BuP was relatively lower than that of other solvents under same conditions.

3.3 Extraction selectivity for metal ions using BuP

Ion solvation extraction using DBC is used for the selective extraction of Au(III) at INCO's (currently Vale) operations [6]. Extraction profiles of various metal ions using BuP of a different concentration of HCl are shown in Figure 6. Pd(II) and Pt(IV) are rarely extracted, in contrast to Au(III) being extracted with increasing hydrochloric acid concentration. Most base metals are not extracted using BuP at all. Fe(III) and Ga(III) are exceptionally extracted under high concentration of hydrochloric acid. Au(III) should be extracted as a tetrachloride complex ($AuCl_4^-$) with proton (H^+) in hydrochloric acid media [7,8]. Fe(III) and Ga(III) should also be extracted as tetrachloride complexes ($FeCl_4^-$ and $GaCl_4^-$) under high HCl concentration [20]. The metal selectivity of BuP is similar to that of various ethers and ketones in previous studies [13,14,16,17]. MIBK extracts In(III) under high concentration of hydrochloric acid, probably due to the higher extractability [14], while BuP does not extract at all. Therefore, BuP can be used for the selective extraction of Ga(III) from the aluminum group. The metal selectivity using BuP is very close to that of an aliphatic ketone 2-NON [17]. These results suggest that BuP can be used for the separation of Au(III), Fe(III), Ga(III) from other metal ions in hydrochloric acid media.

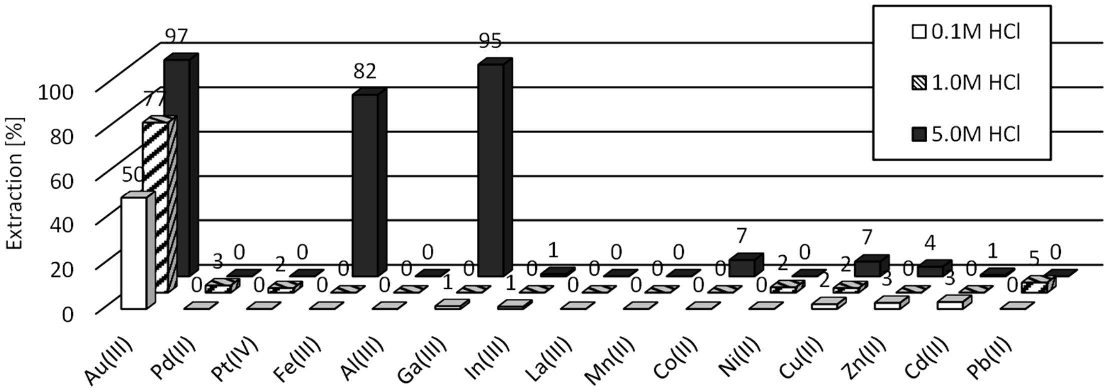

Figure 6. Extraction of metal ions using BuP in HCl media: O/A = 0.2, [metal] = 1.0×10^{-3} mol/dm^3.

3.4 Reductive recovery of gold

Typically extracted Au(III) based on ion solvation is recovered by reduction using oxalic acid according to the eq. (3) [1,14,17]:

$$2HAuCl_4+3H_2C_2O_4 \rightarrow 2Au+8HCl+6CO_2 \tag{3}$$

The reductive recovery of Au(III) extracted using BuP was investigated (Table 2). Au(III) was almost quantitatively recovered by contact with the aqueous solution containing 0.10 mol/dm^3 oxalic acid. As hydrogen chloride is produced in the reduction reaction shown in eq. (3), the recovery decreased with increasing hydrochloric acid concentration. Contact with the solution containing oxalic acid produced a solid material with a metallic luster that should be gold (Figure 7). The XRD pattern of gold recovered by reduction showed four main peaks at 38.26°, 44.52°, 64.63°, and 77.67°. The peaks are originated from gold crystals that correspond to Miller indices of (111), (200), (220), and (311), which agree with those of metallic gold crystals in the database (JCPDS File No. 4-0784). The result indicates that Au(III) extracted using BuP can quantitatively be recovered by reduction as in the conventional process.

Table 2. Reductive recovery of gold from BuP: $[\mathrm{Au(III)}]_{\mathrm{ini}} = 1.0 \times 10^{-3}$ mol/dm^3.

Reagent	Recovery [%]
0.10 mol/dm^3 $(COOH)_2$	98.9
0.10 mol/dm^3 $(COOH)_2$ in 0.10 mol/dm^3 HCl	61.8
0.10 mol/dm^3 $(COOH)_2$ in 5.0 mol/dm^3 HCl	0

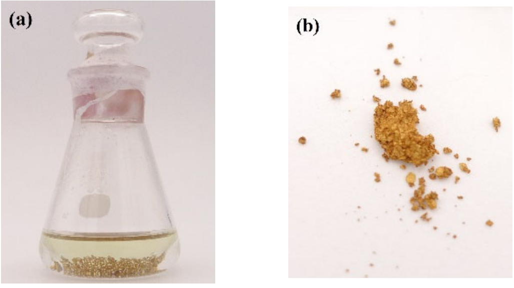

Figure 7. Photograph of gold recovered from BuP by reduction using oxalic acid: (a) a mixture after reduction and (b) recovered metallic solid.

4. Conclusion

Aromatic ketones are found to be available for the extraction of Au(III) based on ion solvation. Extraction using aromatic ketones was rapid and high capacity like DBC. The effect of the alkyl side chains of aromatic ketones on the extraction of Au(III) was similar to those of aromatic diethers and aliphatic ketones in previous studies: More polar aromatic ketones with shorter side chain showed higher extractability. Selective extraction of Au(III) from other metals using aromatic ketones and quantitative reductive recovery of the extracted gold were also satisfactory. The physical properties of BuP, such as low water solubility, low viscosity, and relatively high flash point are favorable for industrial extraction operations. However, specific gravity of aromatic ketones close to that of water is not preferred because it may lead phase inversion.

As the demand for recycling of waste electrical and electronic equipment (WEEE) is expected to increase, more efficient purification processes will be required in future. Aromatic ketones might be alternatives to the currently popular solvents such as DBC due to their high extractability for Au(III) and good physical properties.

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