Korean Chem. Eng. Res., 55(4), 503-509 (2017)
https://doi.org/10.9713/kcer.2017.55.4.503
PISSN 0304-128X, EISSN 2233-9558

Precious Metals Extraction Processing in Chloride Media by Using Ionic Liquids as Novel Extractant Systems

Jyothi Rajesh Kumar, In-Hyeok Choi and Jin-Young Lee†

Convergence Research Center for Development of Mineral Resources (DMR), Korea Institute of Geoscience & Mineral Resources (KIGAM), 124, Gwahak-ro, Yuseong-gu, Daejeon, 34132, Korea
(Received 23 December 2016; Received in revised form 17 January 2017; accepted 31 March 2017)

Abstract – The present experimental study proposed two ionic liquids (ILs) namely [Aliquat 336] [HSO_4] (prepared and characterized at our laboratory) and Cyphos 101 IL (supplied by Cytec Company) dissolved in two different diluents such as DCM (di-chloro-methane) and toluene applied for PMs extraction. The first IL [Aliquat 336] [HSO_4] prepared and confirmed the formation of final product by using FT-IR and TGA studies. The primary experiment in solvent extraction processing is kinetic effect; 0 to 30 time varied for PMs by using two ILs and confirmed the optimized extraction equilibrium time. This study was conducted for PMs (Pt, Rh and Cu) extraction and separation from each other by using proposed ILs. This is the primary study of the utilizing green solvents such as ILs as an extractant system for Pt, Rh and Cu extraction and possible separation.

Key words: Precious metals, Extraction, Separation, Ionic liquids

1. Introduction

Precious metals (PMs) including gold, platinum, palladium, and rhodium have been widely used due to their specific properties such as ductility, noncorrosiveness and high stability. Fig. 1 shows the applications of PMs in various sectors. However, the limited resources and great demand of PMs in industry have led to the urgent recovery of these noble metals from PMs-loaded resources. Many technologies, such as solvent extraction, adsorption, ion-exchange, precipitation and electro-winning, have been extensively used for recovery of PMs from resources. Among them, the solvent extraction process has been receiving great attention owing to fast extraction rate and high loading property (Fig. 2). However, this process has some problems of simultaneously separating and purifying PMs from multi-metal mixtures owing to their similar physical and chemical properties. Therefore, an effective extraction process is needed for the selective separation and recovery of PMs. For this purpose ionic liquids (ILs) have recently attention instead of traditional extractants for recovery of metal owing to their specific characteristics such as negligible vapor pressure with high thermal stabiliy and tunable viscosity and their good properties towards metals.

Ionic liquids (IL's) are salts with melting points below 100 °C and liquids lower temperatures than other salts [1]. The unique properties of the IL's are high ionic conductivity, non-flammability, non-volatility, highly thermally stable with highly solvating wide temperature range for liquid phase (Fig. 3). IL's are separated into two categories: organic and inorganic ions. Organic species exist as cations and organic/inorganic species as anion [1].

The reported literature on IL's as extractant systems (or) solvent media for PM's extraction separation is limited. An application of ionic liquids (IL's) in hydrometallurgy was reported recently [2]. This reviewed synthesis in extraction processing of the metals.

Divalent/tetravalent platinum and divalent palladium extraction with 1-octyl-3-methylimidazolium hexa-fluorophosphate ([Omim] [PF_6]) and di-stearyl-di-methyl-ammonium chloride (DSDMAC) (quaternary ammonium salt) from hydrochloric acid solutions was reported recently [3]. By using both the extractant systems, tetravalent platinum is more favorable to separate from palladium when compared with divalent platinum (separation factor's (SFs): 27 and 13 for Pt(IV), whereas 4.1 and 2.7 for Pt(II)). Undiluted imidazolium

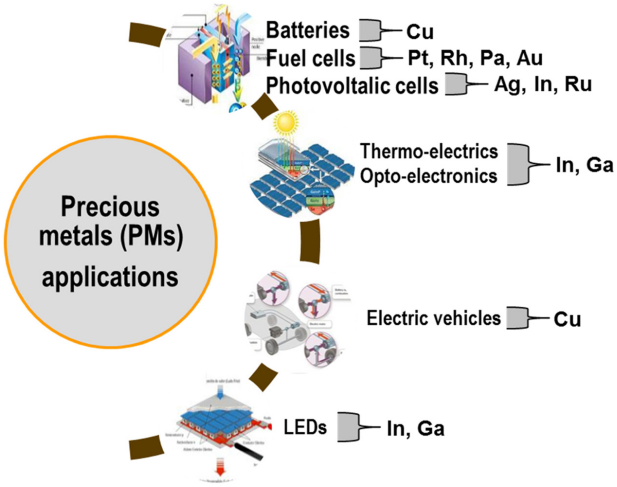

Fig. 1. Applications of precious metals (PMs) in various sectors.

† To whom correspondence should be addressed.
E-mail: jinlee@kigam.re.kr
‡ This article is dedicated to Prof. Choon Han on the occasion of his retirement from Kwangwoon University.

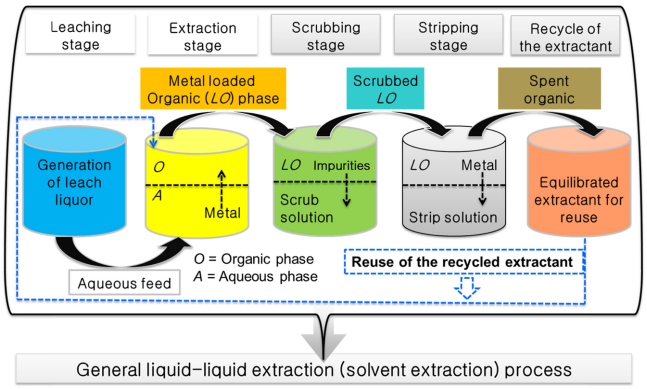

Fig. 2. The overall liquid-liquid extraction (solvent extraction) process for metal ions separation and recovery.

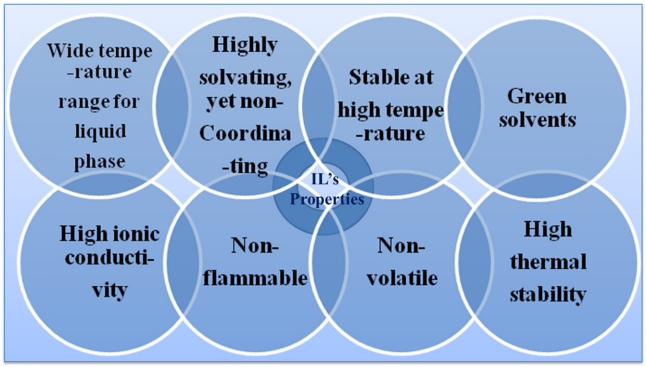

Fig. 3. Properties of ionic liquids (IL's).

based IL's with Tf_2N^- as anions are utilized for Pt and Pd separation in chloride media [4].

Various platinum compounds such as $PtCl_6^{2-}$, $PtBr_6^{2-}$, $PtSCN_6^{2-}$ have been liquid-liquid extracted or precipitated by hydrophobic IL's in HBr or HCl solutions. Three-liquid phase system for extraction and separation of Pt(IV) from Pd(II) and Rh(III) was developed [5]. Platinum(IV) was stripped with 1 or 3 mol dm^{-3} nitric acid 56.7% and 68.5% at a phase ratio is 1:12 [6]. Two IL's mixtures (tri-octyl-ammonium bis(tri-fluoro-methane-sulfonyl) amide ([TOAH] [NTf_2]) and trioctylammonium nitrate ([TOAH][NO_3])) were utilized for palladium and platinum selective extraction from hydrochloric acid solutions [7]. With IL phase and aqueous phase ratio 1:2 up to 8 mol dm^{-3} HNO_3 was tested for back extraction process, and it was reported that advantageous to Pt recovery when compared with Pd [7].

Two commercial IL's such as Cyphos IL 101 and 104 chemical names trihexyl(tetradecyl)phosphonium chloride and trihexyl-(tetra-decyl) phosphonium bis-2,4,4-trimethylpentylphosphinate were implemented for selective extraction of Pd(II) from Ni(II), Cu(II), Pb(II), Fe(III), Rh(III), Ru(III) and Pt(IV) in presence of toluene diluent system [8]. Betainium bis-(trifluoromethanesulfonyl) imide IL was used for extraction of Pd(II), Rh(II) and Ru(III) from nitric acid solutions and the order of extraction efficiency reported, Pd(II) > Rh(III) > Ru(III) [9]. Lower acidic conditions (0.01 mol dm^{-3} HNO_3) are much favorable to distribute the rhodium (D_{Rh} is 16.9) from aqueous phase to organic phase in presence of hydrophobic ammonium based ionic liquid with CMPO extractant system [10].

80% of 8.0 mmol dm^{-3} copper was extracted from 800 µL of IL (3-butylpyridinium bis(trifluoromethanesulfonyl)imide [3-BuPyr] [NTf_2]) [11]. At room temperature selective extraction of copper from other metal ions such as mercury, silver and palladium was performed by using hydrophobic ionic liquids (IL's contains cations 1-octyl-4-methylpyridinium[4MOPYR]$^+$, 1-methyl-1-octylpyrrolidinium [MOPYRRO]$^+$, or 1-methyl-1-octylpiperidinium [MOPIP]$^+$ and anions tetra-fluoroborate [BF_4]$^+$, trifluoromethyl sulfonate [TfO]$^+$, or nonafluorobutyl sulfonate[NfO]$^+$) [12].

We tested two ionic liquids, [Aliquat 336][HSO_4] and Cyphos 101 IL, dissolved in two different diluents, DCM (dichloro-methane) and toluene utilized for PMs extraction and separation.

2. Experimental

2-1. Apparatus and reagents

An inductively coupled plasma optical emission spectrometer (ICP-OES) manufactured by Thermo Scientific, USA model iCAP 6000 Series ICP Spectrometer was used to analyze the precious metals such as platinum, rhodium and copper from aqueous solutions. The operative conditions of ICP-OES were as follows: RF power = 1350 w, pump rate = 45, Aux. gas flow = 0.5 dm^3/min, Neb. Gas flow = 0.6 dm^3/min and Purge gas flow = normal. A Thermo scientific pH meter (supplied by USA) was used for pH measurements and every day. Tt was standardized by following standards: pH = 1.68, 4.01, 7.00 and 10.01. Temperature controlled shaking incubator (Model: SI-300/300R/600/600R) was used only for liquid-liquid extraction studies (Fig. 4).

The present study used one commercial ionic liquid, Cyphos IL 101 (Cy101), chemical name trihexyl(tetradecyl)phosphonium chloride molecular formula $C_{38}H_{68}ClP$ with formula weight 519.31. The physical properties of the Cy101 are density 0.8819 and viscosity is 1824 at 25 °C temperature. The other ionic liquid prepared from Aliquat 336 and the physical appearance of both the ILs is presented in Fig. 5. The ionic liquid [Aliquat 336] [HSO_4] was prepared and characterized based on the reported literature [13].

Fig. 4. Photo of the shaking incubator used for liquid-liquid extraction studies.

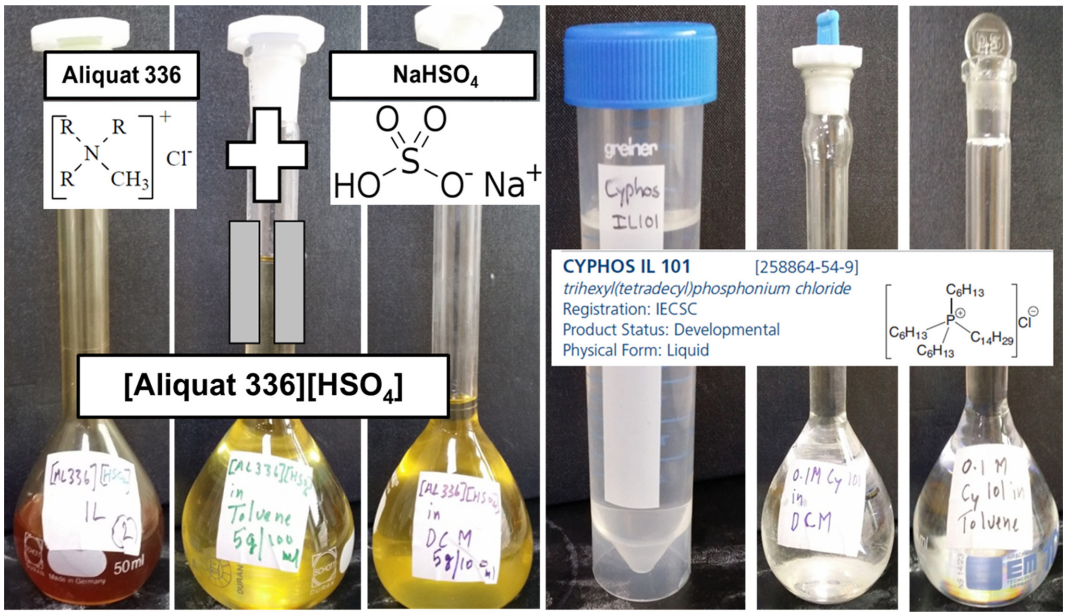

Fig. 5. The [Aliquat 336] [HSO_4] ionic liquid and Cyphos 101 IL ionic liquid original and dissolved in toluene and di-chloromethane diluents for present study.

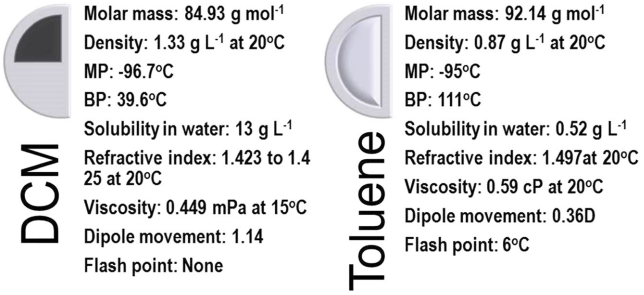

Fig. 6. Chemical properties of diluents (Di-chloro-methane (DCM) and Toluene.

2-2. Diluents properties

The stability of a given diluent [14] for an extraction depends on two distinct groups of properties: a) the properties of practical significance, and b) the properties affecting the mechanism. The present study utilized two diluents: DCM (di-chloro-methane) and toluene. The chemical properties of these diluents are presented in Fig. 6.

2-3. Liquid-liquid extraction procedure

For liquid-liquid extraction studies, 1:5 phase ratio of the organic phase and the aqueous phase was taken in glass separating funnels at different time intervals (0 to 30 min) in a shaking incubator with 250 rpm speed with 25 °C temperature. After extraction with time, we separated the aqueous phase and the organic phase and analyzed the metal content using ICP-OES. The amount of metal ion transferred into the organic phase was calculated by the difference of metal concentration before and after extraction equilibrium. The distribution ratio (D) of the metal between the aqueous phase to organic phase was calculated by using the following equation: $D = [Metal]_{org}/[Metal]_{aqueous}$ at equilibrium. The separation factor (β) refers to the possibility of separation of two metals from each other; $\beta = D_1/D_2$. The general solvent extraction processing flow-sheet is presented in Fig. 2.

3. Results and Discussion

3-1. Characterization studies of [Aliquat 336] [HSO_4] ionic liquid

Liquid-liquid extraction (solvent extraction) processing of PM's used [Aliquat 336] [HSO_4] ionic liquid dissolved in di-chloro-methane (DCM) and toluene diluents and tested for PMs such as copper, platinum and rhodium at room temperature (25 °C) with five phase ratio (Aqueous : Organic). Metal ions concentration was 0.0005 mol dm^{-3}.

The method of [Aliquat 336] [HSO_4] ionic liquid preparation was followed by the reported methodology [13], and further the yield was characterized by Fourier transfer infrared spectroscopy (FTIR) and thermo-gravimetric analysis (TGA) spectra and compared with the reported yield, and it was confirmed (Fig. 7). Aliquat 336 (quaternary ammonium salt) is a commercially available water insoluble extractant. Its molecular formula is $[R_3NCH_3]^+[Cl]^-$; from Aliquat 336 replacement of chloride ion with suitable sodium-bi-sulfate ($NaHSO_4$) by reported preparation methodology [14] it forms the [Aliquat 336] [HSO_4] ionic liquid. This IL was further tested for feasibility to apply as extractant system for PMs (copper, platinum and rhodium) extraction and possible separation.

Liquid-liquid extraction processing of PM's using [Aliquat 336] [HSO_4] ionic liquid was dissolved in di-chloro-methane (DCM) and toluene diluents. Then was tested for PM's extraction and possible separation from each other at room temperature (25 °C) with five phase ratio (Aqueous phase: Organic phase). Metal ion concentration was 0.0005 mol dm^{-3} and IL concentration was 5 g dissolved in 100 ml of diluent.

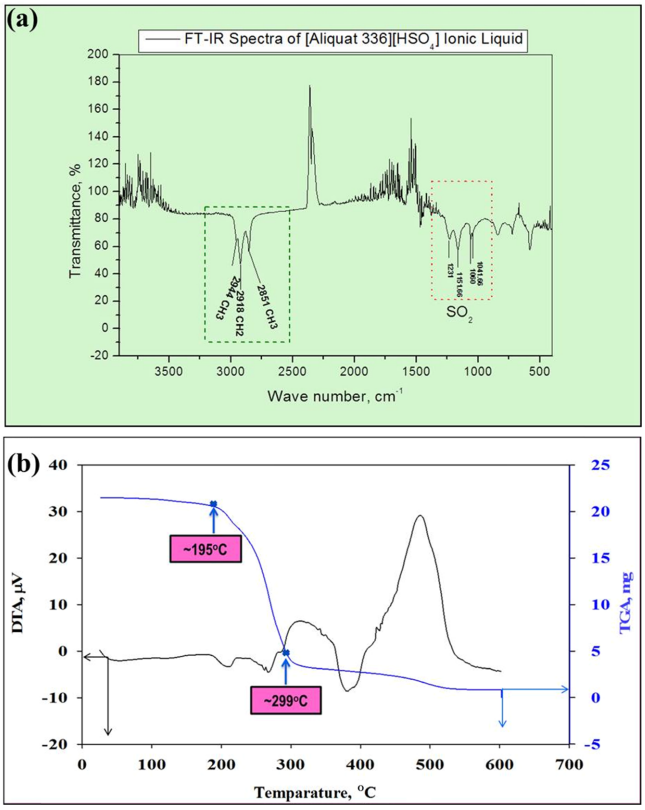

Fig. 7. Preparation and characterization studies of [Aliquat 336] [HSO_4] ionic liquid (a) FT-IR spectra of the [Aliquat 336] [HSO_4] ionic liquid (green color figure), (b) TGA analysis data spectra of the [Aliquat 336] [HSO_4] ionic liquid (white color figure).

3-2. Extraction of the copper by [Aliquat 336] [HSO_4] or Cyphos 101 ionic liquid

The two IL's [Aliquat 336] [HSO_4] (AL336 IL) and Cyphos 101 (Cy IL 101) were separately dissolved in two different diluents such as di-choloro-methane and toluene tested with the variation of the time 1 to 30 min for copper extraction. The experimental conditions were fixed as temperature, 25 °C with five phase ratio (Aqueous :

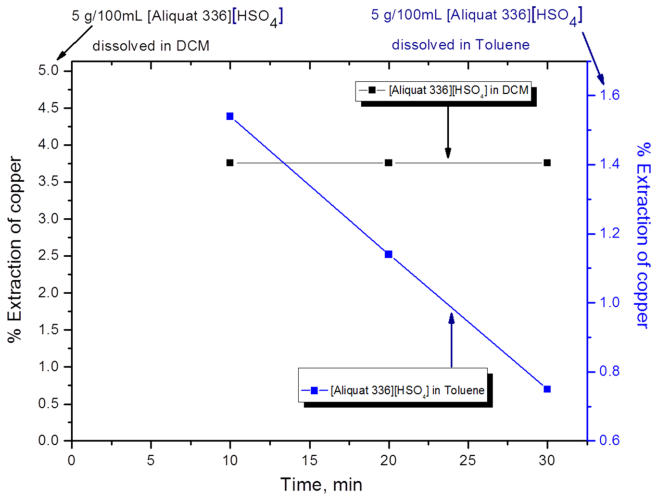

Fig. 8. Extraction of copper by using [Aliquat 336] [HSO_4] ionic liquid as an extractant system.

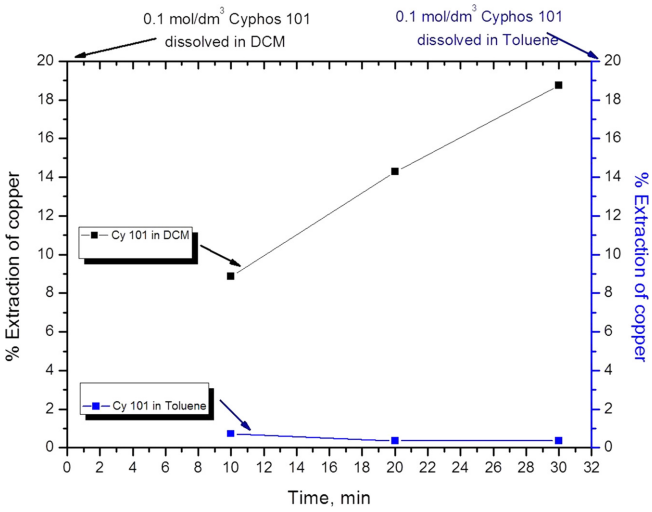

Fig. 9. Extraction of copper by using Cyphos IL 101 ionic liquid as an extractant system.

Organic phases). The obtained experimental results are presented in Fig. 8 and 5.0 g/100 mL AL336 IL maximum was extracted 3 in between 4% of copper by DCM as diluent system, whereas toluene system was up to 4.5% within 1 min the rising the time slightly decreasing the % extraction of copper (Fig. 8). The kinetic study in liquid-liquid extraction was a function of various chemical reactions occurring in the system and the rates of diffusion of the various species that control the chemistry of the extraction process. For slow kinetics the retention of the extraction stages must be superior to a system involving fast kinetics [14]. The formation of an extractable complex may be much slower than the rate at which the complex is extracted into the organic phase [14].

$$\text{Slow kinetic reaction: } M^{n+}_{(aq)} + nHA_{(org)} = MA_{n(org)} + nH^{+}_{(aq)}$$

$$\text{Fast kinetic reaction: } MA_{n\,(aq)} = MA_{n(org)}$$

A commercial ionic liquid, Cy IL 101, gave good indication for the copper extraction. With time increases, % extraction also increased up to 18 to 19% within 30 min in DCM as diluent system, whereas for other diluent toluene system the percentage of copper was nil (Fig. 9). The obtained data clearly indicate that Cy IL 101 will be suitable for copper extraction in DCM system.

3-3. Extraction of the platinum and rhodium by [Aliquat 336] [HSO_4]

The laboratory -prepared [Aliquat 336] [HSO_4] ionic liquid was tested for PMs like platinum and rhodium mixture solutions in two different diluents such as DCM and toluene. The obtained results are presented in Fig. 10. Extraction time varied in the range from 10 to 30 min and the obtained data make known that both the diluent systems are suitable for extraction of platinum as well as separation of rhodium. Platinum extracted ~100%, whereas rhodium extracted between ~4.7 to 7% within 10 to 30 min time. The results indicate that both the diluent systems are suitable for Pt and Rh separation with the [Aliquat 336] [HSO_4] ionic liquid (Fig. 10).

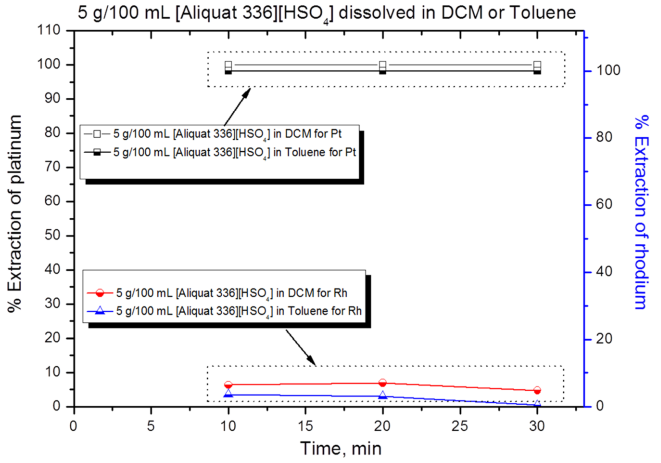

Fig. 10. Extraction of Pt and Rh by using [Aliquat 336] [HSO_4] ionic liquid as an extractant system.

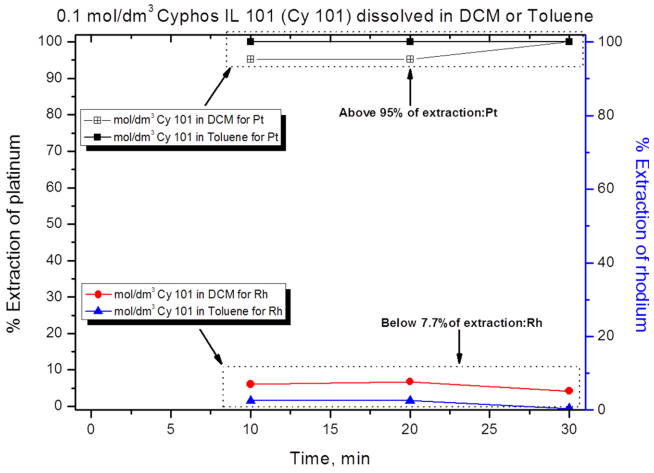

Fig. 11. Extraction of Pt and Rh by using Cyphos IL 101 ionic liquid as an extractant system.

3-4. Extraction of the platinum and rhodium by Cyphos IL 101

In the present study Cyphos IL 101 was dissolved in two different diluent systems such as DCM and toluene. Based on the formula weight proper dilutions were made by the molar solutions and 0.1 mol dm-3 concentration was utilized for platinum and rhodium separation with varying the extraction equilibrium time 10 to 30 min. And similar results were found with Cy IL 101 systems. With the Cyphos IL 101 in DCM system 10 to 20 min time up to ~95% platinum was extracted, whereas rhodium extracted up to ~7%. The extraction time reaching 30 min platinum extraction was reached quantitatively means up to ~100%. The other system Cyphos IL 101 in toluene even 10 min time of extraction reached to ~100% extraction of platinum, whereas rhodium was extracted ~2.6%. The extraction reaching to 30 min time platinum was completely extracted and rhodium was below 1% co-extracted. Comparing both diluents, toluene proved better than DCM for platinum and rhodium separation (Fig. 11).

The present developed extraction and separation methodology was compared with reported data and presented in table form (Table 1).

A summary of the developed extraction and separation methodologies is presented in Fig. 12.

4. Conclusions

The obtained experimental results strongly support that the objects are fulfilling with fruitful data. Green solvents (IL's) were utilized as extractant systems via diluents like di-chloro-methane and toluene, successfully. IL's utilized for Pt / Rh extraction by A:O phase ratio was 5. The preparation and characterization studies of [Aliquat 336] [HSO_4] ionic liquids were confirmed by FTIR and TGA spectra and compared with the reported yield and it was confirmed. The two IL's, [Aliquat 336] [HSO_4] and Cyphos IL 101, were dissolved in two diluents, DCM and toluene. Lower acidity like 0.1 mol dm^{-3} HCl is the most suitable and efficient acidic condition for Pt and Rh separation by using two ionic liquids. With 0.1 mol dm^{-3} Cyphos IL 101 concentrations above 95% of platinum was extracted with ~8% of Rh co-extracted with 10 to 20 min time in both the diluent systems. Whereas, 5 g/100 mL

Table 1. Comparisons of present method with already developed methodologies

Name of the ionic liquid	Diluent	Media	Selectivity	Reference
1-Octyl-3-methyl-imidazolium hexafluorophosphate ([Omim] [PF_6] and Dis-tearyl-di-methyl ammonium chloride (DSDMAC) [A quaternary ammonium salt]	-	HCl	Pt selectively extracted from Pd	[4]
1-Methyl-3-octylimidazolium bis (trifluoromethylsulfonyl) imide ([Omim] [Tf_2N]	-	HCl	The highest separation factor reported in between Pt(IV) and Pd(II) is 312	[5]
1-Butyl-3-methylimidazolium hexafluorophosphate ([C_4mim] [PF_6])	S201	HCl	Pt(IV), Pd(II), Rh(III)	[7]
Tri-octyl ammonium bis (trifluoromethan esulfonyl) amide ([TOAH] [NTf_2]) and tri-octyl ammonium nitrate ([TOAH] [NO_3])	-	HCl	At lower acidic condition Pd and Pt were quantitatively extracted; at the same condition other metals slightly extracted (Na, Mg, K, Ca, Mn, Fe, Co, Ni, Cu, Zn, Ru, Rh and Cd)	[8]
Cyphos IL 101 and Cyphos IL 104	Toluene	HCl	Pd(II) was selectively extracted over Ni(II), Cu(II), Pb(II), Fe(III), Rh(III), Ru(III) and Pt(IV)	[9]
Bis(tri-fluoromethanesulfonyl) imide		HNO_3	Separation factors between Pd/Ru is 4500, Pd/Rh is 1100 at lower acidic range	[10]
[Aliquat 336] [HSO_4] ionic liquid / Cyphos 101 IL	DCM (or) Toluene	HCl	The SFs calculated in between Pt/Rh is 267.5 and 237.9 at 10 and 20 min extraction time with 0.1 mol dm^{-3} Cyphos IL 101 diluted in DCM whereas toluene diluent system two ILs completely extracted Pt with 2.6 to 3.6% of Rh	Present work

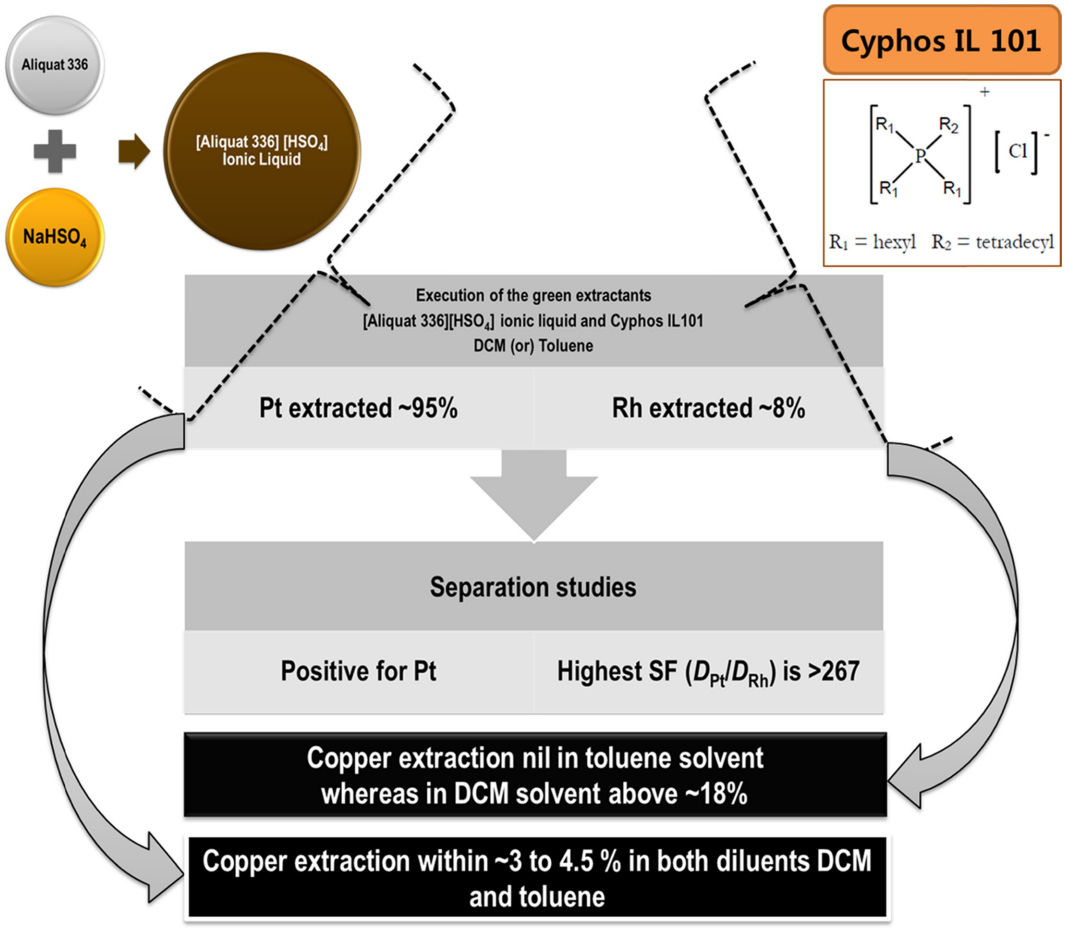

Fig. 12. Summary of the developed extraction and separation possibilities of the PMs using ILs.

[Aliquat 336] [HSO_4] ionic liquids were nearly 100% pt extracted with below ~5% Rh co-extracted by 10 to 20 min time in DCM and toluene systems.

Other precious metals like copper were also tested for both IL's in two diluent systems such as DCM and toluene and it was found that DCM is more suitable than toluene. Up to 18% copper was extracted in DCM system, whereas toluene was not more that 1 to 2% by using Cyphos IL 101 extractant system. The laboratory prepared IL like [Aliquat 336] [HSO_4] was not in a position to extract copper 4 to 5% in both diluent systems.

Acknowledgments

This research was supported by the Convergence Research Project (CRC-15-06-KIGAM) funded by the National Research Council of Science and Technology (NST). The authors give their sincere thanks and gratitude to Korea Institute of Geoscience and Mineral Resources (KIGAM), Daejeon, Korea and NST, Korea.

References

1. Freemantle, M., "An Introduction to Ionic Liquids, RSC Publishing," Cambridge, UK, 2010.
2. Park, J., Jung, Y., Kusumah, P., Lee, J. Y., Kwon, K., Lee, C. K., "Application of Ionic Liquids in Hydrometallurgy," *Int. J. Mol. Sci*. **15**, 15320-15343(2014).
3. Kakoi, T., Kawagoe, M. and Goto, M., "Separation of Platinum and Palladium from Hydrochloric Acid Solutions with 1-octyl-3-methyl-imidazolium Hexa-fluro-phosphate as An Extractant," *J. Chem. Eng. Jpn*., **47**(8), 666-670(2014).
4. Yang, J., Kubota, F., Baba, Y., Kamiya, N. and Goto, M., "One Step Effective Separation of Platinum and Palladium in An Acidic Chloride Solution by Using Undiluted Ionic Liquids," *Sol. Extr. Res. Dev*., **21**(2), 129-135(2014).
5. Génand-Pinaz, S., Papaiconomou, N. and Leveque, J. M., Removal of Platinum from Water by Precipitation or Liquid–liquid Extraction and Separation from Gold Using Ionic Liquids," *Green Chem.*, **15**(9), 2493-2501(2013).
6. Zhang, C., Huang, K., Yu, P. and Liu, H., "Ionic Liquid Based Three-liquid-phase Partitioning and One-step Separation of Pt (IV), Pd (II) and Rh (III)," *Sepn. Puri. Tech*., **108**, 166-173(2013).
7. Katsuta, S., Yoshimoto, Y., Okai, M., Takeda, Y. and Bessho, K., "Selective Extraction of Palladium and Platinum from Hydrochloric Acid Solutions by Trioctylammonium-Based Mixed Ionic Liquids," *Ind. Eng. Chem. Res*., **50**(22), 12735-12740(2011).
8. Cieszynska, A. and Wisniewski, M., "Selective Extraction of Palladium(II) from Hydrochloric Acid Solutions with Phosphonium Extractants," *Sep. Puri. Tech*., **80**(2), 385-389(2011).

9. Sasaki, K., Takao, K., Suzuki, T., Mori, T., Arai, T. and Ikeda, Y., "Extraction of Pd(II), Rh(III) and Ru(III) from HNO_3 Aqueous Solution to Betainium Bis-(trifluoromethanesulfonyl)imide Ionic Liquid," Dalton Trans., **43**(15), 5648-5651(2014).
10. Bell, T. J. and Ikeda, Y., "Efficient Extraction of Rh(III) from Nitric Acid Medium Using a Hydrophobic Ionic Liquid," *Dalton Trans*., **41**(15), 4303-4305(2012).
11. Reyna-Gonzalez, J. M., Galicia-Perez, R., Reyes-Lopez, J. C. and Aguilar-Martinez, M., "Extraction of Copper(II) from Aqueous Solutions with the Ionic Liquid 3-butyl-pyridinium Bis(trifluoromethanesulfonyl)imide," *Sep. Puri. Tech*., **89**, 320-328(2012).
12. Papaiconomou, N., Lee, J. M., Salminen, J., Stosch, M. V. and Prausnitz, J. M., "Selective Extraction of Copper, Mercury, Silver, and Palladium Ions from Water Using Hydrophobic Ionic Liquids," *Ind. Eng. Chem. Res*., **47**(15), 5080-5086(2008).
13. Mikkola, J. P., Virtanen, P. and Sjoholm, R., "Aliquat 336-a Versatile and Affordable Cation Source for An Entirely New Family of Hydrophobic Ionic Liquids," *Green Chem*., **8**(3), 250-255(2006).
14. Kumar, J. R. and Lee, J. Y., "Liquid-liquid Extraction of Tetravalent Platinum VDM Publishers, Saarbrücken," Germany, 2010.