Short Communication:

Extraction of Au(III), Pt(IV), and Pd(II) from Aqueous Media with Deep Eutectic Solvent Dissolved in *n*-Heptane as Extractant

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Abstract: *Due to the scarcity, studying precious metals extraction such as gold, platinum, and palladium is very critical. Solvent extraction is one of the established methods due to its simplicity and quickness but the low operational cost. In this study, a deep eutectic solvent (DES) consisting of decanoic acid and lidocaine in the molar ratio of 2:1 was applied as an extractant to extract Au(III), Pt(IV), and Pd(II) from aqueous media. Au(III) was solvated and extracted with DES in the form of $AuCl_3$. Pd(II) was extracted by the cation exchange reaction between Pd^{2+} and H^+. Complete extraction of Au(III) 98.2% and Pd(II) 100% can be achieved using 500 and 300 g/L DES, respectively. This finding opens new opportunities for improving Au(III) and Pd(II) extraction using an environmental friendly and inexpensive extractant.*

Keywords: *Au(III); deep eutectic solvent; Pd(II); Pt(IV); solvent extraction*

■ INTRODUCTION

Valuable metals like gold (Au), platinum (Pt), and palladium (Pd) become strategic elements due to the scarcity of resources and uneven distribution of metal production. They are extensively used not only for jewellery but also for the production of various advanced materials like fuel cells and electronic devices, as well as for medical use [1]. Therefore, the resources' scarcity and extensive applications encourage researchers to study the separation process of precious metals intensively.

Liquid-liquid extraction is a very established method due to its simplicity and quickness but the low operational cost [2-4]. In most cases of metal extraction, hydrophobic extractants such as chelating reagents and acidic organophosphorus compounds were needed to partition metal ions into the organic solvent phase [5]. Recently, ionic liquids have been successfully applied as extractants in this technique for separating precious metals [6-10]. However, the complexity of their synthesis, particularly in the purification step, causes ionic liquids to be high cost and will limit their practical use for larger-scale applications [11]. A comparable solvent called deep eutectic solvent (DES) was developed to address the ionic liquid's restrictions.

DES is identified by a notable reduction in its melting point upon combining two or three affordable and safe compounds, which function as a hydrogen bond donor (HBD) and a hydrogen bond acceptor (HBA), respectively [12]. The melting point of DES is notably decreased compared to its components, primarily because of a large, asymmetrical ion with low lattice energy [13-14]. Because mixing HBD and HBA to form DES is performed at a moderate temperature and does not need the purification step, DES synthesis is easier than that of ionic liquid. In addition, because most HBD is a natural product; DES is environmentally benign, safe, and sustainable [15]. An extensively explored application of DES involves its utilization as an extractant of metal ions within the solvent extraction technique. In our previous study, DES, which is composed of decanoic acid and lidocaine dissolved in *n*-heptane was successfully employed as an extractant to

extract transition metal ions, including Fe(III), Mn(II), Co(II), Ni(II), and Cu(II) [16-17]. *n*-Heptane was employed as a diluent agent for DES because water was transferred to the DES phase without dilution, generating a considerable change in the volume of both phases from before to after equilibration [18]. In this study, we examined the extraction of valuable metals such as Au(III), Pt(IV), and Pd(II) from aqueous solutions using a DES consisting of lidocaine and decanoic acid dissolved in *n*-heptane as the extracting agent, and the discussion was focused on the extraction mechanism.

■ EXPERIMENTAL SECTION

Materials

The Wako Pure Chemicals company provided decanoic acid, lidocaine, and sodium acetate trihydrate. Fig. 1 shows the molecular structure of the DES components. We bought $HAuCl_4$, $HPtCl_5$, $PdCl_2$ from Nacalai Tesque, Inc. in Kyoto. Without additional purification, all GR-grade compounds were utilized.

Instrumentation

This work used a thermostat water bath in the shaking process. The metal concentration in the aqueous phase was determined using inductively coupled plasma atomic emission spectroscopy (ICP-AES, ICPS-8100, Shimadzu, Kyoto, Japan). A pH meter (F-52, Horiba, Kyoto, Japan) was used to measure the pH value of the aqueous solution.

Procedure

DES preparation

DES was prepared by mixing decanoic acid as HBD and lidocaine as HBA following the procedure according to the previous paper [19]. HBD and HBA were weighed in a beaker at a predefined molar ratio (lidocaine:decanoic acid = 1:2), and covered with parafilm to avoid water contamination. The mixture was stirred at a temperature of 323 K until a transparent and consistent liquid was witnessed. Subsequently, the DESs were left at room temperature overnight to ensure the prevention of any recrystallization.

The procedure of solvent extraction

Due to the DES structure, hypothetically, the pH of the metal ion solution highly influences the metal ion extraction. This study investigated the impact of the pH of the initially prepared metal ion solution on extractability. The data can also be used to predict the extraction mechanism. The detailed procedure for extracting three kinds of metal ions is as follows: the required concentration of the organic phase was prepared by dissolving an exact amount of DES diluted in a certain volume of *n*-heptane. The aqueous phase was prepared by mixing 0.1 mol/L of nitric acid, 0.1 mol/L of acetic acid, and 0.1 mol/L of sodium acetate containing 10 mmol/L of metal ion, which made this media buffered by acetate at the pH of higher than 1. A thermostat water bath set at 303 K was used to mix and shake 2 mL of each phase at 120 rpm. ICP-AES spectroscopy was used to determine the metal content in the aqueous solution after 3 h of shaking to reach equilibrium. A pH meter was used to measure the aqueous solution's pH values. Percentage extraction (%E) and distribution ratio (D) were calculated using Eq. (1) and (2):

$$\%E = \frac{[M]_{aq,int} - [M]_{aq,eq}}{[M]_{aq,int}} \times 100 \tag{1}$$

$$D = \frac{[M]_{aq.int} - [M]_{aq.eq}}{[M]_{aq.eq}} \tag{2}$$

where [M] denotes the metal concentration, aq is the aqueous phases, int and eq are the initial and equilibrium states.

■ RESULTS AND DISCUSSION

In our previous study, the maximum extractability to transition metals was shown by DES, which consisted of decanoic acid as HBD and lidocaine as HBA in a 2:1

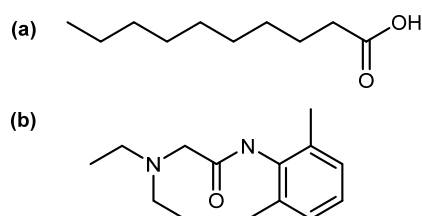**Fig 1.** DES components' molecular structures: (a) decanoic acid, (b) lidocaine (2-(diethylamino)-*N*-(2,6-dimethylphenyl)acetamide

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molar ratio compared to the combinations of other DES constituents, dodecanoic acid and DL-menthol [17]. Therefore, we employed this type of DES as an extractant to extract precious metals in this work.

Extraction of Precious Metals

Firstly, we evaluated the effects of DES concentration and initial pH on %E of Au(III), Pt(IV), and Pd(II), which is shown in Figs. 2 and 3. From Fig. 2, metal extractabilities were in the following order Pd(II) > Au(III) >> Pt(IV). Pt(IV) was scarcely extracted with DES. Fig. 3 shows that

Au(III) percentage extraction reached 95%, far higher than the percentage extraction of Pt(IV) (lower than 9%) at initial pH = 1 and the percentage extraction increased in decreasing the initial pH for Au and Pt. Structurally, decanoic acid can donate a proton, and lidocaine is a proton acceptor, so the pH of metal ion solution highly affects the percentage extraction of metal ions. Considering the dependency of percentage extraction on the initial pH of Au(III) solution, experiments were attempted at higher hydrochloric acid concentrations (≥0.5 mol/L) to dissolve Au(III). In this case, the %E
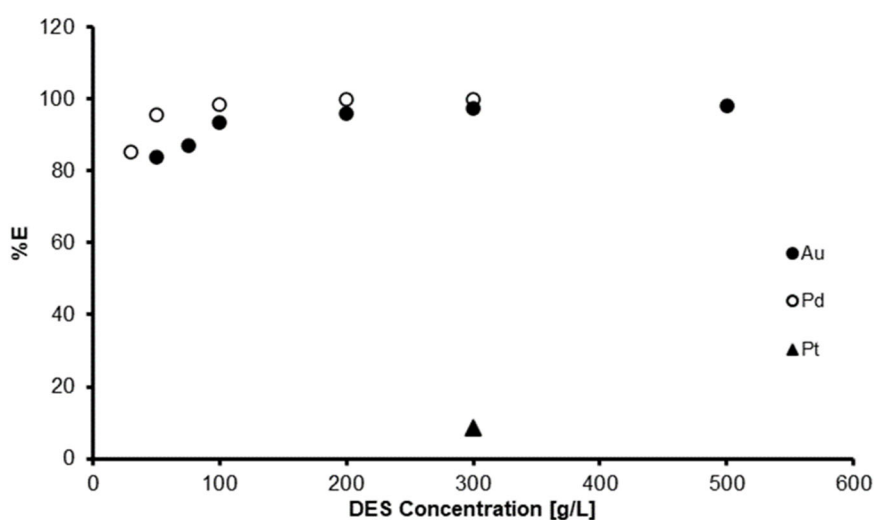

Fig 2. Effect of DES concentration on the percentage extraction of Au(III) (initial pH 1), Pt(IV) (initial pH 1), and Pd(II) (initial pH 4.4)
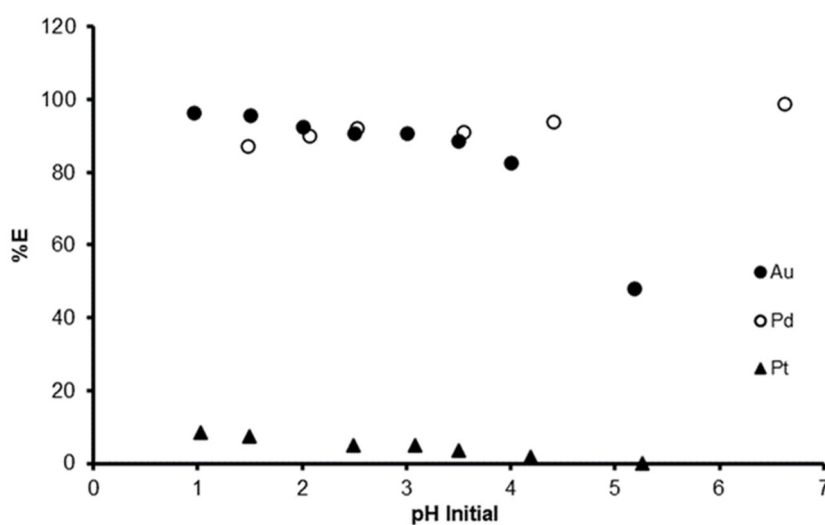

Fig 3. Effect of the initial pH of the metal ion solution on the percentage extraction (DES conc. = 300 g/L for Au(III) and Pt(IV), 50 g/L for Pd(II))

reached 97%, but the solution tended to emulsify. On the other hand, the %E increased with the initial pH for Pd(II). This suggests that Au(III) and Pt(IV) have distinct extraction mechanisms than Pd(II). We also used a solution of lidocaine and decanoic acid as the sole extractant to extract Au(III) to help explain the extraction mechanism, and the results are given in Fig. 4. From Fig. 4, it can be thought that the extraction of Au(III) by DES shown in Fig. 3 was contributed by lidocaine as HBA. Fig. 4 also shows that %E of Au(III) with lidocaine solutions as an extractant reached 85%, approach to the Au(III) percentage extraction using DES as an extractant. However, the mixture of lidocaine solution and Au(III) solution was emulsified; and then, DES was still superior to lidocaine.

Extraction Mechanisms

The %E in Figs. 2 and 3 were converted to D value and the relations between D and pH at equilibrium or DES concentration to clarify the extraction mechanism of Au(III) and Pd(II) were shown in Figs. 5 and 6, respectively, with a logarithmic scale.

From Fig. 5, the slopes between log D of Au(III) and Pd(II), and pH at equilibrium were −3.8 and 0.37, respectively. From Figs. 3 and 5, the pH values changed significantly between initial and equilibrium states and
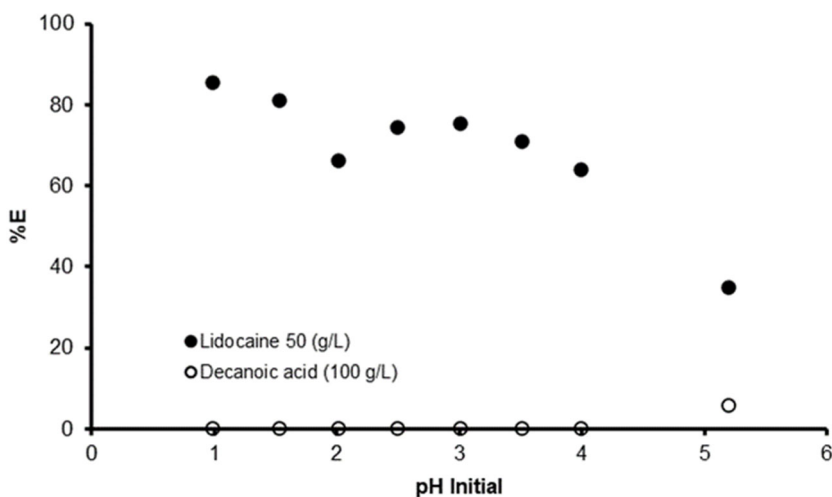

Fig 4. The extractability of Au(III) using decanoic acid solution (100 g/L) and lidocaine solution (50 g/L) with *n*-heptane as solvent
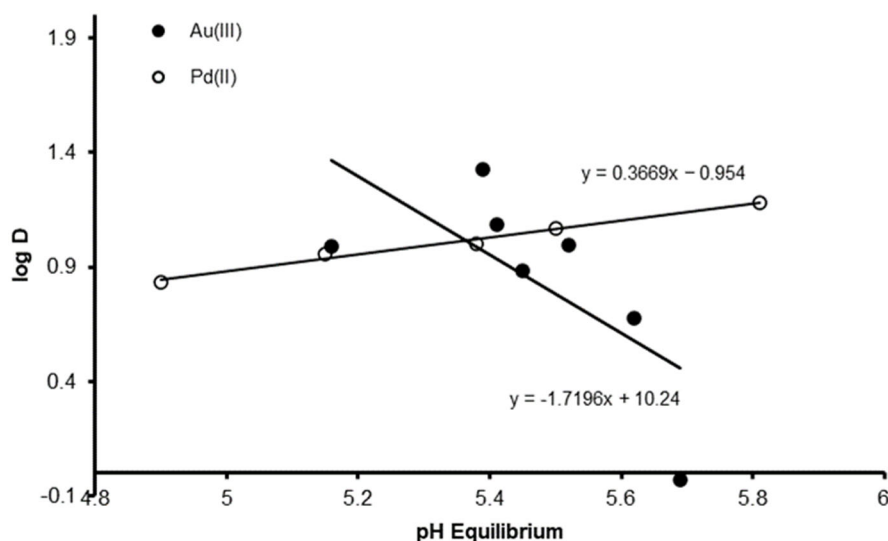

Fig 5. Relation between D of Au(III) and Pd(II) and equilibrium pH in the extraction with DES
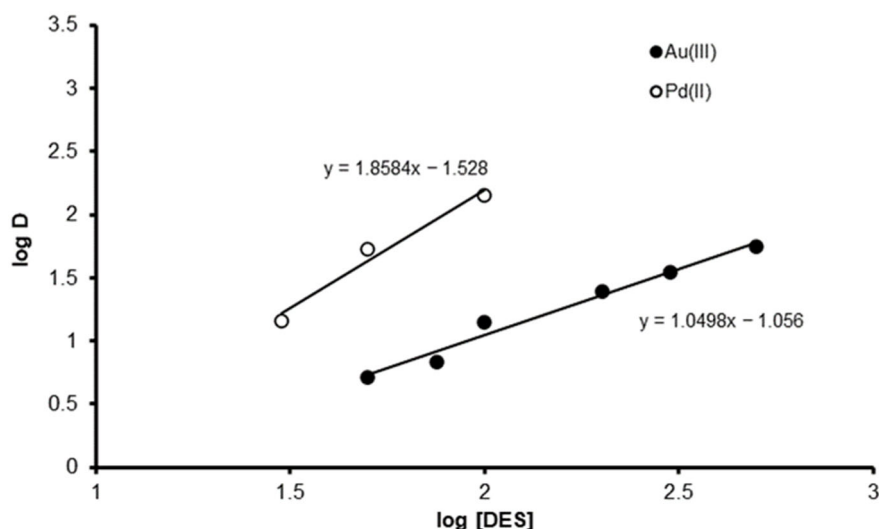
Fig 6. Relation between D of Au(III) and Pd(II) and DES concentration in the extraction with DES

pH values at equilibrium were regulated within a narrow range from 4.8 to 5.8. This may be caused by the strong buffering effect of lidocaine solution [19]. Because pH dependency in a narrow pH range possesses lower reliability, what we found in Fig. 5 is a negative correlation between D and pH for Au(III) and a positive correlation between D and pH for Pd(II). Generally, a positive correlation between D and pH indicates the extraction reaction contains the ion exchange between the metal cation and proton. In the Au(III) extraction, HAuCl$_4$ is prone to hydrolyze in the aqueous solution to form AuCl$_3$OH$^-$.

Fig. 6 clearly shows that the slopes between D and DES concentration were 1 for Au(III) and 2 for Pd(II). Based on these results, Au(III) and Pd(II) were extracted with DES ((RCOOH)$_2$·Lid) according to the following reactions:
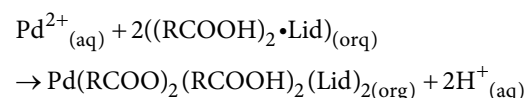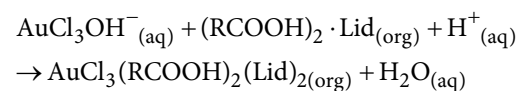
$$AuCl_3OH^-_{(aq)} + (RCOOH)_2 \cdot Lid_{(org)} + H^+_{(aq)}$$
$$\rightarrow AuCl_3(RCOOH)_2(Lid)_{2(org)} + H_2O_{(aq)}$$

$$Pd^{2+}_{(aq)} + 2((RCOOH)_2 \cdot Lid)_{(orq)}$$
$$\rightarrow Pd(RCOO)_2(RCOOH)_2(Lid)_{2(org)} + 2H^+_{(aq)}$$

Table 1. Comparison of Au(III) and Pd(II) extraction in this work with those in the previous work

Metal	Extractant	Diluent	Aq. solution	D	%E	Ref.
Au(III)	500 g/L DES (Lidocaine + decanoic acid)	*n*-Heptane	Acetate media	55.7	98.2	This work
	Cyphos IL 109	Xylene	Chloride media	45.7	99.4	[20]
	2-Octylaminopyridine	Xylene	Malonate media	-	99.5	[21]
	MBIMTT	Chloroform	Chloride media*	-	99.6	[22]
	PKFAD	No diluent	Chloride media	-	99.0	[23]
	[C$_{16}$mim]$^+$Cl$^-$	Chloroform	Chloride media	-	99.6	[24]
Pd(II)	300 g/L DES (Lidocaine + decanoic acid)	*n*-Heptane	Acetate media	∞**	100.0	This work
	[P$_{66614}$]$^+$Br$^-$	Toluene	Chloride media	-	100.0	[25]
	[P$_{66614}$]$^+$Cl$^-$	Xylene	Chloride media	-	98.0	[26]
	N-Hexadecylpiperidinium chloride	Toluene	Chloride media	-	±100.0	[27]
	N-Hexadecylpyridinium chloride	Chloroform	Chloride media		98.8	[28]

MBIMTT: (4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol

*Chloride media in the presence of other metal ions

PKFAD: palm kernel fatty acid distillate

∞**: The equilibrium aqueous metal concentration was not detectable through ICP

We also compared the extraction efficiency and/or distribution ratio with the other extractants, as shown in Table 1. Table 1 shows that the extraction efficiency and/or distribution ratio with DES composed of lidocaine-decanoic acid as extractant to extract Au(III) and Pd(II) was not inferior to the other extractants. However, DES is superior from an economic and ecological point of view because lidocaine and decanoic acid can be found in natural products. Then, DES is cheaper and more environmentally friendly.

■ CONCLUSION

This study demonstrates that extracting valuable metals using a deep eutectic solvent (DES) composed of lidocaine and decanoic acid is notably influenced by the pH of the initial metal ion solution. Gold ion was solvated and extracted with DES in the form of $AuCl_3$. The extractability of platinum ion was very low (<9%). Palladium ion underwent extraction through a cation exchange reaction involving Pd^{2+} and H^+. Au(III) and Pd(II) were fully extracted using 500 and 300 g/L of DES, respectively.

■ ACKNOWLEDGMENTS

■ AUTHOR CONTRIBUTIONS

Pius Dore Ola formulated the idea, performed the experiments and data analysis, wrote the original draft, and revised the manuscript. Michiaki Matsumoto formulated the idea, secured funding, supervised the project, and revised the manuscript.

■ REFERENCES

[1] Aghaei, E., Alorro, R.D., Encila, A.N., and Yoo, K., 2017, Magnetic adsorbents for the recovery of precious metals from leach solutions and wastewater, *Metals*, 7 (12), 529.

[2] Raiguel, S., Gijsemans, L., Van den Bossche, A., Onghena, B., and Binnemans, K., 2020, Solvent extraction of gold(III) with diethyl carbonate, *ACS Sustainable Chem. Eng.*, 8 (36), 13713–13723.

[3] Mahandra, H., Singh, R., and Gupta, B., 2017, Liquid-liquid extraction studies on Zn(II) and Cd(II) using phosphonium ionic liquid (Cyphos IL 104) and recovery of zinc from zinc plating mud, *Sep. Purif. Technol.*, 177, 281–292.

[4] Li, Z., Zhang, Z., Smolders, S., Li, X., Raiguel, S., Nies, E., De Vos, D.E., and Binnemans, K., 2019, Enhancing metal separations by liquid–liquid extraction using polar solvents, *Chem. - Eur. J.*, 25 (39), 9197–9201.

[5] Yudaev, P.A., Kolpinskaya, N.A., and Chistyakov, E.M., 2021, Organophosphorous extractants for metals, *Hydrometallurgy*, 201, 105558.

[6] Lee, L.Y., Morad, N., Ismail, N., Talebi, A., and Rafatullah, M., 2020, Optimization for liquid-liquid extraction of Cd(II) over Cu(II) ions from aqueous solutions using ionic liquid aliquat 336 with tributyl phosphate, *Int. J. Mol. Sci.*, 21 (18), 6860.

[7] Chemat, F., Abert Vian, M., Ravi, H.K., Khadhraoui, B., Hilali, S., Perino, S., and Fabiano Tixier, A.S., 2019, Review of alternative solvents for green extraction of food and natural products: Panorama, principles, applications and prospects, *Molecules*, 24 (16), 3007.

[8] Yang, J., Kubota, F., Baba, Y., Kamiya, N., and Goto, M., 2014, Separation of precious metals by using undiluted ionic liquids, *Solvent Extr. Res. Dev., Jpn.*, 21 (1), 89–94.

[9] Firmansyah, M.L., Yoshida, W., Hanada, T., and Goto, M., 2020, Application of ionic liquids in solvent extraction of platinum group metals, *Solvent Extr. Res. Dev.*, 27, 1–24.

[10] Nguyen, V.T., Riaño, S., and Binnemans, K., 2020, Separation of precious metals by split-anion extraction using water-saturated ionic liquids, *Green Chem.*, 22 (23), 8375–8388.

[11] Zhou, J., Sui, H., Jia, Z., Yang, Z., He, L., and Li, X., 2018, Recovery and purification of ionic liquids from solutions: A review, *RSC Adv.*, 8 (57), 32832–32864.

[12] Smith, E.L., Abbott, A.P., and Ryder, K.S., 2014, Deep eutectic solvents (DESs) and their applications, *Chem. Rev.*, 114 (21), 11060–11082.

[13] Kalhor, P., and Ghandi, K., 2019, Deep eutectic solvents for pretreatment, extraction, and catalysis of biomass and food waste, *Molecules*, 24 (22), 4012.

[14] Migliorati, V., Sessa, F., and D'Angelo, P., 2019, Deep eutectic solvents: A structural point of view on the role of the cation, *Chem. Phys. Lett.*, 737, 100001.

[15] Dwamena, A.K., 2019, Recent advances in hydrophobic deep eutectic solvents for extraction, *Separations*, 6 (1), 9.

[16] Ola, P.D., and Matsumoto, M., 2019, Use of deep eutectic solvent as extractant for separation of Fe(III) and Mn(II) from aqueous solution, *Sep. Sci. Technol.*, 54 (5), 759–765.

[17] Ola, P.D., Kurobe, Y., and Matsumoto, M., 2022, Extraction of Co(II), Ni(II), Cu(II) and Mn(II) with deep eutectic solvents dissolved in heptane as extractants, *Solvent Extr. Res. Dev., Jpn.*, 29 (1), 31–37.

[18] van Osch, D.J.G.P., Parmentier, D., Dietz, C.H.J.T., van den Bruinhorst, A., Tuinier, R., and Kroon, M.C., 2016, Removal of alkali and transition metal ions from water with hydrophobic deep eutectic solvents, *Chem. Commun.*, 52 (80), 11987–11990.

[19] Pascuet, E., Donnelly, R.F., Garceau, D., and Vaillancourt, R., 2009, Buffered lidocaine hydrochloride solution with and without epinephrine: Stability in polypropylene syringes, *Can. J. Hosp. Pharm*, 62 (5), 375–380.

[20] Griffin, P.J., Cosby, T., Holt, A.P., Benson, R.S., and Sangoro, J.R., 2014, Charge transport and structural dynamics in carboxylic acid-based deep eutectic mixtures, *J. Phys. Chem. B*, 118 (31), 9378–9385.

[21] Nguyen, V.T., Lee, J., Jeong, J., Kim, B.S., Cote, G., and Chagnes, A., 2015, Extraction of gold(III) from acidic chloride media using phosphonium-based ionic liquid as an anion exchanger, *Ind. Eng. Chem.*

Res., 54 (4), 1350–1358.

[22] Suryavanshi, V., Kokare, A., Zanje, S., Mulik, A., Pawar, R., Patil, M., Gaikwad, A., Anuse, M., and Mulik, G., 2018, Ion-pair based liquid–liquid extraction of gold(III) from malonate media using 2-octylaminopyridine as an extractant: Analysis of alloys, minerals, and drug samples, *Turk. J. Chem.*, 42 (4), 1032–1044.

[23] Vidhate, K.N., Shaikh, U.P.K., Arbad, B.R., and Lande, M.K., 2015, Extraction and separation studies of gold(III) with 4-(4-methoxybenzylideneimino)-5-methyl-4*H*-1,2,4-triazole-3-thiol in hydrochloric acid medium, *J. Saudi Chem. Soc.*, 19 (1), 54–58.

[24] Chang, S.H., and Anak Jampang, A.O., 2021, Green extraction of gold(III) and copper(II) from chloride media by palm kernel fatty acid distillate, *J. Water Process. Eng.*, 43, 102298.

[25] Tong, Y., Yang, H., Li, J., and Yang, Y., 2013, Extraction of Au(III) by ionic liquid from hydrochloric acid medium, *Sep. Purif. Technol.*, 120, 367–372.

[26] Regel-Rosocka, M., Rzelewska, M., Baczynska, M., Janus, M., and Wisniewski, M., 2015, Removal of palladium(II) from aqueous chloride solutions with cyphos phosponium ionic liquids as metal ions carriers for liquid-liquid extraction and transport across polymer inclusion membranes, *Physicochem. Probl. Miner. Process.*, 51 (2), 621–631.

[27] Nguyen, V.T., Lee, J., Chagnes, A., Kim, M., Jeong, J., and Cote, G., 2016, Highly selective separation of individual platinum group metals (Pd, Pt, Rh) from acidic chloride media using phosphonium-based ionic liquid in aromatic diluents, *RSC Adv.*, 6 (67), 62717–62728.

[28] Cieszynska, A., and Wieczorek, D., 2020, Efficiency and mechanism of palladium(II) extraction from chloride media with *N*-hexadecylpiperidinium chloride, *J. Solution Chem.*, 49 (4), 486–503.