

Selective liquid-liquid extraction of molybdenum (VI) and rhenium (VII) from a synthetic pregnant leach solution: Comparison between extractants and diluents



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ABSTRACT

A study on the selective solvent extraction (SX) of Molybdenum (Mo) and Rhenium (Re) from a synthetic pregnant leach solution (PLS) has been carried out using two diluents: kerosene and the ionic liquid (IL) 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([omim][Tf2N]) and two extractants: di(ethylhexyl) phosphoric acid (D2EHPA) and the IL trioctylmethylammonium bis(2-ethylhexyl) phosphinate [TOMA] [D2EHP].

It can be concluded that the D2EHPA extractant in kerosene achieved selective Mo-Re extractions, times was achieved when replacing kerosene with [omim][Tf2N], but this time with low extraction percentages.

This work shows how ionic liquids, as extractants or diluents, can improve the selective separations in industrial metal extractions.

1. Introduction

Molybdenum (Mo) and rhenium (Re) are highly valuable metal ions for industry because their alloys with other metals provide excellent properties such as high resistance to corrosion and elevated temperatures, hardness, weldability and toughness. Additionally, these metals are often used as catalysts in the petrochemical industry (Jothimurugesan et al., 1985; Bouchmella et al., 2015; Gonçalves et al., 2017). Mo and Re metals are not found neat in nature but in molybdenite ores. For the release of Mo and Re from this mineral, the leaching of molybdenite is often preferred (Jiang et al., 2012; Lasheen et al., 2015), as it is less energy consuming than roasting, obtaining a leach liqueur with mainly molybdic acid (H_2MoO_4), acid ($HReO_4$), copper (II), iron (III) and other metal ions in smaller proportions (Valenzuela et al., 1995). Finally, the recovery of molybdenum and rhenium is made by solvent extraction (SX).

In common industrial applications, the commercial extractant Alamine 336 is used and it is dissolved in kerosene (Lasheen et al., 2015). In spite of the high extraction percentages obtained, this extractant is not selective, leading to additional purification steps to separate Mo(VI) and Re(VII), increasing the operational costs. An alternative route for the purification of these valuable metal ions is the use

of di(ethylhexyl)phosphoric acid (DEHPA) (Valenzuela et al., 1995), which is selective to Mo(VI) but shows lower extraction percentages than Alamine 336. Therefore, the SX process can have two extraction steps, first the SX of Mo(VI) and then that of Re(VII) in a second SX step, in this way, ensuring selectivity.

However, to achieve higher extraction percentages two options could be followed. First, hydrophobic ionic liquids (ILs) could be used as diluents. Besides showing negligible vapor pressure and, therefore, full recyclability that could allow the use of the IL for many extraction-stripping cycles, recent work has demonstrated that ILs improves the distribution ratios compared to the common organic diluents (Quijada-Maldonado et al., 2017). Thus, the replacement of kerosene with an IL could result in an even more selective SX of Mo(VI) and Re(VII), and second, the use of ILs as extractants has shown the achievement of high extraction percentages with small amounts of these (Platzer et al., 2017; Quinn et al., 2017; Dutta et al., 2017; Rama et al., 2017; Shi et al., 2017; Chen et al., 2017; Sengupta et al., 2013). But these ILs are normally expensive or have difficult syntheses. However, when diluting these ILs in another commercially available and relatively low-cost-ionic liquid (Quijada-Maldonado et al., 2018), a more industrially attractive extracting phase can be proposed.

Recent work on selective Mo-Re separation can be found in the

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literature. Joo et al. (Joo et al., 2012) (Joo et al., 2012) used selective precipitation for Mo-Re separation from PLS, Khoshnevisan et al. (Khoshnevisan et al., 2013) (Khoshnevisan et al., 2013) achieved selective separation of Mo-Re using commercial extractants in kerosene, Kang et al. (2013) selectively recovered Re from Mo using trioctyl ammine (TOA) in kerosene, Kim et al. (2015) separated Re from Mo and Vanadium (V) using TBP in kerosene, and Akram Cheema et al. (2017) extracted selectively Re from Mo and other metal from flue dust leach liquors. However, to our knowledge, work on the selective separation of Mo and Re with ILs as diluents and extractant have not been published so far.

Therefore, in the present paper, two approaches to evaluate selectivity in the SX of Mo(VI) and Re(VII) from a synthetic PLS are presented. First, extraction using the commercial organic extractant D2EHPA diluted in 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [omim][Tf2N], as the diluent and, second, the use of the IL trioctylmethylammonium bis(2-ethylhexyl) phosphinate [TOMA][D2EHP] as the extractant diluted in [omim][Tf2N]. Thus, selectivity will be evaluated as a function of industrial parameters such as initial pH, extractant concentration, and aqueous-organic (A/O) ratio. Finally, the SX using kerosene as diluent will be used as reference.

2. Experimental

2.1. Materials and apparatus

For the preparation of the synthetic pregnant leach solution (PLS), both sodium molybdate dihydrate, with a purity higher than 99%, and potassium perrhenate, with a purity higher than 99%, were purchased from Sigma-Aldrich. Iron trichloride hexahydrate, with a purity higher than 99% was obtained from Merck, and copper sulfate pentahydrate, with a purity higher than 98.9%, was purchased from Biopack. Sulfuric acid, with a purity higher than 99.8%, from J.T. Baker, was used to adjust the pH of the PLS. The extracting solution was prepared using bis(2-ethylhexyl) phosphoric acid with a purity higher than 97% and 1-dodecanol with a purity higher than 98% obtained from Sigma-Aldrich. The ionic liquids 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, with a purity higher than 98%, and methyltrioctylammonium chloride, with a purity higher than 97%, were purchased from Iolitec GmbH. Finally, kerosene was kindly provided by Minera Michilla Chile. The ionic liquid trioctylmethylammonium bis(2-ethylhexyl)phosphinate was synthesized in our laboratory according to a scheme presented previously (Quijada-Maldonado et al., 2018). Schematic structures of the ionic liquids used in this work: [omim][Tf2N] and [TOMA][D2EHP], are depicted in Fig. 1.

2.2. Sample preparation and experimental procedure

The synthetic pregnant leach solution (PLS) was prepared by weighing the above mentioned salts and diluted in milliQ water (18.2 M Ω .cm). The initial pH of the PLS was adjusted with a dilute solution of sulfuric acid. At the same time, the extracting solution was prepared by weighing an amount of extractant and diluent that can be either kerosene or [omim][Tf2N]. Table 1 summarizes the concentrations of all the components in the synthetic PLS. These concentrations are normally found in PLSs obtained from the leaching of Chilean molybdenite (Valenzuela et al., 1995). The initial pH was set at 0.5.

The liquid-liquid extractions were carried out at 25 °C in an open flask where 2 mL of the aqueous solution was mixed with 2 mL of extracting solution and stirred for 40 min. After this step, the mixture was centrifuged for another 40 min to assure complete phase separation. The pH of the aqueous PLS was monitored using a HANNA HI4212 pH meter with a microelectrode. Finally, the aqueous phase was withdrawn from the vial and the concentration of all remaining metal species in the PLS were quantified by ICP-AES. The liquid-liquid extraction tests were carried out in duplicate.

The performance of the liquid-liquid extractions was determined by Eqs. (1)–(3) as the extraction percentage (E (%)), the distribution ratio of the specie i (D_i), and the selectivity of the specie i over j (S_{ij}):

$$E_i(\%) = \frac{D_i}{D_i + V_{aq}/V_{org}} \cdot 100 \quad (1)$$

$$D_i = \frac{C_{org,i}}{C_{aq,i}} \quad (2)$$

$$S_{ij} = \frac{D_i}{D_j} \quad (3)$$

where V_{org} and V_{aq} represent the volume of the organic and aqueous phases respectively. $C_{org,i}$ and $C_{aq,i}$ are the concentrations of species i in the organic or ionic liquid phase and in the aqueous phase, respectively.

3. Results

Effect of the diluent: kerosene vs. [omim][Tf2N]

The first liquid-liquid extraction experiments were carried out using the extractant D2EHPA diluted in kerosene. This is the reference case because this extracting solution is used in industry to extract Mo(VI). Fig. 2 shows the extraction percentages of all the metal ions as a function of the concentration of the extractant in kerosene.

Fig. 2 shows that the extractant D2EHPA extracted high percentages of Mo(VI), but with relatively large amounts of D2EHPA, above 80% when the concentration of the extractant is higher than 10% (v/v) while the rest of the metal species were extracted to a much lower extent. This can be explained by the fact that D2EHPA is a pH-selective cation-exchange extractant for Mo(VI) and other metal species (Mohammadi et al., 2015; Wang and Lee, 2016; Chen et al., 2015). At low pH values, Mo(VI) is preferably extracted, while Cu(II) and Fe(III) are also extracted in a sulfate medium (Rao et al., 2000; Aminian and Bazin, 2000; Staszak et al., 2012; Senapati et al., 1994) but with higher pH values. On the other hand, in Fig. 2, a negligible extraction of Re(VII) is reported when the concentration of the extractant is low. Re(VII) can be extracted at low pH values (Valenzuela et al., 1995), even though the extractants used for this are amines or neutral extractants (Srivastava et al., 2015; Fang et al., 2010). The extraction at low pH values could be explained by the fact that a reduced species of Re(VII) would exist (ReO_3^+) and it is extracted by D2EHPA when chloride ions are present at very low pH values (Sato and Sato, 1990). Chloride ions indeed come from the ferric salt that was used to prepare the synthetic PLS.

Then, kerosene was replaced by the IL [omim][Tf2N] to study the effect of the diluent on selectivity towards Mo(VI). Fig. 3 depicts the extraction percentages as a function of D2EHPA concentration.

Fig. 3 shows that the extraction percentages of Mo(VI) increased as expected compared to previous cases where the diluent was kerosene, reaching almost 100% extraction when using 10% (v/v) of D2EHPA. The extraction percentages of the rest of the metal species were below 30%, representing a marginal increase in extraction percentages compared to the case of using kerosene. In our previous work (Quijada-Maldonado et al., 2017) we showed that the use of [omim][Tf2N] as diluent in the SX of Mo(VI) could increase the distribution ratios because of a low extractant-diluent interaction. When the extractant exhibits low interaction with the diluent, the former can extract metal ions more easily. In this case, D2EHPA does not show a strong interaction with the IL as with kerosene. This result is very relevant from the industrial point of view because it opens the possibility of extracting Mo (VI) and Re(VII) selectively and with a more environmentally benign solvent.

Finally, Fig. 4 summarizes Figs. 2 and 3, but in terms of Mo-Re selectivity.

When using 10% (v/v) of the extractant in [omim][Tf2N], the selectivity increases around five times, and it is even higher at higher extractant concentrations, representing a real candidate for the

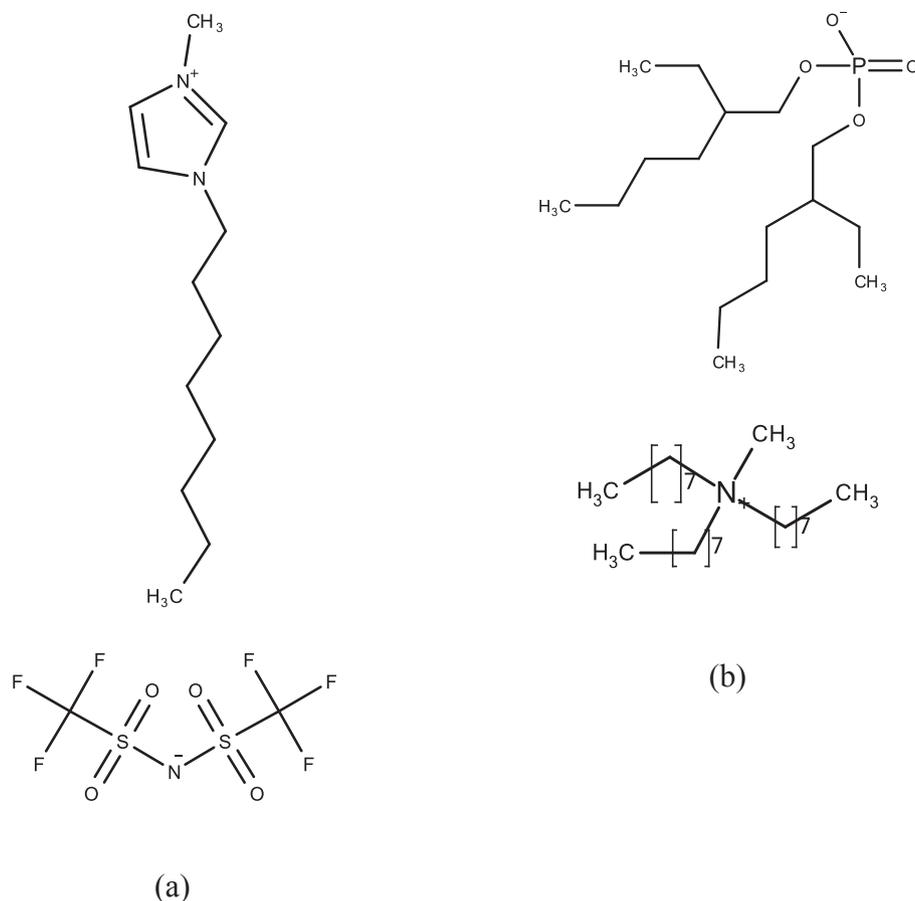


Fig. 1. Molecular structure of the ILs used in this work (a) 1-octyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [omim][Tf2N], and (b) trioctylmethylammonium bis(2-ethylhexyl) phosphate [TOMA][D2EHP].

Table 1
Concentration of the different components in the synthetic PLS.

Metal Species	Concentration (g/L)
Re(VII)	0.2
Mo(VI)	2
Fe(III)	0.3
Cu(II)	1

replacement of kerosene in the hydrometallurgical recovery of Mo(VI) from molybdenite.

Equilibrium stages

Previous results indicated that the use of [omim][Tf2N] improved the distribution ratios, especially those of Mo(VI), and therefore, the selectivity was also enhanced. Thus, from the industrial point of view, it is interesting to see the number of equilibrium stages necessary to recover Mo(VI) from the synthetic PLS. Fig. 5 depicts the McCabe Thiele diagram including the required equilibrium stages for both systems.

Fig. 5 shows that both diluents require around three separation stages to obtain a high purity of Mo(VI). When using kerosene, the Mo(VI) concentration in the aqueous phase after the three equilibrium stages was 0.2 g/L and for the case of [omim][Tf2N] as the diluent 0.1 g/L. However, the A/O ratio in the system containing kerosene requires a level of twice as high more diluent than the system using the IL. In industry, normally two equilibrium stages are accepted. The results could be improved by slightly increasing the extractant concentration. However, these results are interesting for future industrial applications because even though ILs are still expensive on the market, half of the

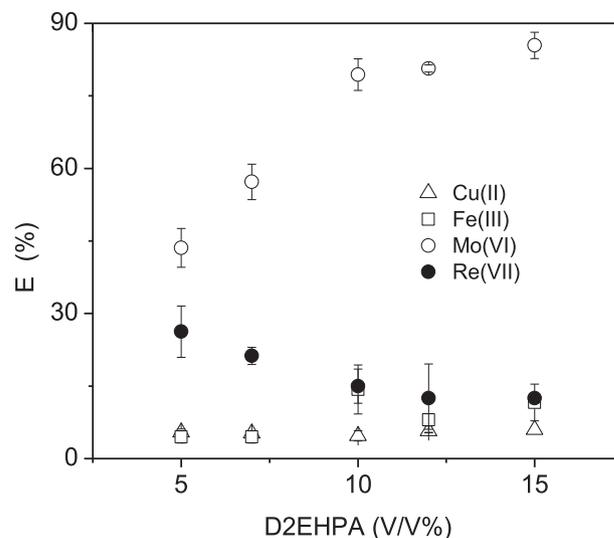


Fig. 2. Extraction percentages of all the components of the synthetic PLS as a function of the extractant percentage when the diluent was kerosene. Initial pH = 0.5. Error bars represent the standard deviation.

volume should be used to decrease the initial costs related to the purchase of the IL. Also, there is the fact that ILs show no volatility which means full recyclability; so, in the long run, lower operational costs could be obtained.

Another important point to mention is that the viscosity of [omim][Tf2N] is 88.6 ± 0.37 mPa·s at 298.15 K (Papović et al., 2016), and the

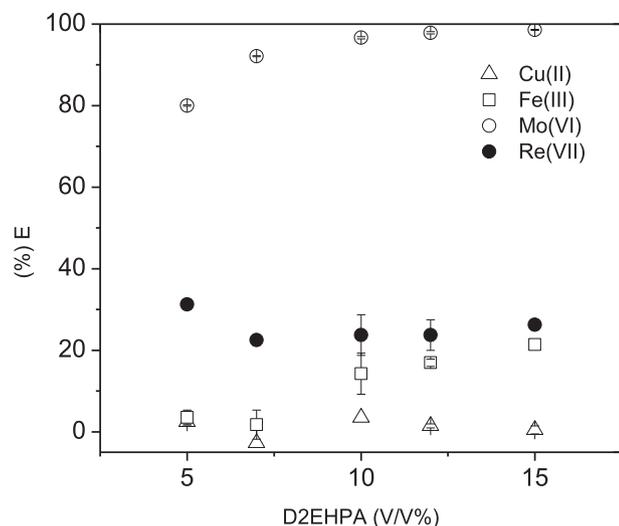


Fig. 3. Extraction percentages of all the components of the synthetic PLS as a function of the extractant percentage when the diluent was [omim][Tf2N]. Initial pH = 0.5. Error bars represent the standard deviation.

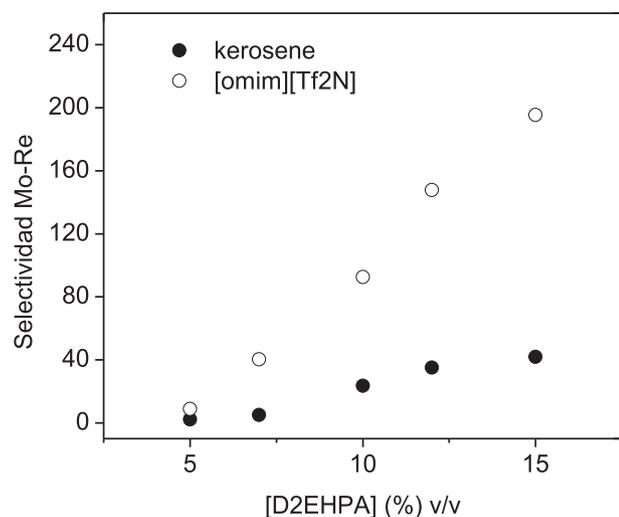


Fig. 4. Mo-Re selectivity as a function of extractant concentration.

viscosity of kerosene is around 1.4 mPa·s at 298.15 K. This last value could vary depending on the brand. This high viscosity could certainly decrease the mass transfer rates of the extraction process which in turn results in more separation stages. However, at 50 °C (323.15 K), which is the processing temperature, the viscosity of the ionic liquid decreases to 32.6 ± 0.15 mPa·s (Papović et al., 2016), having less impact on mass transfer. On the other hand, mass transfer efficiency depends on the transport properties of the solvent and also on the activity coefficients of the solute in the solvent. In this case, the use of the ionic liquid as the diluent could overcome the effect of viscosity because higher extraction percentages were obtained with [omim][Tf2N] than with kerosene, meaning higher solute-solvent interaction when using the ionic liquid as the diluent.

3.1. Ionic liquid as the extractant

Although in previous results the extraction percentages and selectivity obtained were promising, especially when using the IL [omim][Tf2N] as the diluent, the amount of solvent was still relatively high, 10% (v/v) in the diluent. With Alamine 336 in kerosene, a slightly higher performance has been obtained than the results of this work (Coca et al., 1990). However, a reduction in extractant concentration

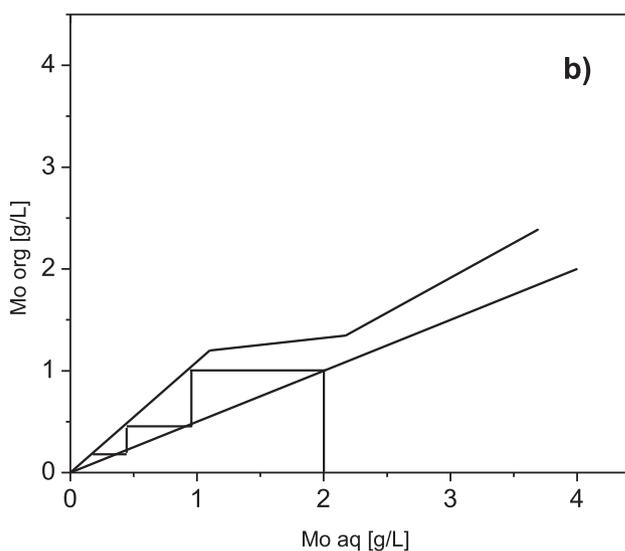
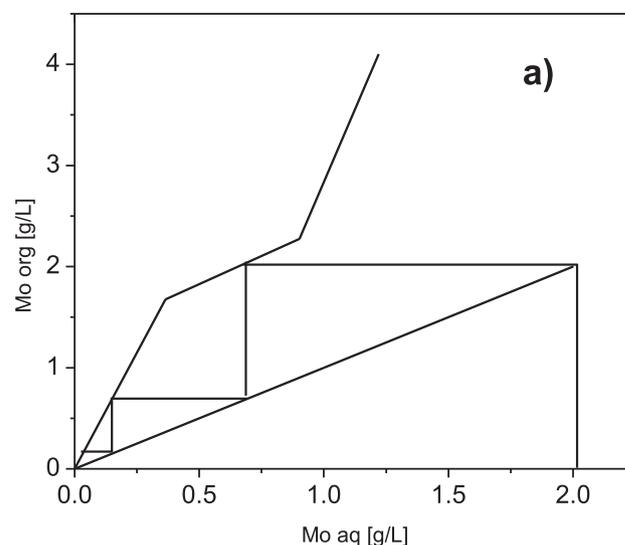
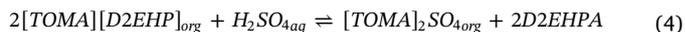


Fig. 5. McCabe-Thiele diagram for the selective separation of Mo(VI) for both diluents: (a) [omim][Tf2N] and (b) kerosene (% extractant).

could yet be achieved maintaining high extraction percentages by the use of ILs extractants. In a previous work, the IL [TOMA][D2EHP] showed very high extraction percentages of Mo(VI) using small amounts of this IL in a diluent, and therefore this would be a good candidate for this selective separation.

To understand if there would be selectivity when using this extractant, the extraction stoichiometry should be understood. At very low pH values, this IL extracts acid in a first extraction step (Quijada-Maldonado et al., 2018) as follows:



This first step results in two reaction products: $[\text{TOMA}]_2\text{SO}_4$ and the organic acid bis(2-ethylhexyl) phosphoric acid (D2EHPA). Therefore, the former, which is basically $[\text{TOMA}]^+$, would extract ReO_4^- and D2EHPA will extract MoO_2^{2+} as the following stoichiometries indicate:



The first stoichiometry has already been demonstrated in a previous report (Quijada-Maldonado et al., 2018). However, the extraction of Re(VII) using [TOMA][D2EHP] as the extractant can be demonstrated in

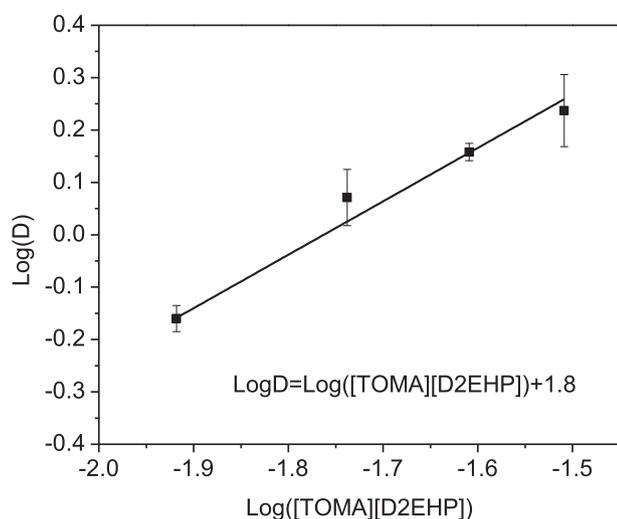
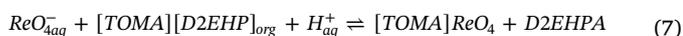


Fig. 6. Log D as a function of log [TOMA][D2EHP] for the extraction of Re(VII). Initial pH = 1, initial [Re(VII)] = 0.5 g/L. Error bars represent the standard deviation.

Fig. 6 by means of the slope analysis.

In the slope analysis depicted in Fig. 6 it is seen that the slope of the linear regression is one. This is because combining Eqs. (4) and (6) results in the following stoichiometry:



where one mole of [TOMA][D2EHP] extracts one mole of Re(VII). This result confirms the extraction of this last metal ion according to Eq. (7).

Although this IL could extract these metal species using low amounts of extractant, the analysis of these stoichiometries shows poor selectivity because both metal species will be extracted. However, as already noted, to extract Mo(VI) with D2EHPA, large amounts of extractant were needed, and on the other hand, one mole of [TOMA]₂SO₄ will extract two moles of Re(VII). Therefore, at low concentrations of [TOMA][D2EHP], selectivity towards Re(VII) could be achieved. A second important point is that the use of [omim][Tf2N] modifies the distribution ratios, and therefore the selectivity can be also modified. Fig. 7 shows the extraction of the metal ions from the synthetic PLS using this IL extractant in both diluents a) kerosene and b) [omim][Tf2N].

In Fig. 7a it is seen that the [TOMA][D2EHP] extractant showed high extraction percentages of both Mo(VI) and Re(VII). Cu(II) and Fe(III) were almost not extracted. As expected, Re(VII) was preferably extracted at low extractant concentrations, followed by Mo(VI); however, no selectivity was achieved. Either way, these results can be considered promising for industry because almost 100% of Re(VII) and Mo(VI) were extracted using small amounts of the extractant. In industry, Alamine 336 is normally used for these metal species (Coca et al., 1990; Moris et al., 1999; Baek and Lee, 2017) and is not selective as [TOMA][D2EHP]. Moreover, large amounts of Alamine 336 are required for the extraction (10% or even higher), and furthermore, a phase modifier is mandatory.

Another observation is that in Fig. 7b the extraction percentages of Mo(VI) and Re(VII) decreased compared to Fig. 7a. This is because of the high extractant-diluent interaction (Quijada-Maldonado et al., 2017), which decreases the extraction percentages of all the metal species. [TOMA][D2EHP] and [omim][Tf2N] are both ILs and show high affinity between them. However, this effect has allowed improvement in Mo-Re selectivity, especially when using low concentrations of extractant in [omim][Tf2N], as expected.

It is worth noting that a selective extraction could be achieved by the use of another IL extractant according to the stoichiometry

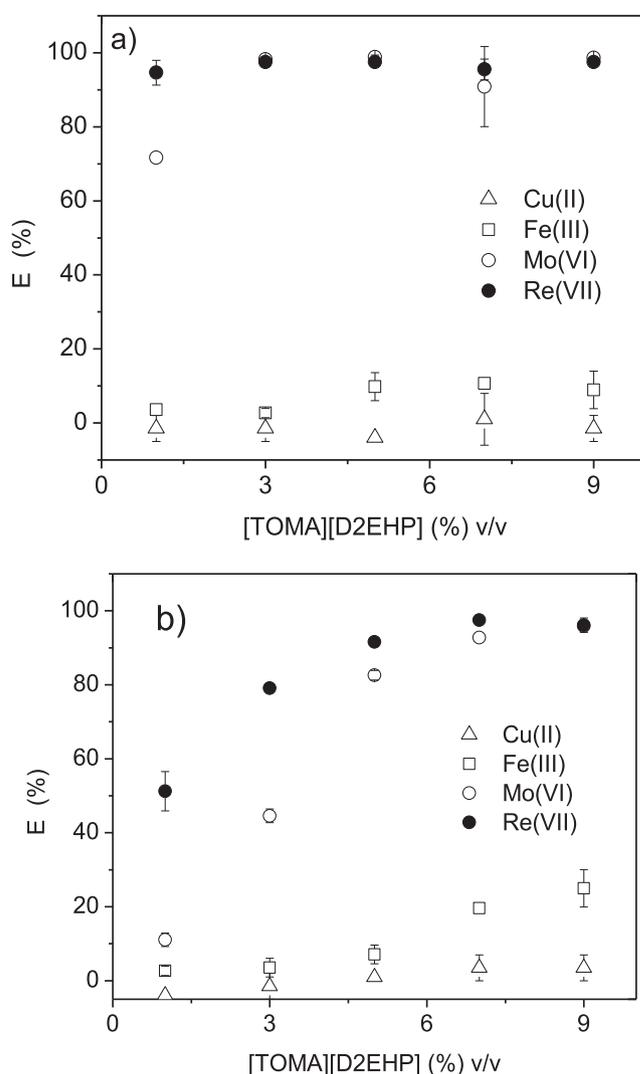


Fig. 7. Extraction percentages of all the metal species as a function of extractant concentration for a) kerosene as the diluent and b) [omim][Tf2N] as the diluent. Initial pH = 0.5. Error bars represent the standard deviation.

presented in Eqs. (4)–(6). For example, the IL trioctylmethylammonium chloride [TOMA][Cl] or Aliquat 336 diluted in either kerosene or [omim][Tf2N] would extract Re(VII) exclusively at low pH (pH < 1). However, extraction of Mo(VI) with Aliquat 336 has been reported before at low pH values (Olazabal et al., 1992). This could be explained by the fact that [TOMA][Cl] or Aliquat 336 extract acid from the aqueous phase at low pH values, increasing the pH of this phase and promoting the presence of poly-anionic species of Mo(VI) (Olazabal et al., 1992) that are extracted by quaternary amines.

Finally, it is important to say that, after the extraction, the stripping of the metal species from the diluent is required. Previous works indicated that a solution of ammonium carbonate would be necessary the recover either Mo(VI) or Re(VII) back to the aqueous phase (Quijada-Maldonado et al., 2017) (Quijada-Maldonado et al., 2018). However, if the SX process is not selective, both metal ions would be extracted from diluent at the same extent. Therefore, the results presented here show that when using [omim][Tf2N], improvements in selectivity are achieved and will enable the subsequent recovery of mainly one metal ion during the stripping process.

4. Conclusions

In this paper the selective extraction of Mo(VI) and Re(VII) from a

low pH synthetic leach liquor was studied.

Extractions with the commercial extractant D2EHPA in either kerosene or [omim][Tf2N] were performed where selective Mo-Re separations were achieved using kerosene as the diluent. Replacing kerosene with [omim][Tf2N] selectivity increases around five times at 10% (v/v) of the extractant.

Three equilibrium stages were needed to achieve highly pure Mo (VI) from the synthetic PLS and a reduction in the diluent volume was observed when using [omim][Tf2N].

On the other hand, when using ionic liquid [TOMA][D2EHP] for the extractions, about 10 times less extractant was required to achieve high extraction percentages, but with poor Mo-Re selectivity. However, when using [TOMA][D2EHP] in [omim][Tf2N] a great increase in selectivity, around five times, was achieved, especially at low extractant concentrations.

This study opens the possibility for selective Mo-Re separation in industry and also shows that ionic liquids are not only non-volatile, but are solvents that improve the separation performance in solvent extraction processes.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.mineng.2019.106060>.

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