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Liquid–liquid extraction of Li^+ using mixed ion carrier system at room temperature ionic liquid

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ABSTRACT

An environmentally benign technique for the separation and recovery of lithium (Li^+) from aqueous streams, containing mixed metal ions was developed via liquid–liquid extraction (LLE). Hydrophobic room temperature ionic liquids (RTIL) were tested as the main extracting solvents. To increase the metal extraction, a proton-ionizable agent bis(2-ethylhexyl) phosphoric acid (DEHPA) was added into the RTIL. To enhance the metal uptake selectivity, three Li^+-selective neutral ion carriers such as 6-hydroxy-dibenzo-14-crown-4, dibenzo-14-crown-4, and tri-n-octyl-phosphine (TOPO) were also used and tested as extractant additives. Among the tested RTILs, phosphonium-based CYPHOS IL 109 was the most stable extractant as it exhibited the lowest loss when contacted with water. Addition of proton-ionizable agent DEHPA in CYPHOS IL 109 afforded a high extraction of multivalent cations with negligible recovery of monovalent metals. On the other hand, the addition of neutral ion carrier TOPO in DEHPA/CYPHOS IL 109 extractant resulted in a selective Li^+ uptake which was maximized when the pH of the aqueous solution was maintained at 13, with TOPO/DEHPA molar ratio = 8. The overall process could be a two-stage LLE system wherein the unwanted multivalent cations are initially removed using DEHPA/CYPHOS IL 109 followed by the selective extraction of Li^+, using TOPO/DEHPA/CYPHOS IL 109 system.

Keywords: Ion carrier; Ionic liquid; Liquid–liquid extraction; Lithium ions; Crown ether; Facilitated transport

1. Introduction

Organic solvent liquid–liquid extraction (LLE) is an established and useful process for the production of concentrated and purified substances in various chemical industries. The technique has also found its niche in analytical chemistry, environmental remediation (i.e. heavy metals removal), and in mining industry (i.e. recovery of precious metals) [1]. The LLE method appeals to many applications due to its simplicity and ease of handling. However, one key

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issue that is yet to be overcome is the use of toxic organic solvents. At industrial scale, significant occupational hazard is perceived as the major drawback of this process [2].

Efforts have been made to develop environmentally benign LLE systems by finding suitable alternative extractants for conventional solvents. One emerging group of compounds is the room temperature ionic liquids (RTIL) which features high solvency power to a wide range of substances, tunable physicochemical properties for specific target compounds, and negligible vapor pressure, which offsets the toxicity problems encountered in volatile conventional solvents [3,4].

For the recovery of precious metals, hydrophobic RTILs can be used to form a stable immiscible phase with the aqueous cation source stream for LLE. The distribution coefficient (K_D) of the metals between RTIL and water would dictate the efficiency of the recovery. Some studies reported that RTILs can extract certain metal ions but the addition of ion carriers in RTILs is typically performed to increase the K_D values such as neutral crown ethers (CEs) and organophosphorus compounds [3–9]. However, it is known that metal extraction using neutral ion carriers would require the transport of the metal ion along with its anion (i.e. as ion pair) towards the organic phase in order to maintain the electroneutrality and stability of the LLE system [10,11].

According to the "hard-soft acid-base" (HSAB) theory, ion pair extraction is convenient in the presence of "soft" anions like thiocynate, picrate, or perchlorate. On the other hand, hard anions such as chloride, nitrate, and sulfate have low solubility in nonpolar solvents; hence it would restrict and limit the extraction of metal ions [12]. Considering that "hard" anions are more commonly present in most of the metal ion source streams, the addition of lipophilic proton-ionizable compounds have been performed in many studies to facilitate the transport of metal ions [13,14]. Proton-ionizable agents in the extractant phase could act as counterions which maintain the electroneutrality of the LLE system during the transport of dissociated metal ions.

Lithium (Li^+) is a precious alkali metal with intrinsically high specific energy density thus it became an important component of rechargeable batteries [15]. Lithium has been typically harvested from brine pools via precipitation. However, the surging Li^+ demand in recent years has diverted research interests on its recovery from various natural reservoirs, such as the seawater, which has been typically performed via adsorption and LLE [16, 17].

Using LLE for Li^+ recovery, Takahashi et al. observed that the addition of alkyl phosphorous acid compounds (as proton ionizable agents) increased the Li^+ extraction efficiency of dibenzo-14-crown-4 (14DBCE4) ethers in chloroform extractant [13]. Onishi reported high Li^+ adsorption on a solvent impregnated resin containing a neutral organophosphorus compound tri-n-octyl-phosphine (TOPO), together with a proton-ionizable agent, β-diketone [14]. Considering the demonstrated abilities of these mixed metal ion carriers, their incorporation in hydrophobic RTILs could result in an effective LLE system for Li^+ recovery.

Herein, a novel LLE system composed of hydrophobic RTILs incorporated with neutral ion carriers and proton ionizable agent is developed for the recovery of Li^+ ions from aqueous streams. Several hydrophobic RTILs were tested depending on their stability when in contact with water. Three neutral ion carriers TOPO, CEs 14DBCE4, and 6-hydroxy-dibenzo-14-crown-4 (14HDBCE4) were selected whereas bis (2-ethylhexyl) phosphoric acid (DEHPA) was used as the proton ionizable agent. Considering the limited information on the selectivity of these mixed ion carriers for Li^+ extraction, competitive metal extraction was performed. The effects of pH and ion carrier compositions on the extraction efficiency were also determined to enhance the selective Li^+ recovery.

2. Materials and methods

2.1. Reagents

Hydrophobic RTILs: (Trihexyltetradecylphosphonium bis(trifluromethylsulfonyl)amide (CYOPHOS IL 109), Trihexyltetradecylphosphonium dicyanamide (CYPHOS IL 105), Methyl-trioctyl ammonium bis (trifluromethyl sulfonyl)imide ($[C_{13}C_8N][Tf_2N]$), and 1-octyl-3-methylimidazolium hexaflurophosphate ($[C_8mim][PF_6]$) were of analytical standards from Sigma (MO, USA). The proton-ionizable carrier DEHPA and HPLC grade chloroform were also procured from Sigma (MO, USA). Neutral ion carriers such as TOPO, was purchased from Sigma (MO, USA), whereas CEs 14DBCE4 and 14HDBCE4 were synthesized according to the procedures described elsewhere [18–20].

2.2. Pretreatment of ionic liquids and crown ethers

Before use, chloroform was washed and stabilized with dionized water. RTIL was freed from metal ion impurities by vortexing it with 2 wt% HNO_3 and washed with dionized water until pH became neutral.

These steps were repeated until all metal ions are removed; the nitric acid washing solution was analyzed for metal content, using inductively coupled plasma mass spectrometry (ICP-MS 7500 series, Agilent, USA). The synthesized CEs 14DBCE4 and 14HDBCE4 were re-dissolved in dichloromethane and the metal impurities were removed similarly as performed in RTIL purification.

2.3. RTIL stability experiments

The selection of the most suitable RTIL was performed by contacting water at 1:5 volume ratio by vortexing. The samples were allowed to stand for 1 h before collecting the aqueous phase for total carbon (TC) analysis using TOC analyzer (Shimadzu, Japan).

2.4. Liquid–liquid extraction

All glasswares and plasticwares used during LLE experiments were acid washed in HNO_3 for 24 h, followed by intensive washing with deionized water. All LLE experiments aside from chloroform systems (i.e. in 5 mL glass vials) were performed in 2 mL centrifuged vials. An LLE system composed of (1) DEHPA and: (2) 14DBCE4, 14HDBCE4 or TOPO in RTIL was vortexed for 2 min with 1 mM aqueous solution of pure Li^+ or in combination with other metals ions such as Na^+, K^+, Mg^{2+}, and Ca^{2+} (1:5 volume ratio). These cations are typically present in seawater, one of the alternative Li^+ sources; hence, were selected for the competitive metal extraction experiments. Extraction experiments at various solution pH and metal ion carrier compositions were also performed for enhanced Li^+ extraction and separation.

After extraction (1 h equilibration), the samples were centrifuged at 5,000 rpm for 10 min to separate the phases. The aqueous phase was recovered, placed in 50 mL centrifuge tubes and acid digested in HNO_3 solution via microwave irradiation (MARS 5 CEM, USA). The digested solutions were diluted in 100 mL polypropylene volumetric flasks and analyzed by via ICP-MS.

3. Results and discussion

3.1. Evaluation of hydrophobic RTILs

The stabilities of hydrophobic ammonium- ($[C_{13}C_8N][Tf_2N]$) and phosphonium-based RTILs (CYPHOS IL 105, CYPHOS IL 109) were determined and compared with those of previously investigated extractants, such as imidazolium-based RTILs ($[C_8mim][PF_6]$) and chloroform. The measured TC in the aqueous phase, as shown in Fig. 1, is proportional to the extractant lost in the aqueous phase after equilibration. But for more accurate extractant stability comparison, the TC data was transformed using Eq. (1) in terms of extractant loss wherein m_{TC} is the measured TC mass in the aqueous phase, χ_C is the carbon fraction in each extractant, and m_{total} is the extractant mass used during the experiment. On the other hand, the loss of CE added in the extractants was estimated using Eq. (2) wherein m_{TC-CE} is the total TC mass measured in the aqueous phase of LLE system containing extractants, χ_{C-CE} is the carbon fraction in each CE whereas m_{CE} is the mass of CE added in the extractant.

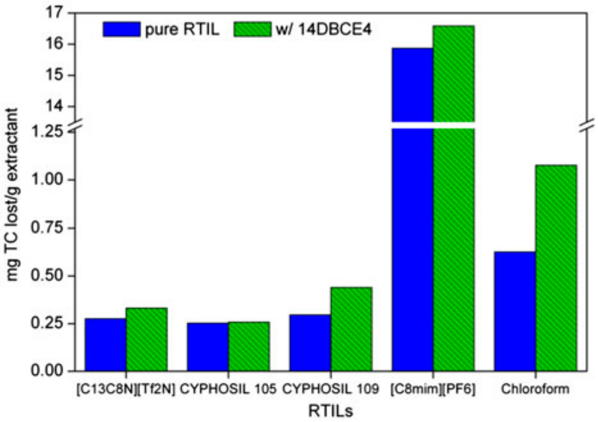

Fig. 1. TC analysis of the aqueous phase during LLE.

$$\text{Extractant loss } (\%) = \left(\frac{m_{TC}}{\chi_C}\right) \times \left(\frac{1}{m_{total}}\right) \times 100 \tag{1}$$

$$\text{CE loss } (\%) = \left(\frac{m_{TC-CE} - m_{TC}}{\chi_C} - \text{CE}\right) \times \left(\frac{1}{m_{CE}}\right) \times 100 \tag{2}$$

It is evident in Table 1 that all extractants exhibited losses <4%; $[C_8mim] [PF_6]$ was found the least stable while all ammonium- and phosphonium-based RTILS showed minimal dissolutions in the aqueous phase. Chloroform also exhibited lower dissolution than $[C_8mim][PF_6]$ but this solvent is unsuitable as an extractant considering its high toxicity profile even at extremely low concentration in water [4]. To further determine the most appropriate RTIL, the percentage of CE loss was examined. Among the extractants tested, CYPHOS IL 109 exhibited the lowest CE elution to the aqueous stream. Though CYPHOS IL 109 is the most viscous extractant, transport resistance due to slower metal diffusion may not be critical

Table 1
Physicochemical properties and stabilities of extractants in LLE systems

Extractant	Chemical formula	M_W (g/mol)	χ_C	Density (g/mL, 20˚C)	Viscosity (cp, 25˚C)	Extractant loss (%)	CE loss (%)
CYPHOS IL 105	$C_{34}H_{69}N_3P$	550.9	0.74	0.90	280.4	0.05	3.97
CYPHOS IL 109	$C_{34}H_{68}F_6NO_4PS_2$	764.0	0.53	1.07	292.5	0.03	0.15
$[C_{13}C_8N][Tf_2N]$	$C_{27}H_{54}F_6N_2O_4S_2$	648.9	0.50	1.11		0.06	3.10
$[C_8mim][PF_6]$	$C_{12}H_{23}N_2PF_6$	340.3	0.42	1.21	176.0	3.75	19.9
Chloroform	$CHCl_3$	119.4	0.10	1.48	0.542	0.62	6.27

considering that all LLE systems tested were not kinetically challenged (i.e. short mixing period was needed to achieve maximum extraction). From stability results, CYPHOS IL 109 formed the most stable LLE system with water hence was selected as the main extractant in subsequent experiments.

3.2. Metals extraction in CYPHOS IL 109 with neutral CEs

Extractions of mixed metal ions solutions were evaluated in pure CYPHOS IL 109 and in those with either 14DBCE4 or 14HDBCE4. Table 2 shows the low extraction efficiency of the pure CYPHOS IL 109, for all metals. The intrinsic hydrophobic property of this RTIL limits the transfer of anions thereby lowering its uptake of metals ions [21]. This result further affirms that the addition of an ion carrier is necessary to improve the metal ions recovery of the RTIL extractant.

As shown in Table 2, extraction efficiencies of all metal ions were improved upon the addition of 14DBCE4 or 14HDBCE4 in CYPHOS IL 109. The metal uptake in RTIL with neutral CE ion carriers followed the sequence: $Li^+ > Mg^{2+} \cong > Na^+ > K^+ > Ca^{2+}$. The enhanced metal uptakes were due to their coordination with the oxygen atoms in the CEs, which promoted more metal ion complexation in the extractant phase [13,22]. Based on size-match selectivity theory, a cation with size closest to that of the CE cavity would form the most stable complexation [19]. The cavity size of 14HDBCE4 and 14DBCE4 are known to match best with Li^+ than with other cations. This probably explains the observed metal uptake trend as both CE/CYPHOS IL 109 systems exhibited highest selectivity uptake towards Li^+. Between the two CEs, the higher Li^+ uptake observed in LLE system containing 14HDBCE4 than in 14DBCE4 may be attributed to the additional coordination imparted by the oxygen atom in the hydroxyl group of 14HDBCE4 [17].

The meager improvements in metal ions recovery observed in RTILs with neutral CE ion carriers indicate that its extraction performance remains to be unsatisfactory. Furthermore, the similar extraction efficiencies of metal ions indicate that these LLE systems would not be able to effectively separate Li^+ from other metals ions. Thus, for enhanced uptake and selectivity the effect of proton-ionizable agent DEHPA in RTILs containing CEs or TOPO was tested in another series of LLE experiments.

3.3. LLE of metal ions in CYPHOS IL 109 RTIL containing mixed ion carriers

The LLE performances of extractants containing mixed ion carriers were investigated using CYPHOS IL 109 and chloroform as extracting solvents. In chloroform systems, Fig. 2 reveals remarkably higher metal ion extractions even without the presence of ion carriers such as CEs or TOPO. For DEPHA/$CHCl_3$ system, highest extractions were observed in divalent Ca^{2+} and Mg^{2+} whereas low values were obtained for

Table 2
Metal ion extraction efficiencies of CYPHOS IL 109 LLE systems

Metal ions	Ionic radius (pm)	Pure CYPHOS IL 109/RTIL (%)	CYPHOS IL 109/14DBCE4 (%)	CYPHOS IL 109/14HDBCE4 (%)
Mg^{2+}	72	8.3	10.4	10.2
Li^+	76	6.7	10.9	12.5
Ca^{2+}	100	2.7	8.6	8.6
Na^+	102	8.4	9.9	10.5
K^+	138	5.4	9.3	9.3

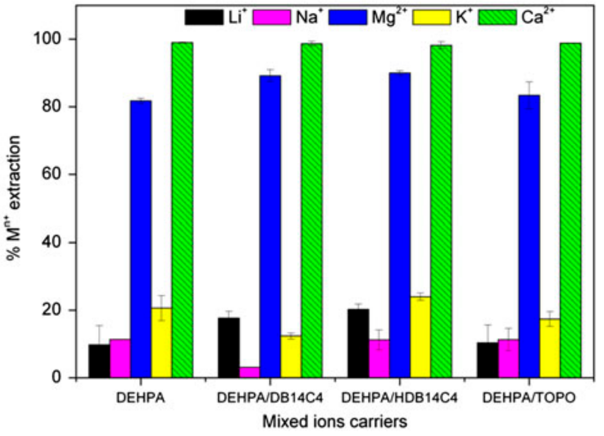

Fig. 2. Extraction of metal ions in chloroform/DEHPA/CE or TOPO system, initial metal ion concentration = 1.0267 ± 0.05 mM (Li^+, Na^+, K^+, hydroxide); $[Mg^{2+}]$ = 0.16 ± 0.04 mM, $[Ca^{2+}]$ = 0.36 ± 0.05 mM; [CE] = 26.19 ± 0.81 mM; and [DEHPA] = 25.20 ± 0.27 mM.

monovalent cations Li^+, Na^+, and K^+. Extraction efficiencies of all metal ions seemed to be unaffected by the addition of neutral ion carriers CEs or TOPO.

In the CYPHOS IL 109 RTIL system, as shown in Fig. 3, the addition of DEHPA alone resulted to approximately 55 and 75% of Mg^{2+} and Ca^{2+} extraction, respectively. While the LLE efficiencies of divalent metals were lower than those measured in chloroform LLE system, the preferential extraction of divalent metal ions over monovalent metals were more remarkable as almost no Li^+, Na^+, and K^+ were recovered.

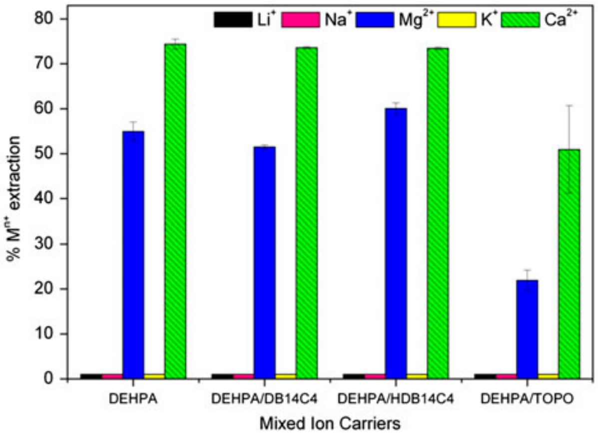

Fig. 3. Extraction of metal ions in CYPHOS IL 109/DEHPA/CE or TOPO system Initial metal ion concentration = 1.0267 ± 0.05 mM (Li^+, Na^+, K^+, hydroxide); $[Mg^{2+}]$ = 0.16 ± 0.04 mM, $[Ca^{2+}]$= 0.36 ± 0.05 mM; [CE] = 26.19 ± 0.81 mM; and [DEHPA] = 25.20 ± 0.27 mM.

Similar with the chloroform system, the presence of CEs in DEHPA/CYPHOS IL 109 apparently did not affect the extraction of all metal ions. On the other hand, the addition of TOPO slightly reduced the extractability of multivalent cations while those of monovalent metals remained unaffected. These findings indicate that DEHPA/CYPHOS IL 109 is highly selective for the removal of multivalent ions. Furthermore as pointed out earlier, chloroform is a known carcinogen whose aqueous concentration is being strictly regulated [4]. On the other hand, CYPHOS IL 109 is a promising alternative extraction solvent as (1) it exhibits minimal aqueous leaching (i.e. environmentally benign) and, (2) facilitates satisfactory and highly selective extraction performances of metal ion carriers. Thus, for the first extraction step, efficient and selective extraction of unwanted divalent metal ions can be performed using DEHPA/CYPHOS IL 109 system.

With the surprising reverse trend observed in both LLE systems (chloroform and CYPHOS IL 109) having high preference towards multivalent ions, it is imperative to elucidate the governing mechanisms during LLE process involving the mixed ion carrier system in RTIL.

Fig. 4 represents a putative extraction mechanism when DEHPA is added as a proton-ionizable agent in CE or TOPO/RTIL system. A similar mechanism has been proposed by Takahashi et al., involving the transport of Li^+ and Na^+ using DEHPA/14DBCE4/Chloroform liquid membrane system [13]. However, the interfering effects of multivalent ions such as Ca^{2+} and Mg^{2+} were not investigated in their work.

The modified mechanism considers the role of CEs or TOPO as solvating and dehydrating agents [13,14]. The CEs have polar interior in which metal ion complexation occurs while its nonpolar exterior facilitates good interaction with the hydrophobic RTIL phase [17]. Similarly, the oxygen atom of TOPO interacts with the extracted metal ion while its hydrophobic tails are aligned outward towards the bulk RTIL phase [14].

Considering the neutrality of both ion carriers, the addition of DEHPA facilitated more metal ion uptake as it maintained the electronic balance between the two immiscible phases [13]. The acid form of DEHPA participated in metal ion extraction (1) by acting as a counterion of metal ions, complexed with CE or TOPO or (2) by being involved in direct ion exchange via deprotonation of its hydroxyl group. Based on the LLE results, it appears that the second mechanism is predominant, while complexation of metals ions on CE or TOPO is a less preferred route. Direct ion exchange seemed to be the reason for the enhanced

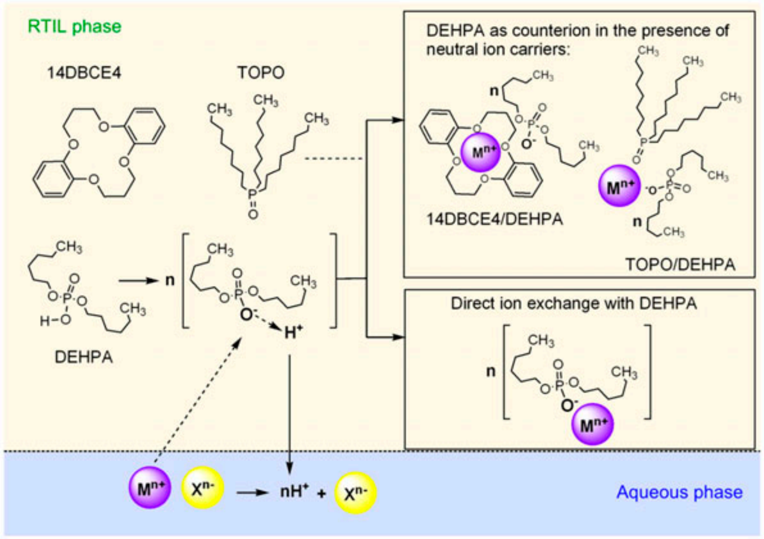

Fig. 4. Putative mechanism for Li^+ and Na^+ transport in liquid membrane.

multivalent cation extraction considering that CEs are more selective towards Li^+ or Na^+.

The results suggest that the strong affinity of DEHPA with divalent metal ions could be an alternative technique to remove interfering ions prior to Li^+ extraction. The obtained results was also observed by a previous study [14], wherein the removal of Li^+ using solvent impregnated resin with TOPO and proton-ionizable β-diketone was diminished in the presence of divalent metal ions. Removal of interfering metal ions prior to Li^+ extraction was also suggested.

3.4. Effect of pH on the extraction of Li^+

With DEHPA/CYPHOS IL 109, established as a suitable LLE system for multivalent cation extraction, subsequent experiments were focused on enhancing Li^+ uptake by DEHPA/CYPHOS IL 109 in the presence of TOPO or CE. In the literature, when using a proton-ionizable carrier such as DEHPA, pH is the most important factor responsible for the extraction efficiency of the system [12,13]. Fig. 5 illustrates the extraction of Li^+ at varied pH between 5 and 13. The extraction efficiency increase with pH was most remarkable with TOPO/DEHPA in CYPHOS IL 109. Both DEHPA and CE/DEHPA did not show significant improvements in Li^+ extraction at any pH level. One possible explanation for the low extraction efficiency of CE/DEHPA was the limited loading of CE due to its lower solubility in CYPHOS IL 109 than TOPO. Based on these results, Li^+ extraction can be maximized by adjusting the pH of the solution to 13, using TOPO instead of CEs.

3.5. Effect of TOPO/DEHPA composition

To further enhance the Li^+ extraction efficiency, experiments with increased TOPO loading or TOPO/DEHPA molar ratio were subsequently performed. Fig. 6a reveals the significant improvements in Li^+ extraction with increase in TOPO/DEHPA ratio.

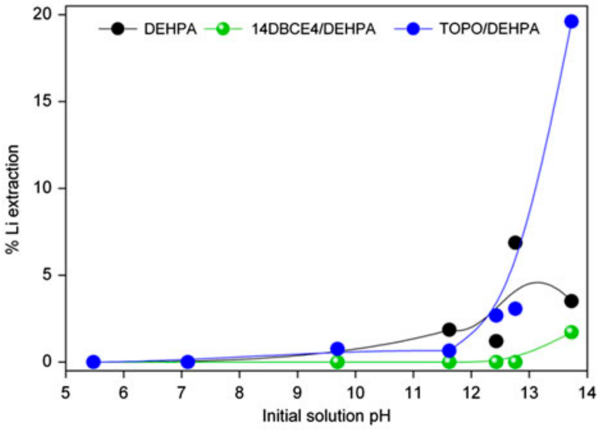

Fig. 5. Effect of pH on the extraction of Li^+ using DB14C4-DEHPA, TOPO-DEHPA, and DEHPA alone system in RTIL Initial concentration $[Li^+] = 0.15 \pm 0.02$ mM; [CE] = 26.19 ± 0.81 mM; [DEHPA] = 25.20 ± 0.27 mM; and [TOPO] = 25.5 ± 0.27 mM.

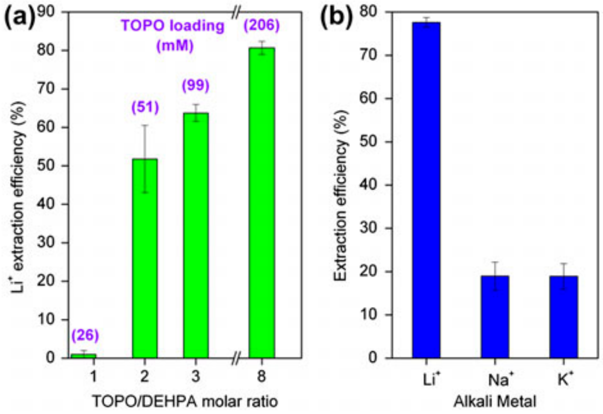

Fig. 6. Li^+ extraction efficiencies at (a) different TOPO/DEHPA compositions: initial $[Li^+] = 0.008$ mM, $[Na^+] = 0.1$ M; and (b) in the presence of other monovalent metal ions: initial $[Li^+] = 0.06$ mM, $[Na^+] = 77.46$ mM, $[K^+] = 76.88$ mM; pH 12.8; $[DEHPA] = 30.2 \pm 0.49$ mM, aqueous phase volume = 1.25 mL, and organic phase volume = 0.25 mL.

Under alkaline environment, the de-protonated DEHPA interacts with Li^+ whereas TOPO combines with DEHPA-Li^+ to form an adduct complex [23]. Specifically, the oxygen group of TOPO coordinates with Li^+. Results indicate that more than one TOPO molecule coordinates with DEHPA-Li^+, as the highest extraction was achieved at TOPO/DEHPA = 8. Thus, satisfactory Li^+ extraction into CYPHOS IL 109 can be achieved if DEHPA-Li^+•nTOPO ($n > 1$) adducts are formed. Similar observation has been reported earlier wherein two TOPO molecules combined with thenoyltrifluoroacetone-Li^+ complex for the efficient extraction of trace Li^+ into m-xylene phase [23].

Revisiting the mechanism presented in Fig. 4, Li^+ uptake in TOPO/DEHPA/CYPHOS IL 109 is considered to be mainly driven by adduct complex formation and not by direct ion exchange with DEHPA, which predominates when multivalent cations such as Ca^{2+} and Mg^{2+} are present in the source stream.

3.6. Li^+ extraction by TOPO/DEHPA/CYPHOS IL 109 in mixed monovalent metal ions

The ability of TOPO/DEHPA/CYPHOS IL 109 to separate Li^+ from other monovalent cations is shown in Fig. 6(b). Highest extraction efficiency was achieved in Li^+ despite having a very low concentration as compared to Na^+ and K^+. The preference of TOPO towards Li^+ is not fully understood but a possible explanation could be that metal complex adducts involves TOPO and Li^+ is more stable than those of Na^+ and K^+. Furthermore, Li^+ has the smallest hydrated size among the monovalent cations present [24]. Removal of surrounding water molecules on Li^+ by TOPO (a dehydrating agent) could have been easiest; hence Li^+ was most conveniently extracted towards the CYPHOS IL 109 phase among the monovalent cations tested. With a multivalent cation-free stream, further separation of Li^+ from Na^+ and K^+ can be achieved, using TOPO/DEHPA/CYPHOS IL 109 LLE system.

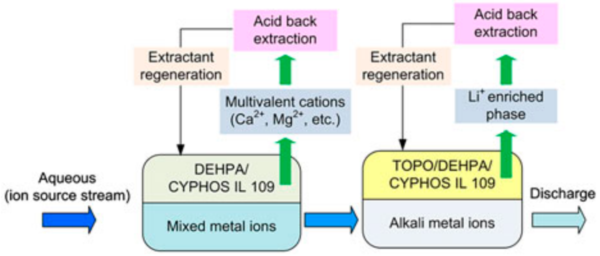

Fig. 7. Proposed two-stage LLE process for the separation of Li^+ from aqueous stream.

3.7. Proposed LLE process for Li^+ recovery

For the entire scheme of Li^+ separation from other metal ions, a two-stage LLE process is proposed as shown in Fig. 7. The first LLE phase would involve the separation of multivalent cations from the source stream, using DEHPA/CYPHOS IL 109 as the extractant. The source stream can be transferred and contacted to a second extractant particularly, TOPO/DEHPA/CYPHOS IL 109 wherein Li^+ extraction can be maximized and preferred by adjusting the pH to 13, at TOPO/DEHPA ratio = 8. A re-extraction experiment using 0.1 M HNO_3 at 1:10 volume ratio with both LLE systems reveals that 80–91% of metals can be recovered from the used organic extractant. Hence, spent LLE systems can be regenerated and re-used by contacting systems in appropriate acid solutions to back extract the recovered metals.

4. Conclusions

A two-stage novel RTIL LLE system is developed for the separation and recovery of Li^+ from aqueous streams containing mixed metal ions. CYPHOS IL 109 is a hydrophobic RTIL than can be used as a stable extractant with water. Addition of proton-ionizable agent DEHPA in CYPHOS IL 109 can selectively separate the multivalent cations. The extracted aqueous phase containing Li^+ ions can be further processed for Li^+ recovery by second extraction, using Li^+-selective

TOPO as a neutral ion carrier in DEHPA/CYPHOS IL 109 system. Maximum Li^+ extraction and separation from Na^+ and K^+ can be achieved at alkaline pH and high TOPO/DEHPA molar ratio.

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