Recovery of lithium from salt lake brine of high Mg/Li ratio using Na[$FeCl_4 * 2TBP$] as extractant: Thermodynamics, kinetics and processes

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ABSTRACT

A systematic investigation on the extraction of lithium from salt lake brine with high Mg/Li using a novel extractant, Na[$FeCl_4 * 2TBP$]$_{org}$, is reported with an emphasis on the extraction thermodynamics, kinetics and process. In liquid-liquid extraction, this extractant shows high separation factor of lithium/magnesium up to 178.4. Thermodynamic analysis indicated that the extraction is an exothermic process. However, when integrated with the kinetic effect, the lithium mass transfer increases at elevated temperature. The kinetics of lithium extraction by this extractant was investigated via a single drop column method. The magnesium, lithium concentration in brine, sodium, ferric concentration in organic extractant were studied, and a linear relationship was found between the rate of lithium transfer and the concentration of each component. The contribution of the formation/coalescence of organic extractant droplets, end-effect, to the lithium mass transfer was investigated. Perturbation at the brine/organic phases was found to promote lithium mass transfer during the rising step of droplets, mainly due to the low interfacial tension. Finally, a process was proposed to extract lithium ions from East Taijinaier salt lake brine and the stability of the new extractant was demonstrated by four extraction/stripping/saponification cycles. These results indicate that the present extractant was suitable for extracting lithium from brines with a high Mg/Li ratio.

1. Introduction

Lithium and its compounds are greatly used in rechargeable batteries (Tarascon and Armand, 2001), nuclear fusion reactions (Soper, 1957) and chemical industries (Peiro et al., 2013). Recent surge in utilization of lithium batteries for consumer appliances and automobiles has led to increasing consumption and demand of lithium (Choubey et al., 2016). Lithium extraction has become a bottle-neck for the sustainable development of energy supply chain. Lithium can be recovered from mine, salt lake brine and seawater (Kesler et al., 2012). Although the conservation of lithium in seawater is 2.31×10^{11} ton, the concentration is very low, e.g. 0.178 mg/L. It will require extensive research investment for the extraction before an economical mature stage is reached (Diallo et al., 2015). The supply of lithium rich mine has been reduced gradually (Kesler et al., 2012); therefore, various technologies to extract lithium from salt lake brine (concentration of lithium, 300 to 7000 mg/L) have been investigated, such as chemical precipitation (lime-soda-evaporation) (Talens Peiró et al., 2013), adsorption technologies utilizing $LiFePO_4/FePO_4$ electrode materials (Zhao et al., 2013), MnO_2 ion-sieve (Xiao et al., 2015), MnO_2/activated carbon hybrid capacitor systems (Kim et al., 2015), membrane processes such as nanofiltration (NF) and reverse osmosis (Somrani et al., 2013), membrane electrolysis (Liu et al., 2015), membrane extraction (Xing et al., 2016, Song et al., 2014, He, 2008, He et al., 2004, He et al., 2002). However, these technologies have not been implemented in large-scale application except chemical precipitation.

The chemical composition of the salt lake brine varies with the geological location. Comparing to the brine in South America, the brine in northwest China typically shows a very high Mg/Li ratio up to a few hundred (Song et al., 2017). Therefore, conventional chemical precipitation, using caustic, consumes a huge amount of chemicals, generates solid wastes, and is economically not viable and environmentally unfriendly. Another promising technology is organic extraction, and it has of low cost and easy operation (Zhang et al., 2016). TBP in kerosene was a typical extractant for lithium extraction from brine characterized by a high concentration magnesium ion (Jin-cai et al., 2005, Zhou et al., 2012a, 2012b, Shi et al., 2015, Shi et al., 2016).

In order to separate the lithium from brine of a high ratio of Mg/Li, ferric chloride ($FeCl_3$) has been utilized as a co-extractant of TBP (Sun et al., 2007, Zhou et al., 2011, Zhou et al., 2012a, 2012b, Li et al., 2015); lithium ions form a complex with ferric chloride and TBP: Li $[FeCl_4 * 2TBP]_{org}$, which is soluble in the organic phase to enable lithium extraction from the brine (Li et al., 2015). The extraction capacity of TBP system followed the sequence: $H^+ > Li^+ > Na^+$ (Zhou et al., 2012a, 2012b), therefore the lithium ion loaded into the organic phase can be stripped by the hydrochloric acid, resulting in $H[FeCl_4 * 2TBP]_{org}$. $H[FeCl_4 * 2TBP]_{org}$ cannot complex with lithium, and a further ion exchange step is necessary to transform the hydrogenated extractant into sodium type, $Na[FeCl_4 * 2TBP]_{org}$, and this step is called saponification. As such, the extracting capability of TBP is recovered and extraction loop is realized (Xing et al., 2016). To the authors' knowledge, the thermodynamics and kinetics of lithium extraction using $Na[FeCl_4 * 2TBP]_{org}$ for extracting lithium ion from salt lake brine of a high Mg/Li ratio has not yet been reported.

In this study, the thermodynamics and kinetics of the lithium extraction using the sodium form of TBP organic extractant are investigated. The kinetics of extraction was explored using single drop techniques (Awwad, 2004, Dziedzic and Bogacki, 2014, Li et al., 2016, Torkaman et al., 2016), instead of Lewis cell (Yang et al., 2013), and rotating diffusion cell (RDC) (Meng et al., 1996). The single rising drop approach was adopted in this research due to its simplicity, as well as the flexibility in operation and quick response. The effect of temperature, droplet size, the concentration of magnesium and other ions in brine was investigated on the rate of lithium extraction. The influence of the formation and coalescence of organic droplets on the rate of lithium extraction was systematically studied, which was correlated to the mass transport in an extraction column scheme. The research in this paper provides a quantitative analysis of the extraction process of $Na[FeCl_4 * 2TBP]_{org}$ for salt lake brine of a high Mg/Li ratio.

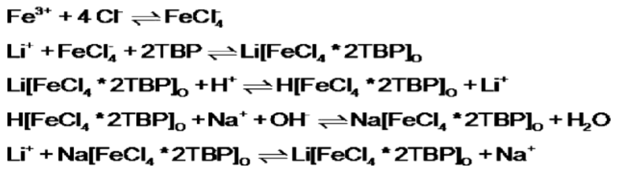
2. Lithium extraction mechanism using $Na[FeCl_4 * 2TBP]_{org}$

In the TBP/kerosene extraction system, the ferric ion is selected as a co-extracting agent to promote the extraction of lithium. As seen Scheme 1, one ferric is associated with four chloride ions to form a complex of $[FeCl_4]^-$ at a high chloride ion concentration. For the investigated salt lake brine, magnesium chloride supplies enough chloride ions. Subsequently the extraction of lithium occurs upon mixing the extractant, ferric and brine in the form of $Li[FeCl_4 * 2TBP]_{org}$ (Reaction 2) (Li et al., 2015). For the recovery of lithium from extractant, an HCl solution is utilized (Reaction 3). After stripping, an extra saponification step (Reaction 4) was employed for the regeneration of the organic phase to sodium form, which is then able to extract lithium (Reaction 5). Then for the next cycle, the process follows Reaction 5 (extraction part), Reaction 3 (stripping part) and Reaction 4 (regeneration of extraction capability) sequentially.

To improve the extraction performance, the concentrations of lithium, ferric, sodium in this system are the key factors. Based on Reaction 4, the extraction rate of lithium ions can be expressed as:

$$R_{Li} = k*[Li^+]^a*[Na^+]^b*[FeCl_4^-*2TBP]^c \qquad (6)$$

where R_{Li} ($mol/cm^2 \cdot s$) is the rate of extraction per unit surface area, and k is the rate constant. a, b, and c represent the corresponding reaction orders.



Scheme 1. Chemical reactions in the extraction (Reactions 1, 2, 4), stripping (Reaction 3) and saponification (Reaction 5) steps for lithium extraction from brine using TBP.

Table 1
Composition of the East Taijinaier salt lake brine.

Substance	Concentration/mol/L
Li^+	0.891
Mg^{2+}	3.810
Na^+	0.060
K^+	0.017
Ca^{2+}	0.015
Cl^-	8.593
SO_4^{2-}	0.012

3. Experimental section

Materials

Tributyl phosphate (TBP), lithium chloride (AR), magnesium chloride, hydrochloric acid (AR), NaOH (AR), and $FeCl_3 * 6H_2O$ (AR) were supplied by Sinopharm Chemical Reagent Co. Ltd. (China) and used as received. Sulfonated kerosene (AR), supplied from Petrochemical Corporation (China), was used without further purification. DI water was used in this experiment.

The main composition of the East Taijinaier salt lake brine is listed in Table 1, as measured in our laboratory. Because the brine solution in our sample was after recovery of potassium, the concentration of K^+ was low, 0.017 mol/L. Slightly higher Na concentration of 0.060 mol/L was observed. Due to the extremely high salinity, the density of the brine is much higher than water, 1.30 g/cm^3. The brine was after acidification for extraction boron, and the pH of brine was 2.38.

Methodology

Preparation of organic phase ($Na[FeCl_4 * 2TBP]$)

The TBP/sulfonated kerosene (v/v 80%, TBP concentration = 2.93 mol/L) and HCl (8 mol/L), $FeCl_3$ (3 mol/L) was mixed using an agitator for 10 min to prepare the $H[FeCl_4 * 2TBP]_{org}$. To wash out the excess HCl in the organic phase, water was added at a volume ratio of organic/aqueous phase (O/A) of 10. Afterwards, a certain volume of NaOH solution (5 mol/L) was added into the organic phase to form a mixed solution. Because the volume of aqueous phase added into the organic phase was small (O/A = 15–50), complete separation of O/A phases was very difficult. When additional $MgCl_2$ solution (4 mol/L) was added to the mixture (O/A = 3), the organic phase quickly separated from aqueous phase. Measurement of the sodium ions in the organic extractant showed that the replaced sodium was marginal.

Liquid-liquid extraction (LLE)

The LLE experiments were conducted using 250 mL flasks at predetermined temperature. The mixture was agitated for 10 min using an oscillator to reach an extraction equilibrium. The lithium extraction efficiency (E%), the separation factor of Li/Mg ($\beta_{Li/Mg}$) were calculated as follows:

$$E_{Li}\% = \frac{C_o - C_{Li\cdot a}}{C_o} * 100\% \qquad (7)$$

$$\beta_{Li/Mg} = \frac{C_{Li\cdot o}/C_{Mg\cdot o}}{C_{Li\cdot a}/C_{Mg\cdot a}} \qquad (8)$$

$$D_{Li} = \frac{C_{Li\cdot o}}{C_{Li\cdot a}} \qquad (9)$$

where C_o (mol/L) is the initial lithium concentration in the brine, $C_{Li,o}$ (mol/L) and $C_{Li,a}$ (mol/L) are the equilibrium concentration of lithium in the organic phase and brine after extraction; $C_{Mg,o}$ (mol/L) and $C_{Mg,a}$

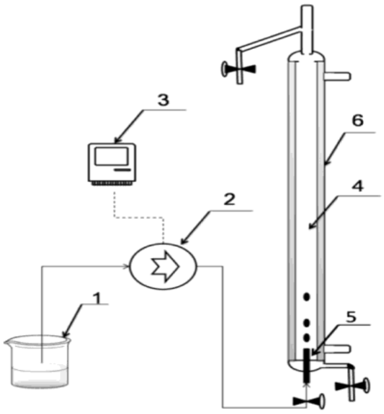


Fig. 1. Schematic of the single-rising drop experimental setup. 1-extractant, 2-syringe pump, 3-pump control, 4-extraction column, 5-capillary, 6-jacket for maintaining constant temperature.

(mol/L) are the equilibrium concentration of magnesium ion in the organic phase and brine after extraction.

Measurement of rate of mass transfer

Single rising drop technique was used to measure the mass transfer of lithium in the extraction process (the experimental setup is shown in Fig. 1). The extractant drop volume was accurately controlled by a micro-syringe pump and connected with capillaries of various dia- meters. The volume and number of droplets were recorded. For one batch of experiment, about 400 droplets were recorded, and the average rising time was calculated. Consequently, the average lithium ion concentration was measured.

The rate of Li^+ transfer in extraction was calculated as follows (Awwad, 2004):

$$R_{\mathrm{Li}^+} = \frac{V}{A} \times \frac{d[C_{\mathrm{Li}:o}]}{dt} \tag{10}$$

where R_{Li} (mol/cm²·s) is the rate of lithium transfer; V (cm³) is the volume of a drop, A (cm²) is the surface area of one drop, and t (s) is the rising time of the droplets of the organic phase.

Measurement of interface intension

Pendant drop method was adopted to measure the interfacial tension (Lee et al., 2008) by a contact angle goniometer (Maist Drop Meter A-100P) equipped with a high speed CCD camera. As shown in Fig. 2, with the shape factor (S) (Eq. (11)), the parameter of H in Eq. (12) can be calculated using the Bashforth-Admas method (Jůza, 1997). Finally, the interfacial tension (γ) can be calculated according to Eq. (12).

$$S = \frac{d_s}{d_e} \tag{11}$$

$$\gamma = \frac{\Delta\rho g d_e^2}{H} \tag{12}$$

where the Δρ (kg/dm³) is the density difference, g is the gravity constant (9.8 N/kg).

3.3. Analysis

The concentration of the cations in the aqueous samples was analyzed using an Inductively Coupled Plasma Atomic Emission Spectrometry/ICP-AES (ICPE-9000, Shimadzu). Lithium in the organic phase was analyzed after being stripped completely into aqueous phase using a 7 mol/L hydrochloric acid solution. Mass balance of lithium in the aqueous and organic phase confirmed that the analysis was accurate (deviation < 5%). The standard deviation of the ICP measurement for triple samples was < 1%. The viscosity was measured by a viscometer (DV-II+ Pro, Brookfield).

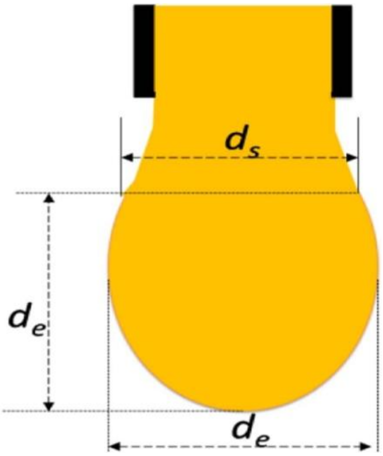


Fig. 2. The schematic diagram of pendant drop method. d_e is the max diameter of pendant drop, the d_s was the diameter which distance of d_e from the apex of drop.

4. Results and discussion

Effect of temperature

Temperature is the most complex factor affecting the equilibrium state in the liquid-liquid extraction process. Located in the northwest China, the temperature in the salt lake brine reaches −20 °C in winter and 25 °C in summer. The effect of the temperature on the reaction is correlated by the change of enthalpy (ΔH) to the temperature based on Van't Hoff equation (Mishra et al., 2011).

$$-\frac{d(\log D)}{(1000/T)} = -\frac{\Delta H\, d}{2303R} \tag{13}$$

By plotting logD against 1000/T, the fitted slope was used to calculate the corresponding ΔH. For the TBP extraction system containing 0.2 mol/L sodium ion, the change of enthalpy (ΔH) in the extraction reaction is −11.5 kJ/mol (Fig. 3A). Obviously, the extraction reaction is an exothermic reaction, and lower temperature favors the extraction step.

Fig. 3B shows the viscosity of brine and organic phase at different temperatures. An increase in temperature causes a considerable decrease in the viscosity. Thermodynamically, low temperature is beneficial for an exothermic reaction; this was reflected in the rate of mass transfer as the temperature decreased from 0 °C to −10 °C (Fig. 3C). The kinetics and the thermodynamic limits are both important for the lithium extraction, but the former is more relevant in an industrial process. And it would be impractical for the extraction process to work at below 0 °C due to the high viscosity. As shown in Fig. 3C, when the reaction temperature was increased from 0 °C to 25 °C, the rate of lithium transfer was enhanced. This probably means that the kinetics of the reaction plays a major role as the viscosity of both brine and extractant decreases significantly at an elevated temperature.

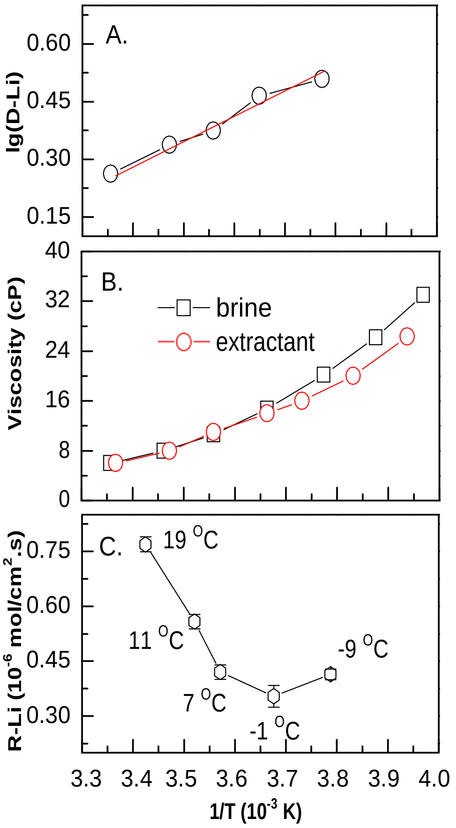


Fig. 3. Effects of temperature on the distribution coefficient, D (A), viscosity of the brine and extractant (B) and rate of mass transfer (C) in extracting lithium ion from brine. Synthetic brine: $MgCl_2$ 4 mol/L, LiCl 0.9 mol/L; organic phase: 0.2 mol/L Na [$FeCl_4 * 2TBP$], the length of extraction column = 90 cm, the diameter of drop = 1.56 mm.

Effects of coalescence and drop break-up

In the liquid-liquid extraction process (Fig. 4A), mass transfer occurs in the process of break-up of organic extractant into droplet (or formation of droplets), coalescence of droplets and the interfacial contact between droplets and continuous phases in the rising step. Identification of the mass transfer in these steps is crucial in designing the extraction equipment, especially the structure of a column (Karr, 1980, Kamp and Kraume, 2015). In an extraction column, the organic extractant droplets experience constantly breakups and coalescence; determination of the critical mass transfer stage is important to optimize the extraction performance. To quantify the contribution of those mass transfer steps, columns of different lengths were used. Fig. 5 shows that the rate of extraction reaction is nearly constant regardless that the length of the column has been nearly doubled, which was attributed to the volume of the brine that was rather large in comparison to the organic phase leading to a nearly constant lithium concentration (driving force) in the aqueous phase.

However, the lithium concentration in the organic phase showed a linear relationship to the length of the column (Fig. 5). By extrapolating the linear relationship to a column length of zero, a concentration of 0.018 mol/L was obtained. This value could be attributed to the lithium ion transfer at the drop formation and coalescence steps, and this effect is called end-effect. And the ratio of the lithium contribution due to end-effect ($C_{Li\text{-}End\text{-}effect}$) to the total lithium concentration ($C_{Li\text{-}Total}$), defined as REE%, was used to describe its performance (Eq. (14)). The lithium transfer caused end-effect ($C_{Li\text{-}End\text{-}effect}$) in this system was 0.018 mol/L.

$$REE\% = \frac{C_{Li-End-effect}}{C_{Li-Total}} \times 100\% \qquad (14)$$

As an example, for a column of 90 cm, the total lithium concentration in the organic was 0.253 mol/L, the REE was 7.19%. This value indicated that the end-effect in the extraction process was minor. A linear relationship of the concentration-column length is a solid support for the observed nearly constant rate of lithium mass transfer as the column length increased from 50 to 90 cm (Fig. 5). The results showed that the transfer mainly occurred in the rising step. It appeared that the droplets behaved like rigid spheres, meaning that macroscopically there was little change occurring at the interface (Fig. 4B). Consequently, the mass transfer occurs slowly at the interface, and so is the rate of mass transfer during the rising step. But for aqueous/organic extractant pairs with a rather low interfacial tension (Fig. A1), the perturbation of the interface can take place frequently, which may promote the mass transfer (Fig. 4B). Therefore, the organic droplets may show disturbance in the organic/brine interface during rising step; due to the disturbance at the organic/brine interface, the extraction reaction is enhanced.

The time for the formation and coalescence of droplets, and the rising speed of droplets were measured to be constant. Although the end-effect for a 90 cm column was low, for a short column, it might be significant. Fig. 6 shows the calculated end-effect in our system at column length below 40 cm. Similar to the above results, a linear relationship between the column length and the lithium concentration in the organic phase was obtained; however, the ratio between the end-effect concentration (0.018 mol/L) to the lithium concentration in organic phase increases as the column length decreases. In a plate column, the gap between two plates resembles the length of the column in this experiment. Because using a plate gap of 90 cm would result in very tall column, it is thus rather useful to reduce the column plate distance and utilize the effect of the mass transfer during the breakage/coalescence step. When the plate gap decreases from 20 cm to 3 cm, the end-effect increased from 25.8% to 69.6%. This means that the end-effect dominates the lithium mass transfer. Since the interfacial tension (Fig. A1) is low, energy for formation of oil droplets in brine is low. Results indicate that the end-effect becomes important in a realistic column where the plate gap is small and the energy consumption would not be significant.

Effects of droplet size

Fig. 7A shows that the rising time of the droplets and the lithium concentration in the organic both declined as the droplet size increases. The rate of extraction increased slightly as the droplets size increased (Fig. 7B). These two observations indicate that as far as the extraction rate is concerned, the droplet sizes appear not critical in the range investigated herein. Observations (Figs. 4 and 5) showed that the organic/brine interface is prone to perturbation. A quick rising speed causes turbulence at the interface. Although smaller droplets are more favorable for extraction due to a larger surface-to-volume ratio, the surfaces may be less prone to disturbance. For larger droplets, the mass transfer due to the turbulence at the interface enhances dynamically the lithium extraction, which overtakes the effect of the surface area, and thus the rate of extraction has been maintained. Nevertheless, to create smaller droplets, more energy is generally required. The findings in this experiment demonstrated that extra energy to break-up the organic into small droplets is not necessary for improved lithium extraction efficiency.

Salting-out effects: contribution of magnesium ion to lithium extraction

The lithium deposit brine in the salt-lake of China is characterized as high magnesium ion concentration. The separation of lithium from magnesium is crucial. It was known that the increase of one salt in

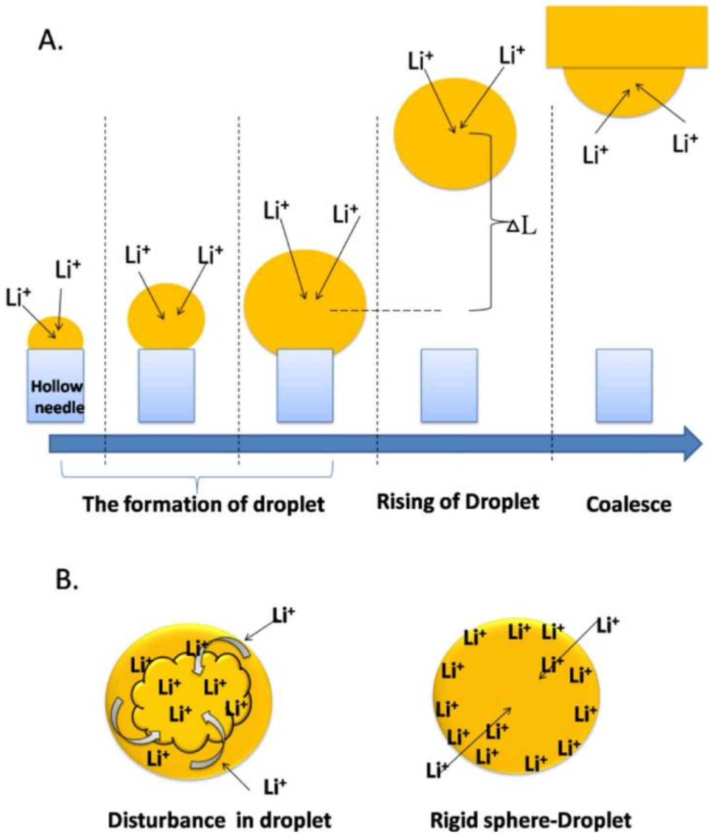


Fig. 4. The schematic of lithium ion transfer during the formation of droplet and rising of droplet (A) and lithium ion transfer in two types of droplet: flexible interface, meaning the perturbation occurs at the interface upon disturbance and rigid interface, meaning that macroscopically very small changes at the interface occurs (B).

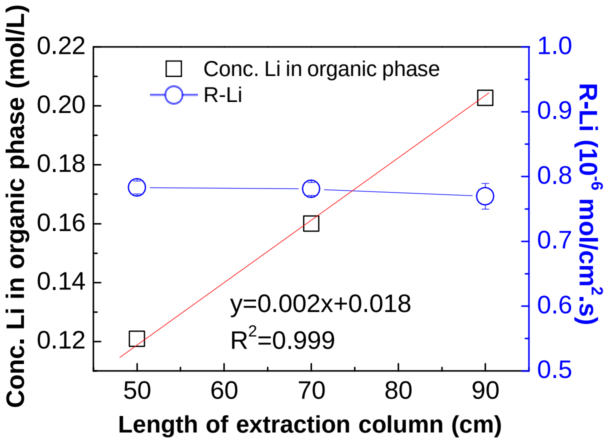


Fig. 5. Effect of extraction column length on extraction rate. Brine: $[Li^+]_{aqu} = 0.9$ mol/L, $[Mg]_{aqu} = 3.8$ mol/L; organic phase: $[Na]_{org} = 0.2$ mol/L, $[Fe]_{org} = 0.4$ mol/L, $[TBP]_{org} = 2.93$ mol/L; diameter of drop was 1.56 mm.

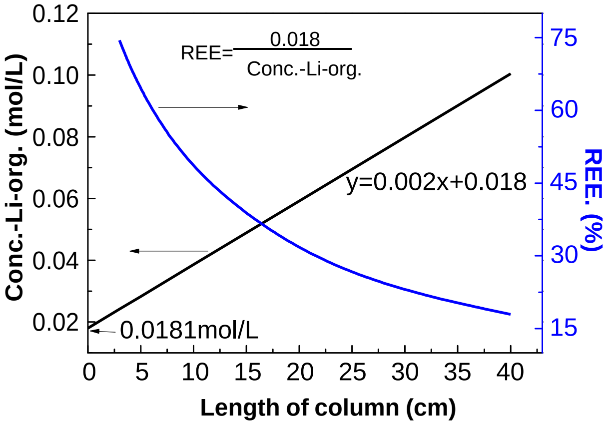


Fig. 6. Effect of extraction column length on extraction (calculated value). Brine: $[Li^+]_{aqu} = 0.9$ mol/L, $[Mg]_{aqu} = 3.8$ mol/L; organic phase: $[Na]_{org} = 0.2$ mol/L, $[Fe]_{org} = 0.5$ mol/L, $[TBP]_{org} = 2.93$ mol/L; diameter of drop was 1.56 mm.

aqueous phase would decrease the activity of other solutes, or called the salting-out effect (Morrison, 1944). Theoretically, the coefficient of salting-out effect can be calculated as follows (Tun, 2010).

$$k_s = (V^o_w/2303)*(h^o_G - v) = 0.0078(h^o_G - v) \qquad (15)$$

where V_W^O is molar volume of water; h_G^O is the number of hydrated ions and v is the number of ions. When $h_G^O > v$, $k_s > 0$, the salting-out effect occurs. In the salt lake brine, the magnesium ions were highly concentrated up to 4 mol/L (Han, 2001). Literature reported that the hexaaquated magnesium ion, $Mg[H_2O]_6^{2+}$, exists in the presence of various anions or chelating groups (Bock et al., 1994). Thus h_G^O was assumed to be 6; and k_s was calculated to be 0.39. The salting-out effect occurs in the brine. Generally, when the brine contains hexaaquated magnesium ions, part of the water molecules loses their translation freedom, and the content of free water molecules in brine declines, and consequently, the actual lithium concentration increased, resulting in an increased driving force of mass transfer and consequently increased

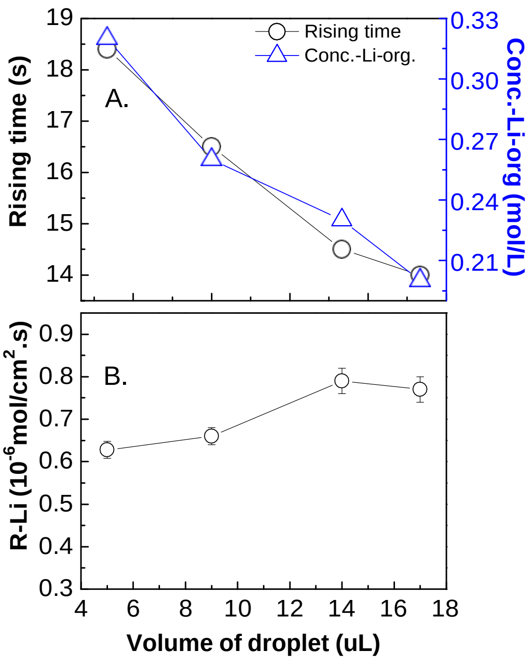


Fig. 7. Effect of drop size on extraction. Brine: $[\mathrm{Li}^+]_{aqu}$ = 0.9 mol/L, $[\mathrm{Mg}]_{aqu}$ = 3.8 mol/L; organic phase: $[\mathrm{Na}]_{org}$ = 0.2 mol/L, $[\mathrm{Fe}]_{org}$ = 0.5 mol/L, $[\mathrm{TBP}]_{org}$ = 2.93 mol/L; length of column = 90 cm.

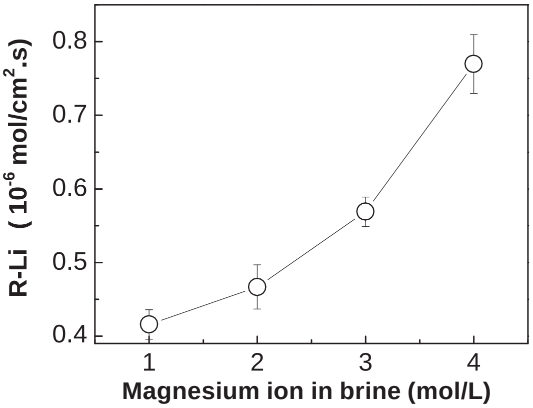


Fig. 8. Effect of magnesium ion concentration on extraction rate. Brine: $[\mathrm{Li}]_{aqu}$ = 0 0.9 mol/L; organic phase: $[\mathrm{Na}]_{org}$ = 0.2 mol/L, $[\mathrm{Fe}]_{org}$ = 0.5 mol/L, $[\mathrm{TBP}]_{org}$ = 2.93 mol/L; diameter of drop = 1.56 mm; length of column = 90 cm.

rate of lithium extraction (Fig. 8)

The extraction performance of $\mathrm{Na[FeCl_4 * 2TBP]}$ system was studied as shown in Fig. 9. The results showed that the $\beta_{Li/Mg}$ increases linearly with the concentration of magnesium. At C_{Mg2+} = 4 mol/L, the $\beta_{Li/Mg}$ was 178.4 (Fig. 9). A high $\beta_{Li/Mg}$ is a prerequisite for a good extraction system. Meanwhile, the ratio of lithium extraction was in a linearly relationship to the concentration of $\mathrm{Mg^{2+}}$. The $\mathrm{Mg^{2+}}$ concentration in the salt lake brine is close to 4 mol/L (Table 1), which could be beneficial to the lithium extraction according to results shown in Fig. 9.

Effects of lithium, sodium, ferric ions concentration

Lithium concentration in brine phase plays an important role in the mass transfer. As shown in Fig. 10A, the rate of lithium ion transfer increased from 0.11 × 10^{-6} mol/cm²·s to 0.77 × 10^{-6} mol/cm²·s when the concentration of lithium in brine increased from 0.1 mol/L to 0.9 mol/L.

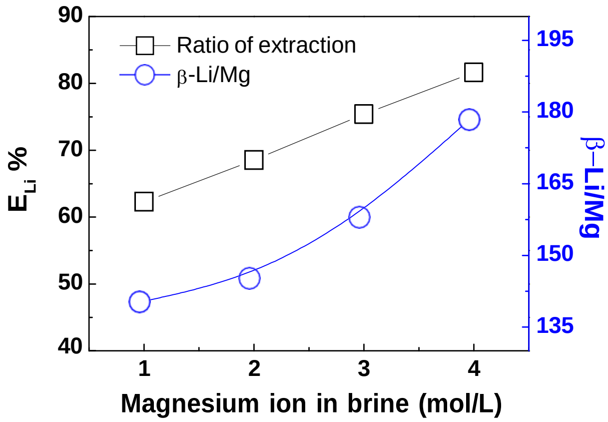
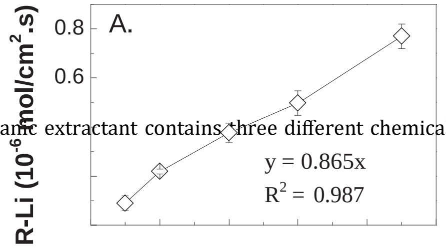


Fig. 9. Effect of concentration — magnesium in brine on extraction rate. Brine: $[\mathrm{Li}]_{aqu}$ = 0.9 mol/L; organic phase: $[\mathrm{Na}]_{org}$ = 0.2 mol/L, $[\mathrm{Fe}]_{org}$ = 0.5 mol/L, $[\mathrm{TBP}]_{org}$ = 2.93 mol/L; O/A = 4.



The organic extractant contains three different chemicals, the active

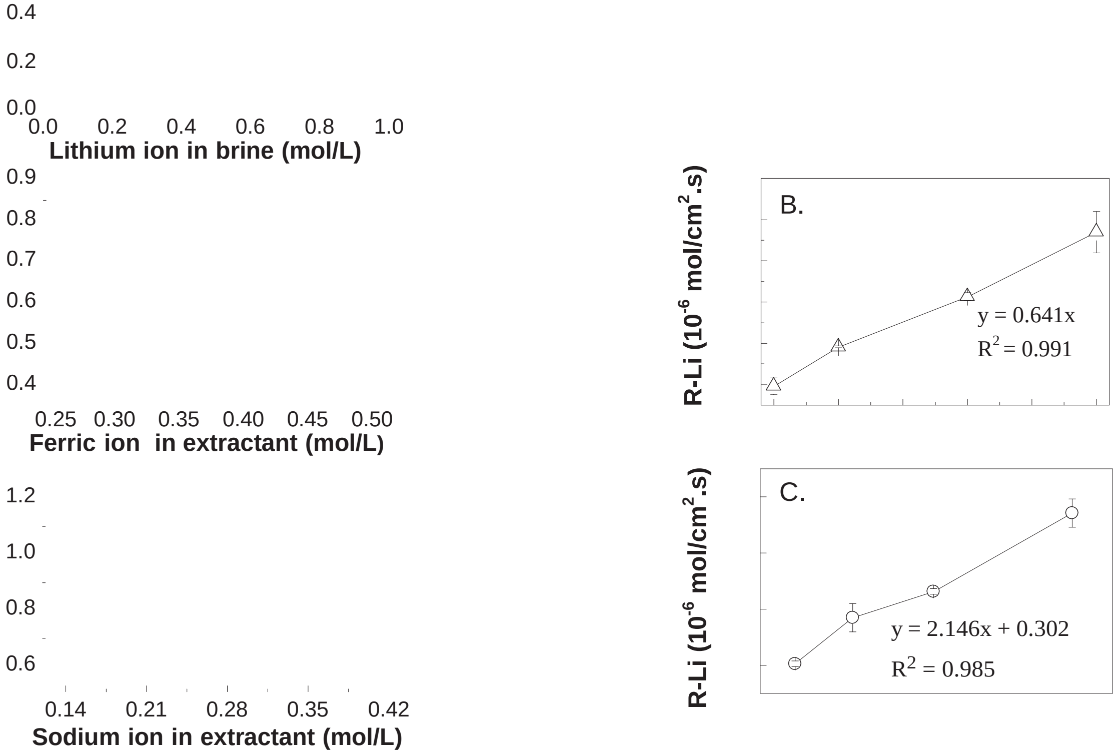


Fig. 10. Effects of lithium (A), iron (B) and sodium (C) concentration on the extraction rate. A: Brine: $[Mg]_{aqu} = 3.8$ mol/L; organic phase: $[Na]_{org} = 0.2$ mol/L, $[Fe]_{org} = 0.5$ mol/L, $[TBP]_{org} = 2.93$ mol/L; B: brine: $[Li]_{aqu} = 0.9$ mol/L, $[Mg]_{aqu} = 3.8$ mol/L; organic phase: $[Na]_{org} = 0.2$ mol/L, $[TBP]_{org} = 2.93$ mol/L; C: brine: $[Li]_{aqu} = 0.9$ mol/L, $[Mg]_{aqu} = 3.8$ mol/L; organic phase: $[Fe]_{org} = 0.5$ mol/L, $[TBP]_{org} = 2.93$ mol/L. Diameter of droplet = 1.56 mm; length of column = 90 cm.

extractant, $Na[FeCl_4 * 2TBP]$, $H[FeCl_4 * 2TBP]$, and $Mg[FeCl_4 * 2TBP]_2$ (Reaction 5). High ferric concentration (Fe^{3+}) in the organic phase is associated with a high content of $[FeCl_4 * 2TBP]^-$. Because of the high $\beta_{Li/Mg}$ (Figure10), $Mg[FeCl_4 * 2TBP]_2$ actually promotes lithium extraction due to preferential exchange of lithium with magnesium. Therefore, increase in ferric concentration results in enhanced lithium extraction rate (Fig. 10B).

The extraction of lithium using $Na[FeCl_4 * 2TBP]$ is in practice an

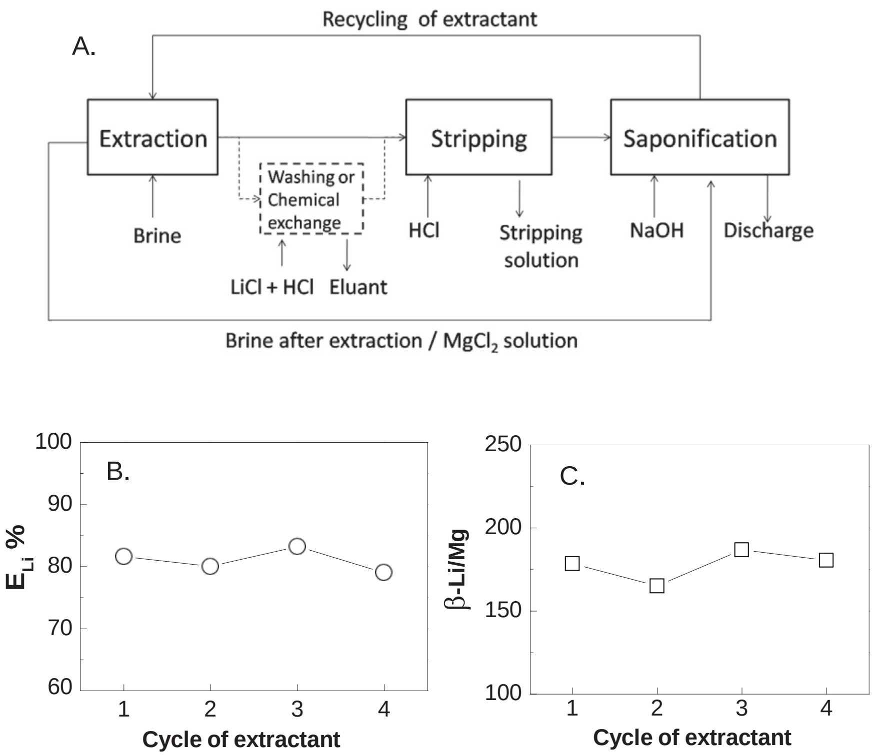


Fig. 11. Schematic illustration of lithium recovery from brine and recycling of the extractant (A), and the performance of re-used extractant (B, C). Brine: East Taijinaier salt lake brine — Table 1; organic phase: $[\mathrm{Na}]_{org}$ = 0.2 mol/L, $[\mathrm{Fe}]_{org}$ = 0.5 mol/L, $[\mathrm{TBP}]_{org}$ = 2.93 mol/L. Extraction-O/A = 4.

ion exchange process between of $\mathrm{Na^+}$ in the organic and $\mathrm{Li^+}$ in the aqueous phase. Hence, the increase of sodium concentration in the organic phase leads to increased driving force of extraction and increased rate of mass transfer (Fig. 10C).

From Fig. 10C, a linear relationship of lithium transfer ratio against lithium in brine and $\mathrm{Na[FeCl_4 * 2TBP]_{org}}$ was obtained. Therefore, the reaction order appears to be close to 1. Based on Reaction 5, the experimental rate equation can be obtained as follows:

$$R = (8.63 \pm 1.05*10^{-6}) \times [\mathrm{Li}]_{aqu} \times [\mathrm{Na}]_{org} \times [\mathrm{FeCl_4{\cdot}2TBP}]_{org} \qquad (16)$$

Extraction of lithium from brine: stability of extractant and process

Fig. 11A shows a schematic process for lithium extraction from salt-lake brine using $\mathrm{Na[FeCl_4 * 2TBP]}$. After extraction, the lithium is stripped by a concentrated acid HCl (Zhou et al., 2012a, 2012b) using a counter-current stripping process (4 stages using 6 mol/L HCl and the O/A was 5). The excess acid in the organic phase was washed out by deionized water. In the regeneration approach, the organic phased was saponified using NaOH. To further demonstrate the efficiency of the extractant, four cycles were tested and the results are shown in Fig. 11B–C. The extraction efficiency for lithium was about 80% in all 4 cycles, indicating that the process and the extractant were both rather stable. A washing step can be introduced to improve the lithium purity as shown in Fig. 11A (the process in dashed box). Then the complete process for extraction of lithium from salt lake brine can be implemented. Nevertheless, further investigations are still needed for this extraction process to become feasible, such as the washing process, the recovery of lithium, the cost efficiency and so on.

5. Conclusions

In this research, effects of operating parameters on the extraction of lithium from brine with $\mathrm{Na[FeCl_4 * 2TBP]_{org}}$ was studied. A single drop column methodology was adopted for analysis of the extraction process. Thermodynamic studies on the extraction reaction indicated that the extraction is exothermic. However, integrated with the kinetic effect such as diffusion rate and viscosity, the lithium mass transfer increases at elevated temperature. Due to the low interfacial tension between the brine and extractant, perturbation at the interface contributes to the mass transfer as supported by the increased lithium mass transfer with the column length. However, the contribution of the formation/coalescence of organic extractant droplets, end-effect, to the lithium mass transfer is more significant as the column length is shortened. It was observed that larger droplets corresponded to higher rate of lithium mass transfer. The salting-out effect of magnesium ions in brine benefits the lithium extraction due to increased lithium concentration. The concentration of sodium and ferric in the organic extractant showed a linear relationship to the rate of lithium transfer. The relationship between the rate of lithium mass transfer and the lithium concentration in brine, and $\mathrm{Na^+/Mg^{2+}}$ concentration in organic extractant was correlated. A process was proposed to extract lithium ions from brine and the stability of the new extractant was demonstrated by four extraction/stripping/saponification cycles. These results indicate that the present extraction system/methodology could be potentially applied in a scale-up application for extracting lithium from brines with a high Mg/Li ratio.

Appendix A. Appendix

The interfacial tension plays an important role on the process of droplet break-up and coalescence, as well as the integrity of the interface. More energy is needed to generate smaller droplets and to create perturbation at the interface if the surface intension is higher. Fig. A1 shows the interfacial tension of the organic extractant in different chemical form and the brine. Results show that all values of the interfacial tension are in the range of 12–16 mN/m, which is relatively low.

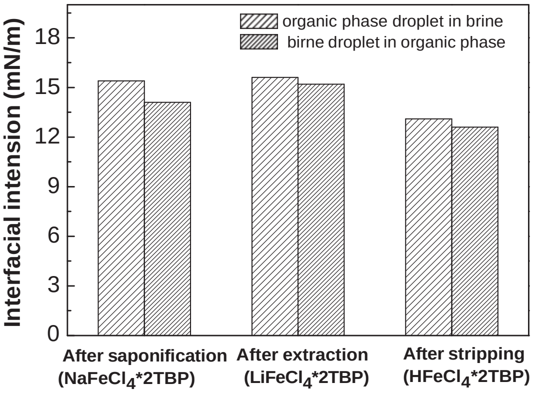


Fig. A1. The surface tension of extractant and brine. (Brine: East Taijinaier salt lake brine — Table 1; organic phase-$NaFeCl_4 * 2TBP$: $[Na]_{org} = 0.2$ mol/L, $[Fe]_{org} = 0.5$ mol/L, $[TBP]_{org} = 2.93$ mol/L; organic phase-$HFeCl_4 * 2TBP$: $[H]_{org} = 0.5$ mol/L, $[Fe]_{org} = 0.5$ mol/L, $[TBP]_{org} = 2.93$ mol/L).

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