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Extractive separations of lithium isotopes with benzo-15-crown-5 and ionic liquids: a comparative study between stirred vessels and small channel contactors

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Abstract

The separation of lithium and the fractionation of the isotopes by solvent extraction was studied, using benzo-15-crown-5 as an extractant dissolved in a diluent of an ionic liquid and anisole. Equilibrium experiments were carried out in stirred vessels while continuous flow experiments were performed in small channels with 0.5 mm diameter. In the flow channels about 8-19% extraction was reached in approximately 1 min with an apparent fractionation factor of 1.032 (±0.005). In comparison, in stirred vessels 10–25% extraction was achieved with a fractionation of 1.026 (±0.002) over an hour. An increase in residence time in the channels increased the extraction percentage but reduced the lithium fractionation. When the ionic liquids were diluted with anisole, equilibrium was reached at an increased rate while the extraction percentage was not affected in stirred vessels. Density Functional Theory (DFT) calculations suggested that the fractionation of the Li isotopes is attributed to different vibrational frequencies of the Li-O bonds with the extractant in the organic solution and with water, while the isotope exchange was spontaneous. The ionic liquid helped the isotope fractionation, while its dilution with anisole did not significantly affect it.

Key words: Liquid-liquid extraction; Lithium isotopes separation; Process intensification; Small channels; Ionic liquids; benzo-15-crown-5

1. Introduction

In natural resources, lithium isotopes can be significantly fractioned by secondary mineral formation and/or adsorption onto particles [1]. Lithium isotopes are important in numerous applications, including nuclear fusion reactions, as a coolant in fusion power plants and for tracing continental weathering processes [2-4]. Producing materials with isotopic concentrations enriched beyond natural levels is essential in many technological fields, such as most contemporary fusion reactor designs, which will use deuterium and tritium as the fuel. While deuterium is readily available, tritium must be generated inside the reactor using lithium-based materials in breeding blankets. It is likely that Li will need to be enriched to Li6 to enable future fusion power plants to be self-sufficient in tritium, which in most design scenarios will require large amounts of lithium enriched to at least 10% lithium-6 [5]. In some other applications, such as in pressurized water reactors (PWRs), lithium hydroxide is added as a coolant to stabilize pH levels and reduce corrosion in the primary water systems. The existence of lithium-6 could create an environment where significant quantities of the radioactive gas tritium is produced. Tritium is a regulated substance, and its small atomic size allows it to permeate through materials more easily than larger molecules, making its containment and capture difficult. Thus, lithium must be enriched to at least 99.995% of lithium-7 to be used in PWRs, as recommended by the Oak Ridge National Laboratory [6].

The enrichment of lithium isotopes to date has predominantly been via the COLEX process which involves the fractionation of the Li isotopes from an acidic solution into a mercury amalgam. The efficiency of the process is characterised by the separation coefficient (also referred to as fractionation factor), α, which is defined as the molar ratio of the heavier to the lighter isotope between the two phases. The mercury amalgam approach has been utilized to enrich lithium isotopes because of its large and compelling single-stage separation factor of $\alpha = 1.054$ (± 0.002) [7]. This method separates lithium-6 and lithium-7 based on their different affinity to mercury, but it raises significant environmental concerns due to mercury vapour emissions [8]. Consequently, there is a growing need to develop sustainable, economic, and more environmentally friendly lithium isotope separation methods. Alternative techniques such as chromatography [9], electromigration [10], membrane separation [11], and use of lasers [12] have been considered. Some of these alternative techniques have shown promise by either demonstrating specific advantages or achieving higher single-step enrichment efficiencies compared to the COLEX method, highlighting the potential for their application in sustainable and economically viable industrial-scale lithium isotope separation. However, challenges preventing the industrial implementation include large number of required stages needed for enrichment, leading to large footprint or energy costs, limited throughput and lack of scale up demonstrators.

Another promising alternative method for lithium fractionation involves its extraction from aqueous solutions to organic diluents using suitable extractants [13, 14]. There are two general aspects to be considered for lithium extractive separations: chemicals and separation units. Considerable research has been directed towards optimising the chemicals for the extraction. For example, by adding specific extractants, the solvation environment for lithium isotopes in the organic phase can become different from that in the aqueous phase and facilitate lithium fractionation [15, 16]. To enable the extraction of lithium ions into the organic phase, macrocyclic ligands have been used which comprise four or more oxygen atoms separated by carbon chains. The crown-shaped conformers of these ligands, with cavity sizes similar to those of the alkali metal cations, act as extractants by encapsulating the ionic substances in the organic phase. Cryptands with suitable sized cavities to accommodate the lithium ion (such as 2. 1. 1-cryptand) are popular for lithium fractionation [17, 18]. An alternative, slightly modified crown ether, the benzo-15-crown-5 (B15C5), is made more hydrophobic by adding a lipophilic group to the carbon atoms. This modification reduces the amount of extractant lost to water through dissolution. B15C5 has demonstrated both high fractionation factors (around 1.040 ± 0.003) and moderate distribution factors (defined as the ratio of lithium in the organic phase to the aqueous phase), indicating efficient lithium fractionation into the organic phase [19-25].

Instead of organic solvents, ionic liquids (ILs) can be used as diluents. Ionic liquids have attributes such as negligible vapour pressure, high polarity, thermal stability, and customizable functional groups which make them attractive alternatives to organic solvents [26]. For example, imidazolium-based ionic liquids have been widely used as diluents in the recycling and separation of metal ions, such as Li(I), Pb(II), Au(III), Pt(IV), Pd(II), Sr(II), U(VI), and other rare-earth elements in liquid–liquid adsorption/extraction and membrane systems [22, 23, 27, 28]. In recent studies, a combination of crown ether, ionic liquids, and organic solvents for dilution has been proposed as an effective and sustainable approach for lithium extraction separations [16, 29, 30]. A few studies have investigated the factors affecting lithium isotope extractions using ionic liquid, including solvent composition, effect of solvent dilution, extractant/lithium concentration, temperature, and pH [31, 32].

The studies discussed above are all limited to equilibrium investigations carried out in batch vessels. Such studies usually have long residence times of a few hours and may not provide information on the kinetics of the separation. Currently, intensification of chemical and separation processes is considered as a means to reduce material usage, residence times, and waste. Processes in small channels can intensify liquid-liquid extractions because they are characterised by thin fluidic films and large specific interfacial areas which enhance mass transfer, reduces residence times, favours the formation of well-defined flow patterns, and simplifies modelling [33, 34]. Based on these advantages, small channel contactors provide a more conducive platform for detailed kinetic studies compared to batch systems.

There are plenty of studies highlighting the promising aspects of using small channel devices for process intensification. For example, Pheasey et al. found that 80% extraction efficiency of Nd was achieved in a 0.5 mm channel in 37.5s, while similar extraction percentage needed about 16 hours in batch separators [35]. Intensified extractions of metal ions, such as uranium[36], lanthanum[37], europium[38], and separations of Co/Ni[39], have already been investigated in small channel contactors, demonstrating high extraction efficiencies in short residence time.

In this work, small channel flow contactors are combined for the first time with ionic liquid-based extraction systems for lithium separation and fractionation. B15C5 is used as an extractant to separate lithium isotopes originally existing in aqueous solutions. An ionic liquid (1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide) is chosen as a diluent because it has a synergistic role in lithium extraction. The ionic liquid is, however, more expensive and viscous compared to traditional solvents. Thus, the effect of diluting the ionic liquid with methoxybenzene (anisole, $CH_3OC_6H_5$) is also studied. The lithium extraction efficiency and Li-6 and Li-7 isotope fractionation are studied in stirred vessels and in small channel devices and the results are compared in terms of residence time, extraction percentage, and fractionation factor. The enhanced lithium separation is explained in terms of vibrational frequencies of the bonds of the possible complexes formed during extraction and of thermodynamic parameters via DFT calculations.

2. Materials, experimental procedure, and models

2.1 Materials

Lithium chloride (CAS number: 7447-41-8, purified > 98%) was purchased from VWR Chemicals; ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide([C4mim][NTf2])) (CAS number:174899-83-3, >98%), benzo-15-crown-5 (B15C5) (CAS number: 14098-44-3, >98%), and anisole (CAS number: 100-66-3, >99%) were purchased from Sigma Aldrich; all chemicals were used as received. The structures of the chemicals used are shown in Figure 1. The aqueous phase consists of lithium chloride dissolved in de-ionized water, while the organic phase is either pure ionic liquid (IL) or ionic liquid diluted with anisole (volume ratio IL: anisole= 3:7). Two liquid phases were prepared at room temperature. Each phase is contacted and pre-saturated with the other phase before lithium salt is added to the aqueous phase. The physical properties of the fluids used in the experiments have been measured in the lab and are listed in Table 1. Viscosity was measured with a Rheometer DV-111 Ultra (Brookfield), with an error of 1%, and surface and interfacial tensions were measured with a DSA100E tensiometer (KRÜSS Scientific), with an error of ± 0.3 mN/m.

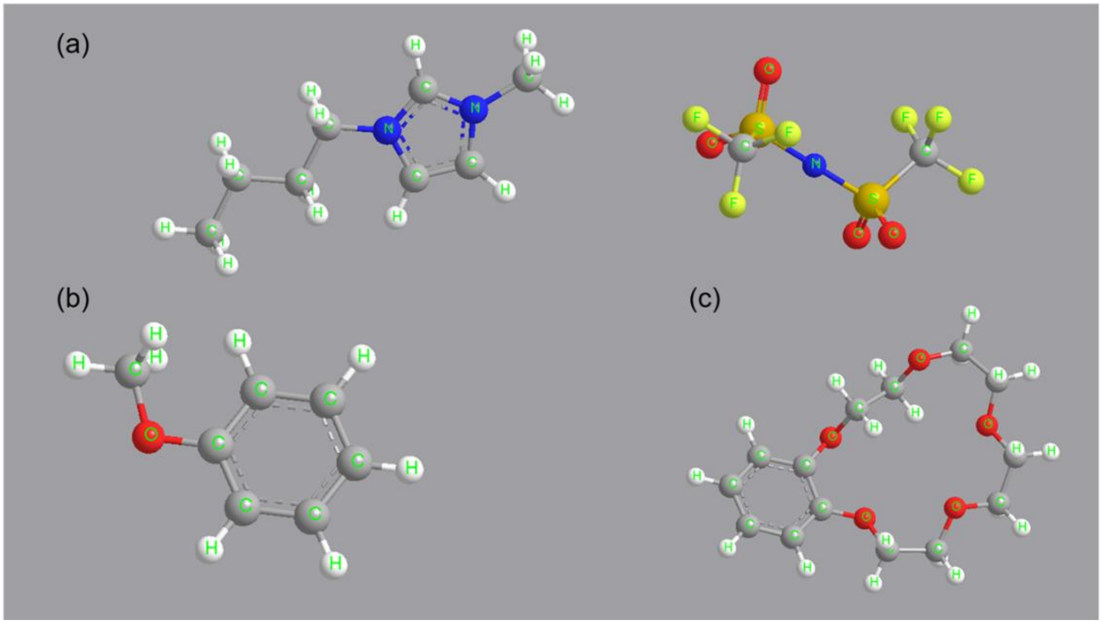

Figure 1. Chemicals used in the experiments constituting the organic phase. (a): 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (referred as [C4mim][NTf2] or ionic liquid below); (b): Anisole; (c): Benzo-15-Crown-5.

Table 1. Physical properties of the fluids used in experiments measured at room temperature (293 K) and ambient pressure.

Fluids	B15C5 Extractant concentration /mol/L	Density /kg·m^{-3}	Viscosity /cP	Interfacial tension with aqueous solution /mN·m^{-1}
LiCl solution	n/a	1007	1.002	n/a
Pure ionic liquid [C4mim][NTf2]	0.2	1415	56.364	12.33
	0.4	1395	62.071	12.25
	0.5	1392	65.689	12.15
IL/Anisole (volume ratio: 3/7)	0.2	1101	3.012	54.11
	0.4	1105	3.250	53.24
	0.5	1113	3.435	53.40

2.2 Experimental methodology

The extraction experiments were carried out at atmospheric pressure and room temperature (T= 293K). With either ionic liquid or anisole-diluted ionic liquid as one phase and lithium chloride solution as the other phase, equilibrium experiments were carried out first in stirred vessels. For these experiments, equal volumes of the aqueous and the organic phase solutions (5 mL) were added in stoppered vessels and then mixed with a magnetic stirrer at constant rotational speed for up to 1 hour. A sample from the aqueous phase was removed from the vessel every 10 mins for the concentration measurements. The same amount of the organic phase was also removed from the vessel to keep the volumes of the two phases equal. Prior studies on lithium separation have indicated that the composition of the organic phase influences the extraction percentage [40]. Here we have considered three extractant concentrations and two solvent compositions in the organic phase, as listed in Table 2. The concentration of lithium chloride in the aqueous phase is constant at 0.5 mol/L for all the cases studied. The extractant B15C5 was dissolved in organic solutions, and the extractant concentrations were 0.2, 0.4, and 0.5 mol/L.

Table 2. Composition of the organic phase for all cases studied.

Cases	B15C5 Extractant concentration (mol/L)	Organic phase composition
A	0.2	IL/Anisole (volume ratio: 3:7)
B	0.4	
C	0.5	
D	0.2	Pure IL
E	0.4	
F	0.5	

Figure 2 shows the experimental set-up for the continuous small channel extraction. The aqueous and organic phases, immiscible to each other, were injected separately by two high precision continuous syringe pumps (Kd Scientific) via polytetrafluoroethylene (PTFE) tubes that had the same diameter (d= 0.5 mm) and joined in a T-junction mixer made of fluorinated ethylene propylene (FEP). The mixture of the two phases was introduced in a tube made of PTFE. The organic phase was the continuous one and entered in line with the main channel, while the aqueous solution containing the lithium salt was fed from the orthogonal direction. At the end of the extraction channel the mixture of the two phases was collected in a narrow glass container and shortly after samples from both phases were taken with a pipette for analysis.

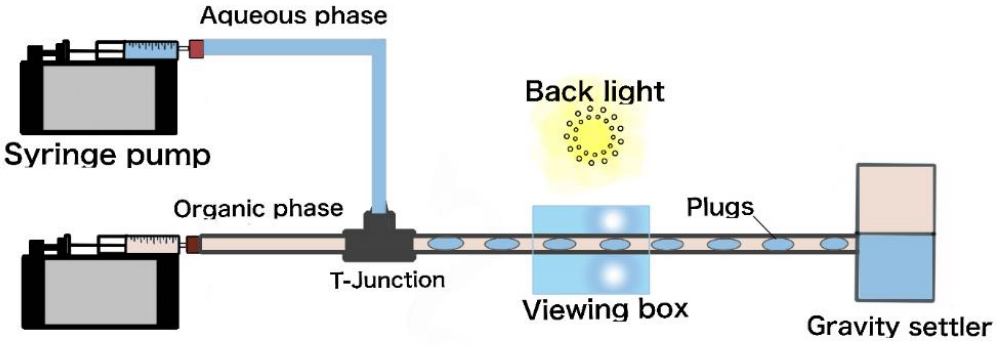

Figure 2. Experimental setup for the continuous flow experiments in microfluidic channels.

The lithium concentrations in the aqueous solutions before and after the extraction were measured using Agilent MP-AES in the Department of Chemical Engineering at UCL. The uncertainty for measurement was 6.07%. Lithium isotope ratios were measured on a Neptune multi-collector ICP-MS using an APEX IR sample introduction system, a 50micl/min PFA nebuliser nickel X cones. ^{7}Li/^{6}Li ratios were normalised to L-SVEC (NIST RM 8545) using standard-sample bracketing and reported using standard delta notation:

$$\delta^7 Li_x = \left[\left(\frac{\left({}^7Li/{}^6Li\right)_{sample}}{\left({}^7Li/{}^6Li\right)_{standard}}\right) - 1\right] 10^3 \qquad (1)$$

Therefore, $\delta^7 Li$ shows how much the composition of the sample deviates from that of the standard. Bracketing measurements are taken for both the standard and the actual samples. This bracketing measurement sequence is designed to minimize the influence of any drift in the instrument beam strength. Since the solutions were pure Li, no ion-chromatography separations were conducted to further purify them. Solutions were diluted to ~0.5 ppb using a 10^{13} Ω resistors on the pre-amplifiers for both ^{6}Li and ^{7}Li. The typical beam size for samples was around 0.3V on ^{7}Li and the background was typically <0.25mV. Accuracy and precision were monitored using ^{6}Li-N and ^{7}Li-N solutions which gave values of -8.1±0.6‰ (2SD, n=59) and 30.3±0.9‰ (2SD, n=50) respectively during the course of the measurements [41, 42]. These values are in agreement with previously published values for these standards (^{7}Li-N = 30.2‰ and ^{6}Li-N = -8.0‰ to -8.3‰).

2.3 Lithium separation calculations

To characterise the overall amount of lithium (including both Li-6 and Li-7) extracted into the organic phase, the extraction efficiency (as a percentage), *E,* and the distribution coefficient, *D*, were used which are defined as follows:

$$E = \frac{n_{org}}{n_{aq,0}} = \frac{C_{org}V_{org}}{C_{aq,0}V_{aq,0}} = \frac{C_{aq,0}V_{aq,0} - C_{aq,eq}V_{aq,eq}}{C_{aq,0}V_{aq,0}} \times 100\% \qquad (2)$$

and

$$D = \frac{n_{org}}{n_{aq,eq}} = \frac{C_{org}V_{org}}{C_{aq,eq}V_{aq,eq}} = \frac{C_{aq,0}V_{aq,0} - C_{aq,eq}V_{aq,eq}}{C_{aq,eq}V_{aq,eq}} \qquad (3)$$

where *n*, *C*, *V* denote the molar amount of lithium, concentration of lithium ion in solution, and volume of the solution used in the experiment, respectively. The subscripts aq and org denote the aqueous phase and the organic phase, while eq and 0 represent liquids at equilibrium and initial liquids, respectively. Following the measurement of $\delta^7 Li$ in the aqueous phase, mass balance was used to determine delta lithium-7 in the organic phase:

$$\delta^7 Li_{org} = \frac{\delta^7 Li_{aq,0} - N_{aq} * \delta^7 Li_{aq}}{N_{org}} \qquad (4)$$

where N stands for the molar fraction of lithium substance remaining in each phase over the overall lithium initial aqueous solution. This can be used to determine the fractionation factor *α* defined as follows:

$$\alpha_{x1-x2} = \frac{\left({}^{7}Li/{}^{6}Li\right)_{x1}}{\left({}^{7}Li/{}^{6}Li\right)_{x2}} \qquad (5)$$

where $\left({}^{7}Li/{}^{6}Li\right)_{x}$ represents the molar ratio of Li-7 to Li-6 in phase x. In this work, x1 stands for the aqueous phase, and x2 denotes the organic phase. For cases where the fractionation factor *α* is close to unity (which is typical of many isotope separation techniques in one stage), the following equation can be used as a close approximation to calculate the fractionation factor *α* [43]:

$$\delta^7 Li_{aq-org} = \delta^7 Li_{aq} - \delta^7 Li_{org} \cong 1000\left(\alpha_{aq-org} - 1\right) \cong 1000 \ln\left(\alpha_{aq-org}\right) \qquad (6)$$

where the $(aq - org)$ represents the two phases between which the fractionation takes place. If $\delta^7 Li_{aq}$ is positive and therefore $\delta^7 Li_{org}$ is negative, it indicates that there is an enrichment of lithium-6 in the organic phase and accordingly a depletion of lithium-6 in the aqueous phase ($\left(\alpha_{aq-org}\right) > 1$).

3. Results and discussion

3.1 Equilibrium studies in stirred vessels.

In the equilibrium experiments in stirred vessels concentrations were measured every 10 minutes from the start of the experiment and for 1 hour, and the results are shown in Figure 3. Solid points denote anisole-diluted IL as the diluent phase, and hollow points stand for pure IL diluent. As it can be seen, equilibrium was established at an early stage for all the anisole-diluted cases and no significant changes of extraction percentage were found over time. However, for the pure IL cases, the extraction percentage shows a delay before equilibrium was reached regardless of extractant concentration. The final values of extraction percentage were mainly influenced by the extractant concentration. Larger concentration of extractant gives larger extraction percentage at equilibrium, which confirms the key role of B15C5 in separating lithium from aqueous solutions. The addition of anisole in the ionic liquid diluent does not affect the final extraction percentage apart from the case of 0.4 mol/L extractant, where it decreases slightly. It seems that the addition of anisole in the ionic liquid shortens the extraction time (by reducing the time to equilibrium) without impacting the final extraction percentage compared to pure ionic liquid. Diluting the IL is favourable in industrial applications for both saving ionic liquid and reducing the viscosity and pumping requirements of the diluent.

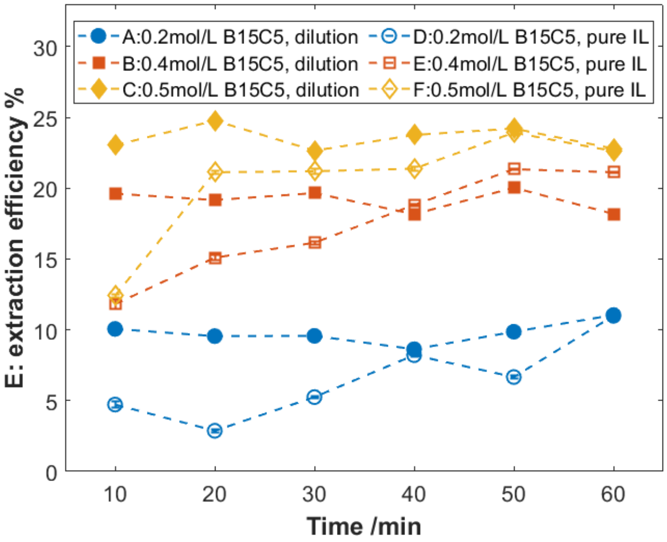

Figure 3. Extraction percentage *E* in the equilibrium tests at different extraction time. In some cases, the size of the error bar is smaller than the size of the symbol.

Some studies have considered the role of organic phase in lithium transfer. For example, Zhang et al. added lithium salts into aqueous solutions of B15C5 and found that only trace amounts of lithium were captured by B15C5 in water [32]. Their findings suggested that B15C5 is less able to combine with lithium ions in aqueous solvation environments. Their experiments could help explain why diluting ionic liquids with anisole increases the rate at which equilibrium is reached. The solvation power of a solvent can be expressed by polarity and can be measured by permittivity (dielectric constant). The permittivity of [C4mim][NTf2] and anisole is 12.7 and 4.3 ($C^2\cdot(N\cdot m^2)^{-1}$) respectively, while water has a high permittivity of 80.2 ($C^2\cdot(N\cdot m^2)^{-1}$) at 20 °C [32, 44] . When lithium chloride is dissolved in water, its corresponding cation, lithium, does not exist on its own. Instead, a tetrahedral-shaped complex with a lithium ion in the centre surrounded by four water molecules is the optimised form in the aqueous environment. The tetrahedral-shaped complex ($[Li(H_2O)_4]^+$) has strong steric hindrances, preventing the combination of lithium with B15C5 outside the complex. With the addition of anisole, the permittivity of the organic mixture decreases from 12.7 (pure ionic liquid) to around 6.8 ($C^2 \cdot (N \cdot m^2)^{-1}$). It is possible that when the $[Li(H_2O)_4]^+$ complex approaches the water-solvent interface, the IL-anisole mixture repels the H_2O molecules of the complex to the water side. This helps to reduce steric hindrances and exposes the lithium ions to the extractant, facilitating its faster transfer to the organic phase.

Some studies have suggested that the extraction is facilitated by forming complexes of lithium-ions and crown ethers through the ion-dipole interactions. The positively charged [*n* (crown ether) - Li]$^+$ complex is paired with bis(trifluoromethanesulfonate) ($[NTf_2]^-$) anions following the Hofmeister series [15]. Assuming a similar mechanism in the extractions here, the reaction formulation for lithium extraction when equilibrium is reached can be written as:

$$LiCl(aq) + \{[C_4mim][NTf_2]\}(org) + n[B15C5](org)$$

$$\Leftrightarrow \{[Li-n(B15C5)][NTf_2]\}(org) + \{[C_4mim]Cl\}(aq) \qquad (7)$$

where the brackets are used to indicate the phase where the complexes are in, the box brackets are for particles under ion-dipole interaction or particles with long formulas when necessary, and the brace brackets are for particles under electrostatic interaction. The equilibrium constant *K*, and the distribution coefficient *D* are defined as

$$K = \frac{\{[Li-n(B15C5)][NTf_2]\}\{[C_4mim]Cl\}}{[LiCl]\{[C_4mim][NTf_2]\}[B15C5]^n} \qquad (8)$$

and

$$D = \frac{\{[Li-n(B15C5)][NTf_2]\}}{[LiCl]} \qquad (9)$$

Arranging the equations for *K* and *D* gives

$$K = D \times \frac{\{[C_4mim]Cl\}}{\{[C_4mim][NTf_2]\}[B15C5]^n} \qquad (10)$$

The following equation can then be used to predict the number of crown ethers *n* that are engaged in caging a lithium ion:

$$\mathrm{Log}\, D = n \times \log[B15C5] + \log\{[C_4mim][NTf_2]\} + \log\mathrm{K} - \log\{[C_4mim]Cl\}$$

$$= n \times \log[B15C5] + constant \qquad (11)$$

The logarithms of the distribution coefficient and the extractant concentration are plotted in Figure 4, where only equilibrium concentrations after 30 min were used for the calculation of *D*. The number of crown ethers is found to be 1.12 for the anisole-diluted cases (D_1) and slightly larger (1.28) for the pure IL cases (D_2) , indicating that there might be a hybrid complex of [*n* (crown ether) - Li]$^+$ with both n=1 and n=2 at a certain proportion, while the one-to-one complex [(crown ether) - Li]$^+$ dominates. The difference between D_1 and D_2 was observed to be significant at low concentrations of extractants while it decreased at high concentrations, indicating that it is possible to optimise the organic concentration related to the lithium concentration in the aqueous phase. Considering that the extraction percentage never exceeds 25% and ignoring the loss of extractants into water, there could still be unoccupied extractants after 1 hour of extraction for all cases. Following the results in Figure 4, the addition of anisole into IL potentially increases the utilisation of crown ethers by reducing the formation of [2 (crown ether) - Li]$^+$.

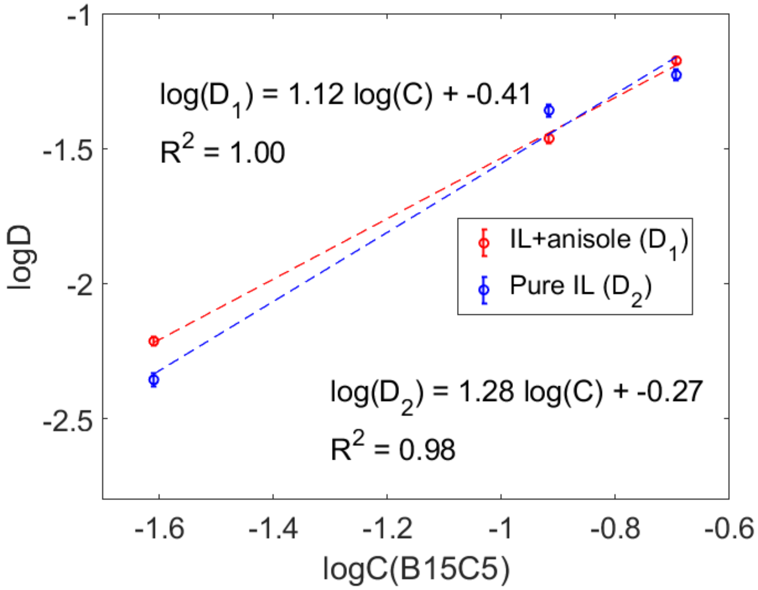

Figure 4. Linear regression of log*D* with log*C*(B15C5). D_1: diluted IL solution, volume ratio= 7 anisole: 3 IL; D_2: pure IL.

To obtain the fractionation of lithium isotopes, samples from the aqueous solutions before and after extraction were ionized and measured. The relative amounts of the two lithium isotopes were given in delta notation defined in equation (1). It was found that all the measured δ^7Li values are greater than those of the initial solution, indicating that lithium-7 is enriched in the aqueous phase during the extraction while lithium-6 is enriched in the organic phase. Combining equations (5) and (6) and rearranging gives

$$\delta^7 Li_{org,eq} = \frac{\delta^7 Li_{aq,0} - N_{aq} * \delta^7 Li_{aq}}{N_{org}} = \frac{\delta^7 Li_{aq,0} - N_{aq} * \delta^7 Li_{aq}}{(1 - N_{aq})} \qquad (12)$$

$$\delta^7 Li_{aq} - \frac{\delta^7 Li_{aq,0} - N_{aq} * \delta^7 Li_{aq}}{(1 - N_{aq})} = 1000(\alpha - 1) \qquad (13)$$

Multiplying $(1 - N_{aq})$ with both sides of equation (13) and rearranging gives:

$$\delta^7 Li_{aq} = 1000(\alpha - 1) * (1 - N_{aq}) + \delta^7 Li_{aq,0} \qquad (14)$$

commonly referred to as the batch equation.

The results for the equilibrium conditions (after 30 min in Figure 3) are plotted in Figure 5. From linear regression the separation factor is found to be 1.026 ± 0.002, while the correlated intercept (12.163) also agrees well with experimentally measured $\delta^7 Li_{aq,0}$ (12.059).

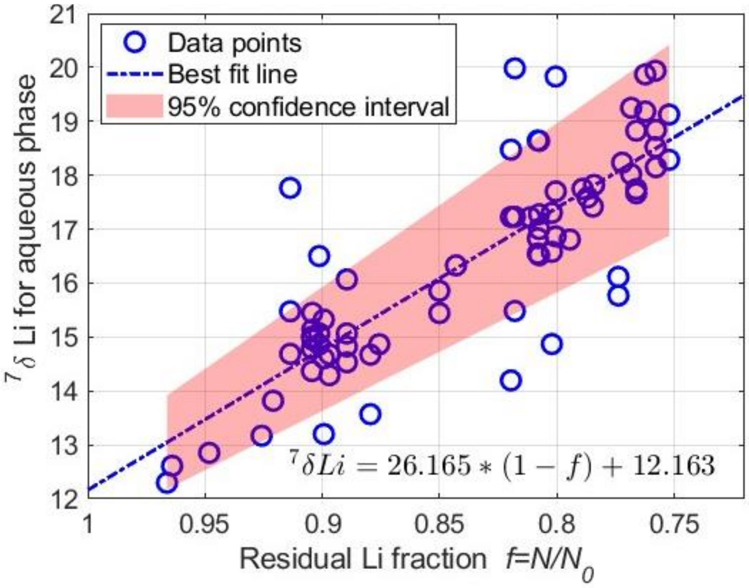

Figure 5. Li isotope separation factor determined in equilibrium experiments. The residual fraction *f* is the ratio of remaining lithium in the aqueous solution in molar concentration (*N*) to that of the overall lithium in the initial aqueous solution (N_0).

Studies using similar chemical systems have been summarized in Table 3. These results, including ours, confirm that the system of ionic liquids, diluting solvents, and extractants (B15C5 and its derivatives) are promising candidates for lithium extractive fractionation and will be considered further in the continuous small channel separators.

Table 3. Summary of extraction results for Li isotope enrichment in experiments in stirred vessels.

Extractant	Solvents	α	Dilution	Safety	Reference
B15C5	Chloroform ($CHCl_3$)	1.017 - 1.044 ± 0.003	/	toxic	Nishizawa, K., et al., Journal of Nuclear Science and Technology, 1984[21] Shokurova, N.A., et al., Russian Journal of Inorganic Chemistry, 2016.[45] Shi, C., et al., Journal of Molecular Liquids, 2016[46]
B15C5	1-(butyl, hexyl, octyl, decyl)-3-methyl-imidazolium-bis(trifluoromethylsulfonyl)imide ([C4,6,8,10 mim]$^+$[NTf2]$^-$)	1.029 ± 0.001	/	nontoxic	Xiao, J., et al., Journal of Molecular Liquids, 2017.[22]
B15C5	1-butyl-3-methylimidazolium hexafluorophosphate ([C4mim][PF6])	1.038 ± 0.002	Chloroform ($CHCl_3$)	toxic	Xiao, J., et al., Journal of Molecular Liquids, 2016[23]
DB15C5	1-Ethyl-3-methyl-imidazolium-bis(trifluoromethysulfonyl)-imide ([EMIm][NTf2])	1.031 - 1.034 ± 0.001	Anisole ($CH_3OC_6H_5$)	nontoxic	Sun, H., et al., Fusion Engineering and Design, 2019[31] Zhang Z., et al., Journal of Molecular Liquids, 2021[32]

DB15C5	1-hexyl-3-methylimidazolium bis(trifluormethylsulfonyl)imide ([HMIM][NTf2])	1.037 ± 0.002	Anisole ($CH_3OC_6H_5$)	nontoxic	Zhang, Z., et al., Fusion Engineering and Design, 2020[47]
B15C5	1-Butyl-3-methylimida-zolium bis(trifluoromethylsulfonyl)imide ([C4mim][NTf2])	1.030 ± 0.002	Anisole ($CH_3OC_6H_5$)	nontoxic	Liu, B., et al., Journal of Molecular Liquids, 2018[28]
B15C5	1-Butyl-3-methylimida-zolium bis(trifluoromethylsulfonyl)imide ([C4mim][NTf2])	1.026± 0.002	Anisole ($CH_3OC_6H_5$)	nontoxic	Current work

3.1 DFT calculations of fractionation mechanisms.

In stirred vessels, equilibrium can be established for long residence time, and the extraction is underpinned by the thermodynamic characteristics. The results above show that the lithium isotopes fractionate during extraction while there is a one-to-one ratio between the extractant molecule and the lithium ion transferred. Yet the mechanism for lithium extractive separation on a molecular level, as well as the role of the organic phase composition remain unknown. Density Functional Theory (DFT) calculations can provide further insights at atomistic level and help interpret the fractionation results found experimentally. The DFT calculations are used to study the mechanism of lithium isotope fractionation with the extractant B15C5, and to investigate the impact of the organic phase composition on the isotope separation. The detailed models can be found in the supplementary material.

As a first step, the configurations of lithium species in both phases are optimised. In the aqueous phase, lithium ions have a hydrated structure which has been verified by many studies [48, 49]. The most stable structure is lithium ion coordinated by four water molecules, as shown in Figure 6(a). In the organic phase, lithium ions are captured by the extractant which has a positive cavity of similar size to the lithium ion, as shown in Figures 6(b) and (c). Detailed information on the optimisation can be found in the Supplementary material.

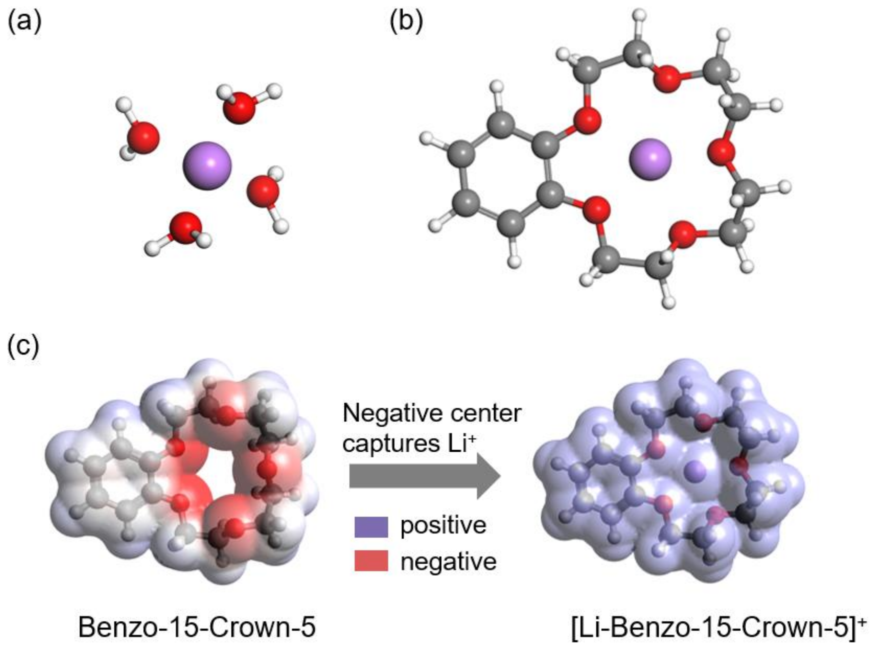

Figure 6. Optimized structures for (a) $Li(H_2O)_4^+$; (b) $[Li\text{-}B15C5]^+$; (c) electrostatic iso-surfaces of $\rho(r) = 0.001\, e/bohr^3$ for B15C5 and $[Li\text{-}B15C5]^+$. Purple, red, white, and grey spheres denote lithium, oxygen, hydrogen, and carbon atoms, respectively.

DFT calculations were then performed to obtain the vibrational frequency of the Li-O bonds in the aqueous and the organic solutions. Hooke's law (equation(15)) shows that the vibrational frequency (ν) of the bond is proportional to the force constant (k).

$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}} \tag{15}$$

where *m* stands for the reduced mass (defined as the ratio of the product of atomic masses to the sum of atomic masses). Table 4 shows that the complex $Li(H_2O)_4^+$ has higher absolute values of Li-O vibrational frequencies, compared with $Li(B5C15)^+$. According to the quantum mechanical solution for an harmonic oscillator (equation(16)), the internuclear potential energy (E_n) is proportional to vibrational frequency (ν) of the bond.

$$E_n = \left(n + \frac{1}{2}\right) h\nu \tag{16}$$

where *n* stands for the non-negative quantum number (0, 1, 2…) associated with the energy level of the oscillator, and *h* represents Planck's constant. Therefore, ^{7}Li-O in the aqueous solution has relatively smaller zero-point energy at the ground state, which increases the energy barrier for breaking the ^{7}Li-O bond. This reduces the likelihood for ^{7}Li to enter the other phase from the aqueous solution compared to ^{6}Li. Hence, it is favourable for ^{7}Li ions to be in the aqueous phase, while ^{6}Li ions are preferentially captured by B15C15 in the organic phase.

Table 4. Harmonic vibrational frequencies of Li-O bond at 0 k with isotopic shifts ($\Delta\upsilon$) between ^{6}Li-O (υ_6) and ^{7}Li-O (υ_7) in complexes Li(H_2O)$_4^+$ and Li(B15C5)$^+$, and average Li-O distance (*d*). The modes refer to specific patterns of atomic motion within a molecule which can be found in supplementary material.

Complex	Modes	υ_6 (cm^{-1})	υ_7 (cm^{-1})	*d* (Å)
Li(H_2O)$_4^+$	B1	536	517	1.98
	B2	529	506	
	E	526	503	
Li(B15C5)$^+$	A	396	390	2.19
	B	345	337	

The influence of diluting the ionic liquid with anisole was also studied with DFT calculations, by considering the change in permittivity, or dielectric constants of the organic phase. The permittivity of a solvent influences the harmonic structure of the molecules within it and can change the thermodynamic characteristics in isotope exchange reactions. We have determined the structures of 1:1 stoichiometric Li-(B5C15) as discussed above. The optimised structure for this is shown in the supplementary material [50, 51]. The isotopic exchange reaction is as follows:

Reaction 1: $^{6}Li(H_2O)_4Cl(aq) + \ ^{7}Li(B15C5)(H_2O)NTf2(org)$

$$\Leftrightarrow \ ^{7}Li(H_2O)_4Cl(aq) + \ ^{6}Li(B15C5)(H_2O)NTf2(org)$$

DFT simulations were performed to quantitively determine the thermodynamic parameters at a temperature of 293.15 K and 1atm to identity the spontaneity of the two isotopic exchange reactions. Table 5 shows the Gibbs free energy change (ΔG), enthalpy change (ΔH), and entropy change (ΔS) for the reaction. The negative Gibbs free energy change shows that the isotopic exchange reaction is spontaneous regardless of the composition of the organic phase. This suggests that lithium-6 in the aqueous phase always tends to exchange with lithium-7 in the organic phase. Comparing the values of ∆G, ∆H, and ∆S for both reactions, it is found that the dilution with anisole has no significant impact on the performance of isotopic exchange from the perspective of thermodynamic parameters. The negative values of enthalpy change show that lithium isotope exchange is exothermic reaction, and the negative entropy change indicates that the reaction favours low temperature. These thermodynamic parameters in Table 5 show that the NTf2 anions help the separation of ^{6}Li/^{7}Li isotopes, and IL dilution with anisole plays an insignificant role from a thermodynamic perspective (i.e., at equilibrium state).

Table 5. DFT calculated the Gibbs free energy change (∆G), enthalpy change (∆H), and entropy change (∆S) for the isotopic exchange reactions (3) and (4) at 293.15 K, with thermal correction to enthalpy. Two different solvation environments are considered by using COSMO, with different dielectric constants ($C^2/(N\cdot m^2)^{-1}$): 11.6 for pure IL and 6.4 for anisole diluted IL.

Environment	Reaction	ΔH (kJ/mol)	ΔS (J/mol/K)	ΔG (kJ/mol)
Pure IL	Reaction 1	-0.115	-0.280	-0.033
7 Anisole: 3 IL	Reaction 1	-0.119	-0.285	-0.036

3.2 Continuous flow extraction in small channels

The patterns obtained in the small channel with a T-junction inlet, are annular, churn, drop, intermittent and plug flow and are plotted in the map in Figure 7. Plug flow occupies a large area of the map for mixture velocities less than 0.01m/s and is characterised by well-defined dispersed phase plugs, with length larger that the channel diameter, separated by continuous phase slugs. This pattern is characterised by the thin film between the plug and the channel wall, recirculation patterns within the phases as well as large interfacial areas which improve mass transfer within and across the phases [52, 53]. Therefore, plug flow has been used for the flow extraction studies reported here.

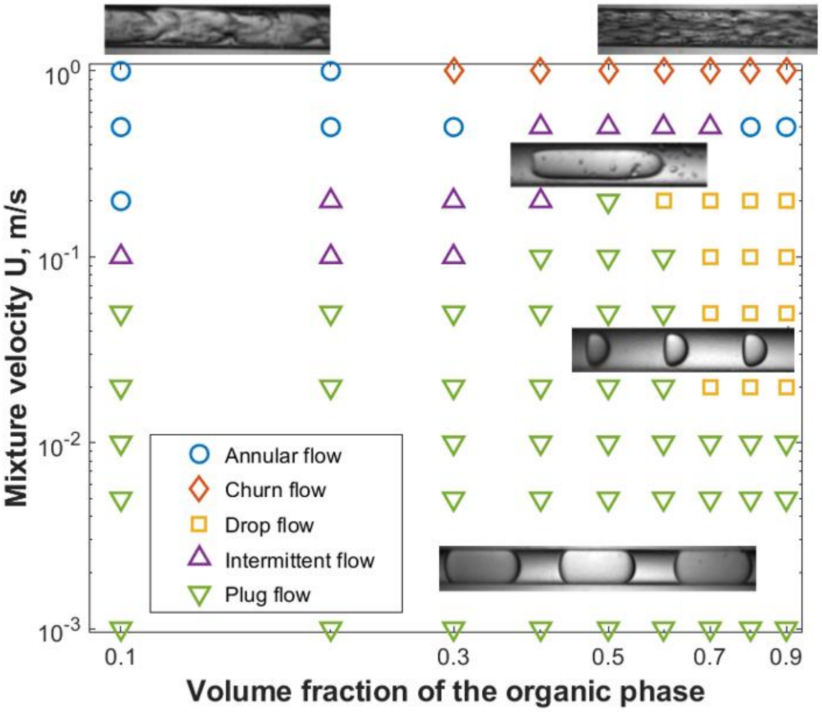

Figure 7. Flow patterns in the small channel. Mixture velocity is defined as $U = (Q_w + Q_o)/\left[\pi\left(\frac{d}{2}\right)^2\right]$, while volume fraction is defined as $\varphi = Q_o/(Q_w + Q_o)$.

To investigate the effects of residence time without influencing the flow patterns, the mixture velocity was kept constant at 0.01 m/s while the length of the test channels varied from 15 to 75 cm with an interval of 15 cm. The amount of lithium extracted is given in terms of extraction percentage E_p, defined as by:

$$E_p = \frac{C_{aq,0} - C_{aq,t}}{C_{aq,0}} \times 100\% \tag{17}$$

where C_{aq} denotes the lithium concentration in the aqueous phase, and subscripts *0* and *t* represent the initial solution and the solution sampled at residence time *t*, respectively. Extraction efficiency E_e is used to measure how much the substance has been extracted at residence time *t* compared to the equilibrium extraction percentage, and is defined as

$$E_e = \frac{C_{aq,0} - C_{aq,t}}{C_{aq,0} - C_{aq,eq}} \times 100\% \tag{18}$$

The results of E_p and E_e are given in Figure 8. As it can be seen in Figure 8(a), for extractant concentration of 0.5 mol/L the extraction percentage has already reached 15% at residence time of 15 s, regardless of the composition of the organic phase. As a comparison, it takes 10 min to reach ~12.5% extraction percentage in the batch system (Figure 4). In the flow channel, the extraction percentage reaches around 19% within 75 seconds. For the low extractant concentration (0.2 mol/l), the extraction percentage increases to 8% at 45 s, while similar extraction percentage is achieved in about 40 min in the batch vessel. From Figure 8(b) it can be seen that at high extractant concentrations (0.5 mol/L), the extraction efficiency E_e exceeds 60% within 15 s. As the residence time increases further, there is a gradual increase towards 80%. When the extractant concentration is low (0.2 mol/L), the extraction efficiency undergoes a sharp increase at the beginning, reaching about 75% at 45 s, followed by a slight increase afterwards. Comparing with stirred vessels, extractions in microfluidic channels can drastically reduce the residence times to achieve required extraction efficiencies, especially for cases with the pure ionic liquids (i.e., no anisole dilution). No significant influence of diluting IL with anisole is observed in terms of extraction percentage or extraction efficiency.

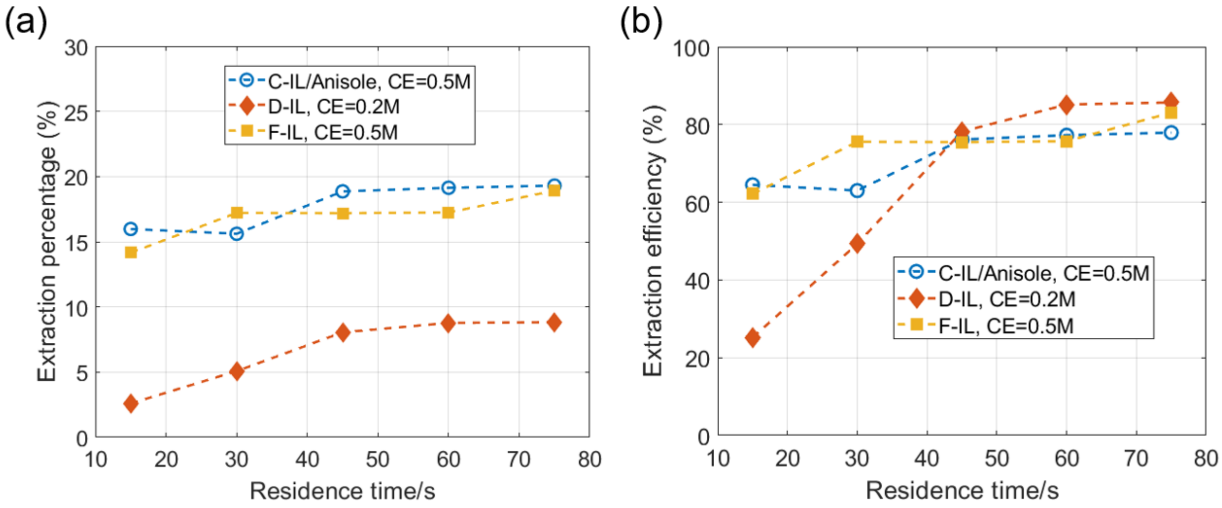

Figure 8. (a) Extraction percentage of lithium ions in microfluidic channels at different residence times. (b) Extraction efficiency of lithium ions in microfluidic channels at different residence times.

The fractionation factors of lithium isotopes during the flow extraction in channels are plotted in Figure 9. As it can be seen, the fractionation factor is 1.032 (±0.005), while the intercept is equal to 11.744, which agrees well the experimentally measured $\delta^7Li_{aq,0}$(12.059). As Figure 8 suggests, equilibrium has not been reached in the small channels as the data points do not reach nearly 100% extraction efficiency before 75s. It seems that for these cases the ‘fractionation factor’ is larger than the one obtained at equilibrium conditions (1.026 ±0.002).

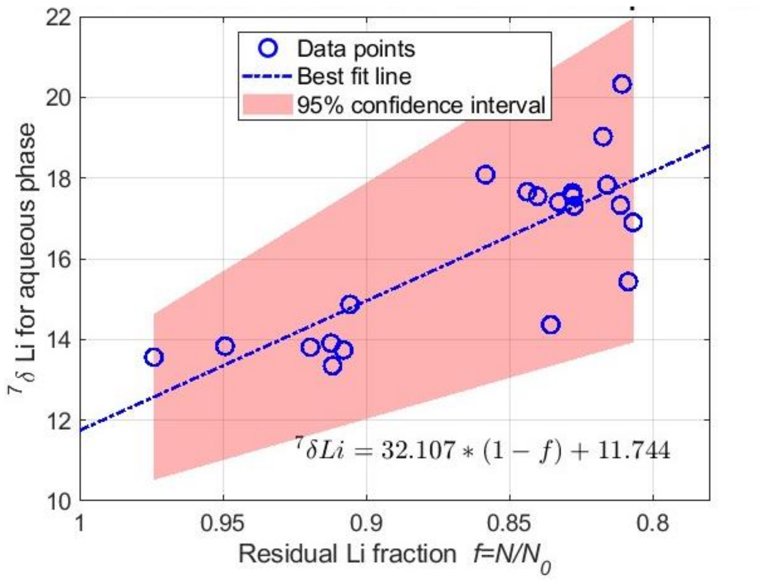

Figure 9. Li isotope separation factor determined in microfluidic channels.

Here, a parameter called apparent fractionation factor $\tilde{\alpha}$ is introduced to quantify the instantaneous difference of the delta lithium-7 values in the two phases, which is defined as

$$\tilde{\alpha} = \frac{\left({}^{7}Li/{}^{6}Li\right)_{aq}}{\left({}^{7}Li/{}^{6}Li\right)_{org}} \tag{19}$$

Results for $\tilde{\alpha}$, plotted in Figure 10 against the residence time in the channel, show that in all cases studied the apparent fractionation factor is higher than α at equilibrium for residence times between 15s and 30s. As residence time increases, the apparent fractionation factor gradually converges around the equilibrium value. It seems that lithium-6 is transported more rapidly from the aqueous to the organic phase especially at the beginning, yielding $\tilde{\alpha}$ larger than the equilibrium value. These results strongly encourage the consideration of kinetic isotopic fractionation in small channel contactors. When measuring the isotopic diffusion in solids (such as ore) and water, researchers have found that the difference in diffusion coefficients of the isotopes depends on the isotope atomic masses and can empirically be described by the following equation:

$$\frac{D_{^6Li}}{D_{^7Li}} = \left(\frac{m_{^7Li}}{m_{^6Li}}\right)^{\beta} \qquad (20)$$

where β represents a parameter that can be experimentally determined for different media. By measuring the arrested diffusion of lithium, it was documented that lithium-6 diffuses up to 3% faster than lithium-7 in both silicate melt and in water [54]. In small channels diffusion is a primary mechanism governing mass transport. This difference in diffusion rates could explain the high apparent fractionation factor at low residence times. By considering the results in both Figures 8 and 10, it can be seen that there is a trade-off between the amount of lithium extracted and the degree of lithium enrichment in the flow separators. Larger residence times result in larger amount of lithium extracted into the organic phase, while the degree of partition/fractionation decreases.

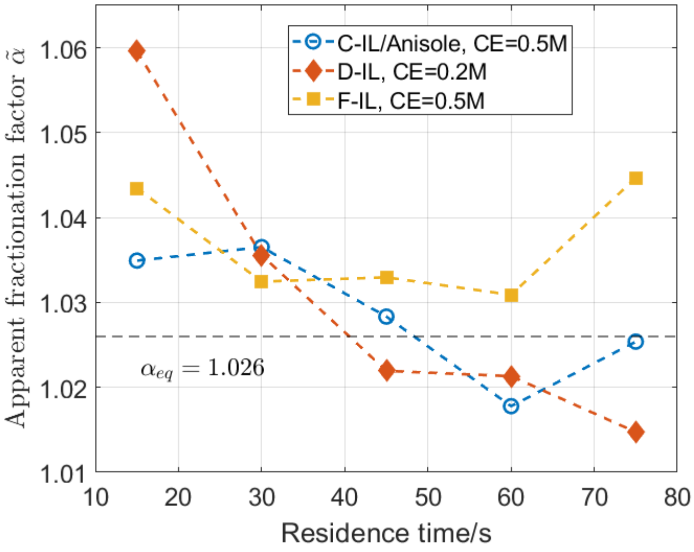

Figure 10. (a) Apparent fractionation factor α̃ at different residence times *t* in microfluidic reactors. (b) extraction efficiency over residence times in microfluidic reactors. The dotted horizontal line represents the fractionation factor at equilibrium state.

4. CONCLUSIONS

The study explored the separation of lithium isotopes using liquid-liquid extraction, where the organic phase comprised either ionic liquid (1-butyl-3-methylimidazolium bis (trifluoromethyl sulfonyl) imide([C4mim][NTf2])) alone or combined with anisole, with Benzo-15-Crown-5 included as the extractant. Experiments were carried out in stirred vessels and in small channels. Extractant concentrations of 0.2, 0.4, and 0.5 mol/L were used while the initial LiCl concentrations in the aqueous phase was 0.5mol/L. In the equilibrium experiments in the vessels, it was found that the extraction percentage increased with extractant concentration, and a maximum of about 23% lithium in the organic phase was reached for extractant concentration of 0.5 mol/L. Diluting the ionic liquid with anisole did not change the extraction percentage at equilibrium, but it decreased the time required to reach the equilibrium concentration. The fractionation factor was found to be α = 1.026 (±0.002), which agrees well with previous studies for this system and other similar systems in stirred vessels.

Calculations with Density Functional Theory (DFT) suggested that lithium isotopes are separated due to different vibrational frequencies of Li-O bond in crown ether (350 cm^{-1}) and in water (520 cm^{-1}). Both the experimental results and the DFT calculations support the mechanism that the extractant forms a one-to-one complex with lithium ions in the organic phase during extraction. In addition, it was found that the ionic liquid helps the isotope fractionation, while its dilution with anisole does not significantly affect it. The dilution with anisole, however, reduces the viscosity of the diluent and the usage of the ionic liquid.

For the continuous extractions in the flow channels, flowrates that resulted in plug flow were chosen (0.01 m/s). The extraction efficiency reached about 80% within 1 min, which is significantly reduced from the hours required in the stirred vessel experiments. An apparent fractionation factor of 1.032 (±0.005) was found which is higher than that in stirred vessels, due to enhanced diffusion of the lithium-6 isotope. With an increase in residence time in the microfluidic channels, the apparent fractionation factors were found to decrease and converge around the equilibrium values. This suggests that small channels could enhance lithium-6 enrichment compared to stirred vessel separators by taking advantage of differences in the diffusion of the isotopes.

The results show that the separation of lithium by solvent extraction in small channels is significantly faster than in batch systems. In addition, the apparent fractionation of the lithium isotopes at very short times in the small channels is larger than the equilibrium one, which is advantageous for enrichment. Further studies can explore the trade-off between the extraction percentage and the fractionation of the isotopes as well as the scale up of the small channel contactors.

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Author CRediT statement

Cong Duan: Methodology, Formal analysis, Investigation, Writing – Original Draft. **Haoyu Wang:** Conceptualization, Validation, Investigation. **Shijia Sun:** DFT modelling. **Mohd Tarique:** Investigation. **Edward Tipper:** Resources, Investigation, Methodology. **Tamsin Whitfield:** Conceptualization, Supervision, Writing - Review & Editing. **Mark Gilbert:** Conceptualization, Funding acquisition, Supervision, Writing - Review & Editing. **Panagiota Angeli:** Conceptualization, Funding acquisition, Supervision, Project administration, Writing - Review & Editing.

Conflict of interest declaration

The authors have no conflicts of interest to declare. All co-authors have seen and agree with the contents of the manuscript and there is no financial interest to report. We certify that the submission is original work and is not under review at any other publication.

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