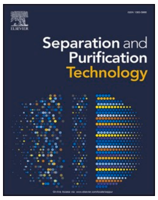
Separation and Purification Technology 389 (2026) 136835

Contents lists available at ScienceDirect

Separation and Purification Technology

journal homepage: www.elsevier.com/locate/seppur



Short communication

Investigations into a ternary liquid-liquid-solid extraction system for partitioning of lithium, with a view to potential isotopic enrichment applications

Thomas J. Robshaw [a,*], Magali Goncalves Rego [b], Stephen Reid [c], Alastair Baker [a], Timothy Hunter [a], Kathryn George [b]

[a] *School of Chemical and Process Engineering, University of Leeds, Leeds LS2 9JT, United Kingdom*
[b] *Department of Chemical Engineering, University of Manchester, Manchester M13 9PL, United Kingdom*
[c] *School of Earth & Environment, University of Leeds, Leeds LS2 9JT, United Kingdom*

ARTICLE INFO

Editor name: M Freire

Keywords:
Fusion
Lithium
Isotopic enrichment
Solvent extraction
Ion-exchange
Crown ether
Organosilica

ABSTRACT

The fractionation of lithium isotopes is of great importance to the nuclear industry. Solvent extraction (SX) methods using benzo-15-crown-5 ether (B15C5) are one of the more mature and easily scalable technologies to achieve this. However, the isotopic enrichment (α) possible for SX has not been significantly improved for >40 years. Here, we present an investigation into a novel three-phase (liquid-liquid-solid) system, combining B15C5, dissolved in an imidazolium ionic liquid, with two organosilicas with ethyl/butyl phosphonic acid (EBPsil) and sulfonic acid (SULFsil) functional groups. The aqueous Li mass transfer was investigated, initially in two-phase systems, which suggested that Li was favourably extracted as complexes involving two of the extracting ligands. The B15C5 organic phase produced the highest distribution coefficient (K_D), followed by SULFsil. In three-phase experiments, it was found that increasing the effective ligand concentration in either the liquid or solid phase increased Li transfer into that phase, but not at the expense of transfer into the other non-aqueous phase. Li extraction could not be well controlled by initial aqueous pH, due to buffering by contact with the ionic liquid in the organic phase. The addition of Mg^{2+} as a competing ion was strongly suppressive for solid-phase adsorption, but not SX. A maximum α of 1.035 ± 0.004 was achieved for ^{6}Li enrichment in the organic phase, at a Li/B15C5 ether molar ratio of ~2.5. Surprisingly, increasing the organosilica mass in the system appeared to enhance the α value for the organic phase, which is contrary to almost every other study involving Li isotope fractionation via cation-exchange. This result was believed to be due to the hydrophilicity of the silica-based matrix and suggests that a pathway is possible to significant improvement in isotope fractionation efficiency, using a three-phase methodology.

1. Introduction

Elemental lithium naturally occurs as two stable isotopes: lithium-6 (^{6}Li) at a natural abundance of 7.5% and lithium-7 (^{7}Li) at an abundance of 92.5%. There is substantial interest across the nuclear industry in separation and enrichment of lithium isotopes. In fission plants, ^{7}Li, at 99.95% enrichment, finds a use in pressurised water reactors (PWRs) as a coolant pH modifier (at ~2 mg L^{-1}), preventing corrosion [1]. It is also projected to be important in next-generation molten salt reactors (MSRs), as certain designs utilise LiF as the principal salt component [2]. In both cases, the attractive feature of ^{7}Li is its low neutron absorption cross-section.

On the other hand, ^{6}Li is of seminal importance to developing fusion technology. While having no direct role in the fusion reaction, ^{6}Li is used to establish tritium breeder blankets, by reaction with slow neutrons, in the reaction: $^6Li + {}^1n_{slow} \rightarrow {}^4He + {}^3T$ (+ 4.8 MeV). Technical estimates on the actual ^{6}Li enrichment necessary for this purpose vary between 30 and 90%. However, all sources agree that a process for procuring ^{6}Li, at tonne scale, is urgently required within the next 15 years [3]. Currently, there is no large-scale provision for this need in Europe.

Elsewhere in the world, lithium isotopic separation is achieved by the COLEX (COLumn EXchange) process, used at the Oak Ridge Y-12

---

* Corresponding author.
E-mail address: t.j.robshaw@leeds.ac.uk (T.J. Robshaw).

https://doi.org/10.1016/j.seppur.2026.136835
Received 28 October 2025; Received in revised form 6 January 2026; Accepted 7 January 2026

National Security Complex in the US on an industrial scale in the 1950s and 1960s [4]. COLEX is based on contacting an aqueous LiOH phase with liquid Hg amalgam, and because of historical environmental releases and extreme toxicity of Hg to health and environment, the methodology is not considered feasible to implement in many countries [5].

An economically viable chemical lithium isotope splitting process requires relatively high values for both the distribution coefficient (K_D, Eq. 1) and more importantly, the isotopic enrichment factor (α, Eq. 2):

$$K_D = \frac{[Li_{(solv)}]}{[Li_{(aq)}]} \tag{1}$$

$$\alpha = \frac{[6Li_{(solv)}]/[7Li_{(solv)}]}{[6Li_{(aq)}]/[7Li_{(aq)}]} \tag{2}$$

$[Li_{(solv)}]$ is the Li concentration in the non-aqueous phase at equilibrium (mg L^{-1}, or M) after the forward-extraction and *$[Li_{(aq)}]$* the equilibrium Li concentration in the residual aqueous phase (mg L^{-1}, or M) after the forward-extraction. *$[^6Li_{(solv)}]$* refers specifically to the ^{6}Li concentration in the non-aqueous phase and so on for the similar terms in Eq. 2. The equations are equally applicable to liquid-liquid and liquid-solid separation processes. The α parameter for the COLEX process has been quoted as ~1.020–1.050 across literature sources [6]. More recently, new approaches have been developed, to attempt comparable separation in a more safe and sustainable manner. These have included electrochemical insertion [7], electromigration [8], direct centrifugation of aqueous solutions [9] and selective bioaccumulation of ^{6}Li by algae [10]. Nonetheless, for confidence in scalability, the chemical separation processes of adsorption and solvent-extraction are popular choices, as they have both been widely demonstrated industrially for hydrometallurgical applications and specifically for the reprocessing of spent fission fuel rods [11] (albeit not yet for the purpose of Li isotope separation).

For conventional (non-isotopic) Li hydrometallurgy, the most common extracting ligands are β-diketones and phosphines [12]. However, they are not isotopically selective. The only extractants to exhibit such selectivity so far have been crown ethers and cryptands. The selectivity of 12-crown-4 (12C4), 15-crown-5 (15C5), 18-crown-6 (18C6) and cryptand 2B, 2, 1 systems for ^{6}Li was first studied in the 1980s by Nishizawa and co-workers [13–16]. However, only the crown ethers have merited sustained investigations, likely because of more facile synthesis and greater availability. The highest α value ever reported for such systems was by Nishizawa in 1988 for solvent-extraction via 12C4 in chloroform (1.057). Nonetheless, this achievement is of questionable real-world value, as it was recorded at 0 °C, accompanied by an extremely low K_D value of 2×10^{-5} and used a partially water-soluble crown ether. In later years, benzo-15-crown-5 ether (B15C5) has become preferred, offering slightly poorer α, but superior K_D and the addition of the aromatic moiety improves organic phase solubility [5,17].

The addition of imidazolium-based ionic liquids (ILs) to the organic phase has also been widely investigated more recently, especially those of the general formula $[C_nmim][NTf_2]$ ($n = 4$–12), with n indicating the number of carbons on the imidazolium sidechain. ILs boost the overall Li extraction by ionising the organic phase, while maintaining hydrophobicity. It has been shown that the extraction mechanism is cation-exchange between Li^+ and Imidazolium$^+$. This results in a neutral organic phase complex of, Li^+, the crown ether ring and the IL anion, which is a more favourable ion-pairing in the organic phase than Li^+, crown ether and the anion from the aqueous phase Li salt [18]. Despite this, IL-based organic phases often (though not always) decrease the crown ether selectivity for ^{6}Li versus the classical halogenated solvents first used (examples in Supplementary Information (SI), Table S1 [5,16–20].

Authors have also shown that the choice of counter-anion in the aqueous Li salt is also a meaningful parameter, with larger, more hydrophobic cations, such as iodide and bis(trifluoromethane)sulfonamide, producing more favourable mass transfer of the Li/crown ether$^+$ cations to the organic phase than harder bases, such as nitrate and chloride [13,19]. Since ^{6}Li is a more hydrophobic cation than ^{7}Li, the effect is more pronounced and can produce increased isotopic selectivity in the organic phase [21]. Zhang and co-workers showed that matching the anion of the Li salt to that of the organic-phase ionic liquid (NTf_2) produced more favourable extraction than other anions and may also serve to simplify downstream processes (recovery of the ionic liquid) [21]. Again, see Table S1.

It is also a known strategy to immobilise crown ethers onto a solid-phase, creating a ^{6}Li-selective adsorption system. This has been achieved with a solid matrix of silica, with α values of 1.013–1.046 [22,23]. Organic polymeric supports have also been trialled with crown ethers grafted onto polysulfone ($\alpha = 1.031$) [24] and biopolymers such as chitosan ($\alpha = 1.036$) [25]. Nonetheless, liquid-solid systems perform optimally at rather low flow-rates [6], which currently restricts their real-world applicability. Clearly overall, neither liquid-liquid, nor liquid-solid crown ether systems currently offer the step-change in process efficiency necessary for universal acceptance over COLEX type methods.

A potential strategy is to combine three different phases (liquid-liquid-solid) in a single contact stage, with one non-aqueous phase being ^{6}Li-selective and the other being ^{7}Li-selective, the objective being enhancing the α value above what is currently feasible for two-phase models. This would offer a potentially huge reduction of the carbon footprint of the isotopic enrichment plant, as fewer contact stages would be required to reach the desired ^{6}Li enrichment ratio. Furthermore, the engineering options to allow implementation at scales beyond laboratory are already available, in the form of centrifugal tricanters, which can simultaneously separate two liquid and one solid phase. Nonetheless, this strategy is a difficult undertaking, as there are very few chemical species known to be selective for ^{7}Li isotopes. A rare exception is a ruthenium based 12-metallocrown-3 complex, which was shown by Severin and co-workers to preferentially coordinate the more massive ^{7}Li ion by sterically hindered access to the binding site [26]. Before such a process can be designed, it is necessary to fundamentally investigate the particulars of Li mass-transfer in a liquid-liquid-solid system.

This paper therefore presents what is believed to be the first attempt at studying lithium partitioning behaviour in a three-phase system. We chose a popular solvent phase of B15C5 ether and a commercially available ionic liquid 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ($[BMIm][NTf_2]$), also using anisole as a diluent to reduce viscosity and facilitate pumping [20,27]. For the solid phase, organosilicas were an attractive choice, as they feature a small, yet consistent particle size, which is important for efficient column packing (though no hydrodynamic experiments would be attempted at this stage) and to minimise the mass-transfer resistance reported in Li isotope separation by column systems [28]. They are also commercially available, with a consistent functional group concentration, improving the repeatability of data. The results reported herein, we believe, are of significant relevance to the field of Li isotopic separation.

2. Materials and methods

2.1. Chemical reagents

All reagents used were commercially available from UK vendors and were employed without further purification. Anisole (≥99%) and hydrochloric acid (J.T. Baker grade, 99.99%) were purchased from Fisher Scientific. B15C5 (97%) and $[BMIm][NTf_2]$ (≥98%), were purchased from Selleck Biotechnology. LiCl and $MgCl_2$ (≥99%) were purchased from Flurochem.

Two different organosilicas, in dry, granular form, were supplied by PhosphonicS Ltd. These were ethyl/butyl phosphonic acid silica (EBPsil) and ethyl sulfonic acid silica (SULFsil). The former has been noted by the manufacturer to exhibit high selectivity for Li^+ ions in mixed-metal solutions for hydrometallurgical applications, while the latter is a more general-purpose functionality for a wide range of ion-exchange applications. The different components of the extraction systems are shown in Fig. 1.

Unlike most adsorption studies, we did not use an equivalent mass of adsorbent across compared experiments. Rather, the masses of each silica were chosen so that the effective functional group concentration was equivalent. This allowed a direct assessment of the relative affinities of the phosphonic acid and sulfonic acid groups for aqueous Li. The manufacturer-quoted functional group concentrations for the EBPsil and SULFsil, as received, were 1.14 and 0.95 mmol g^{-1} respectively.

2.2. Li partitioning experiments

An initial aqueous phase was made up by dissolving LiCl in the required volume of deionised water. Adjustments to initial pH, as required, were achieved by addition of HCl or NaOH (0.0001–0.1 M), but pH was not controlled during the phase contact. Likewise, the organic phase was made up by dissolution of a certain mass of B15C5 in a co-solvent of [BMIm][NTf_2] and anisole (1:9 *v*/v ratio). In most cases (unless varying the [B15C5] or quantity of solid-phase functional groups was the subject of the experiment), the [B15C5] was chosen so that the number of mmol B15C5 in the system matched the number of mmol of phosphonic acid or sulfonic acid ligand in the solid phase. The initial Li and B15C5 concentrations were chosen to allow accurate quantification of the mass of Li transferred between phases and it is accepted that these would not be representative of an isotopic enrichment plant.

All experiments were performed in duplicate. The two liquid phases were added to 50 mL polypropylene tubes, containing a pre-weighed mass of the organosilica. The three-phase system was equilibrated for 60 min, at 850 rpm, using an Eppendorf SE ThermoMixer® C with Smartblock™ Thermoblock accessory, set at 25 °C unless otherwise stated. Li partitioning in crown ether systems is generally acknowledged to be very rapid to reach equilibrium (seconds, rather than minutes) [13] Therefore the kinetics of Li adsorption via the organosilicas was the limiting factor in the experimental timeframe. From studies on ion-adsorption by similar materials [29] these systems are known to reach >95% equilibrium within 60 min.

The two liquid phases were allowed to disengage (~20 min), after which the upper (aqueous) phase was removed by pipette and an aliquot of the organic phase was back-extracted, to transfer the organic Li back into an aqueous phase for analysis, achieved by contact of 1.00 mL Li-loaded organic phase with 20.0 mL 0.5 M HCl and otherwise followed the same technique as the forward extraction. It was ascertained by a repeat of the process that all organic Li was back-extracted successfully in this way.

The barren aqueous phase and back-extracted organic phase could then be analysed for overall Li concentration. The back-extracted organic phase after certain experiments was also analysed for the Li6/7 isotopic ratio to determine the extent of ^{6}Li enrichment that occurred. The overall partitioning of Li between the phases in three-phase experiments was worked out by mass-balancing:

$$Li_{ads} = Li_{aq,initial} - Li_{aq,equilib} - Li_{org} \tag{3}$$

where Li_{ads} is the equilibrium Li mass in the solid phase, $Li_{aq,\ initial}$ is the initial mass in the aqueous phase, $Li_{aq,\ equilib}$ the mass in the aqueous phase after equilibration and Li_{org} the equilibrium mass in the organic phase. K_D and α were calculated as per Eqs. 1 and 2. Uncertainty values were calculated from an approximation of the 95% confidence interval (2 x standard deviation) and propagated as necessary.

2.3. Quantification of total li mass transfer and Li6/7 isotopic ratio

Quantification of the total Li concentration in aqueous samples was performed using flame atomic absorption spectroscopy (AAS). Li isotopic ratio of aqueous samples was achieved using inductively coupled plasma mass spectrometry, using a certified reference material and a specific mode of analysis, to mitigate mass bias effects. Full methods and ICP-MS method development are found in the SI, p2).

It must be noted that data treatment for three-phase experiments used a modified version of Eq. 2 (Eq. 4):

$$\alpha = \frac{\left[6Li_{(solv)}\right] / \left[7Li_{(solv)}\right]}{\left[6Li_{(res)}\right] / \left[7Li_{(res)}\right]} \tag{4}$$

where $[^6Li_{(res)}]$ and $[^7Li_{(res)}]$ refer to the respective residual (non-solvent phase) isotopic concentrations (mg L^{-1}), which are cumulative values, taking into account both the aqueous and solid phases (i.e. the actual individual isotopic ratios of the aqueous and solid phases are not determined from this equation).

2.4. Modelling of Li adsorption data

The focus of this work was investigations of the three-phase system. However, Li uptake has not been reported previously for these two specific organosilicas. Therefore, it was of interest to produce fundamental isotherm data for two-phase liquid-solid systems. These data were fitted to isotherm models introduced and described in the SI, p5. [30–33] Non-linear least squares fitting was used, employing the Microsoft SOLVER data analysis tool. Uncertainty values were calculated using the Microsoft Solvstat add-in [34].

3. Results and discussion

3.1. Two-phase experiments

Two-phase (liquid-liquid and liquid-solid) systems were assessed, with varying initial concentrations of Li and an equal number of mmol ligand/functional group (Fig. 2). All three systems showed a gradual and approximately linear increase in Li removal from the aqueous phase, corresponding to increasing initial Li concentration, with the crown ether-based liquid-liquid system showing greater affinity for Li than the two silicas (Fig. 2a) and adsorption for SULFsil seemingly approaching monolayer saturation (Fig. 2b-d). The seeming greater affinity of the

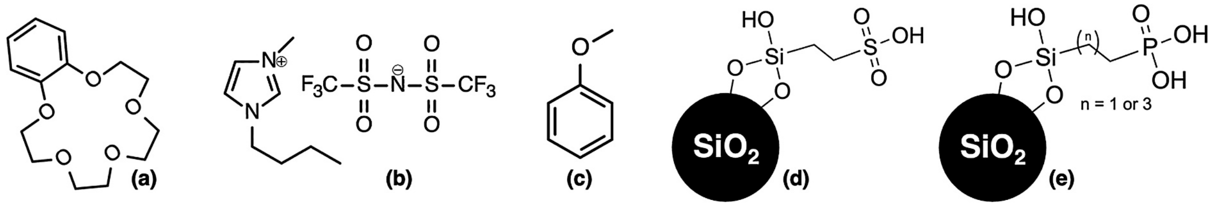


Fig. 1. The molecules and functionalised adsorbents used to conduct the reported Li separation experiments. (a) Benzo-15-crown-5 ether (the extracting ligand in the organic phase). (b) 1-Butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ionic liquid (the organic phase modifier to increase bulk Li extraction). (c) Anisole (the organic phase diluent). (d) Ethyl sulfonic acid-functionalised silica. (e) Ethyl/butyl phosphonic acid-functionalised silica.

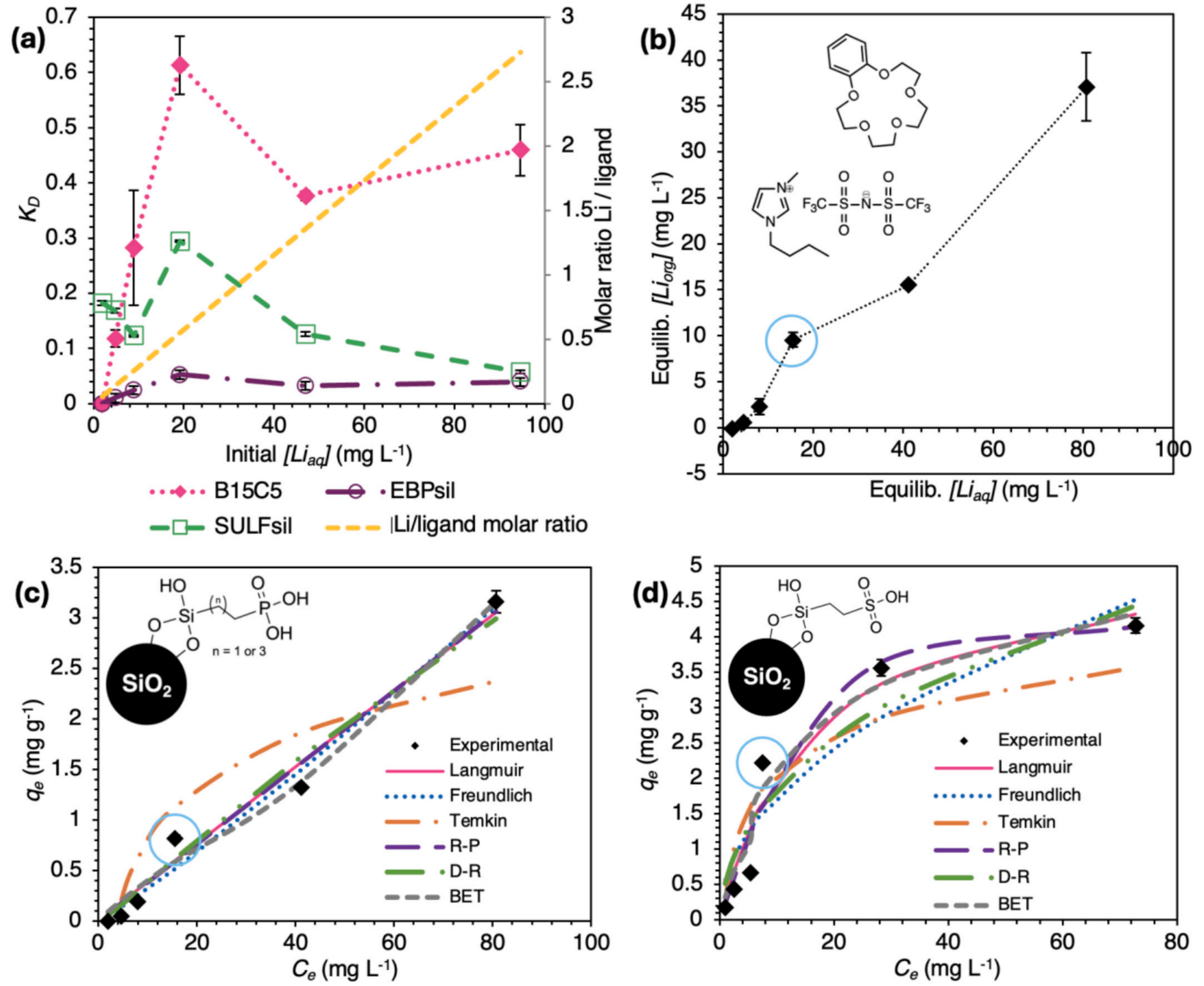


Fig. 2. Mass transfer of Li in two-phase systems. (a) Variation of Li distribution coefficient with initial [Li] for all systems. (b) Variation of Li distribution between aqueous and organic phases with increasing initial Li (20 mL aqueous phase, 7.5 mL organic phase [B15C5] = 13.3 mmol L^{-1}). (c) Li loading isotherm and model-fitting for EBPsil (20 mL aqueous phase, silica mass = 88 ± 1 mg). (d) Li loading isotherm and model-fitting for SULFsil (20 mL aqueous phase, silica mass = 105 ± 1 mg). In (b-d), datapoints where the initial Li/ligand molar ratio was 0.5 are circled in blue.

crown ether for Li can be ascribed mainly to the ionic liquid in the organic phase, which has been shown to increase the K_D value of the extraction by orders of magnitude (Table S1). An interesting feature of the data for all systems is a significant spike in the K_D value at the point where the initial aqueous Li concentration is approximately half that of the ligand concentration, indicating a favourable binding interaction (most obvious in Fig. 2a). It is well-known that Li^+ ions form stable "sandwich complexes", where the ion coordinates simultaneously to two crown ether rings [35]. The favourability of sandwich complex formation is somewhat complex and influenced by choice of solvent and Li salt anion [36]. However, Xiao et al. [27] found evidence that such complexes are preferentially formed in a B15C5/IL system, even when the ligand concentration remains below that of Li [27]. We were not able to find any literature examples of instances where Li extraction is specifically boosted at a crown ether: Li ratio of 2:1. This is because the majority of other researchers have not presented data over a full range of crown ether:Li ratios, but rather choose to keep either the crown ether or Li concentration much higher than the other component across the experimental range [18,37,38].

It appears that in liquid-solid systems, the most stable complexes formed are also between Li^+ ions and two adjacent functional groups. This behaviour frequently occurs in ion-exchange media [29,39], though is not always observable from isotherm data.

Because of the suspected 2:1 ligand:Li^+ binding behaviour, none of the six isotherm models employed provided an excellent description of the solid-phase uptake data (Fig. 2c&d, Table S4). For both silicas, the Brunauer–Emmett–Teller (BET) model provided the best R^2 value (EBPsil = 0.985, SULFsil = 0.961). However, this is likely a result of the anomalous datapoints previously mentioned where the Li/ligand molar ratio is ~0.5. This gives the isotherms, particularly for EBPsil (Fig. 2c), the superficial appearance of adsorption proceeding in discrete monolayers. If we discount these anomalous datapoints, It can be seen that the adsorption of Li by EBPsil produces an almost linear isotherm, implying weak physisorption, whereas SULFsil produces a parabolic isotherm more suggestive of chemisorption. This is shown by the Freundlich R^2 values (EBPsil = 0.981, SULFsil = 0.857) and the Dubinin-Radushkevich (D-R) desorption energies (EBPsil = 7.25 kJ mol^{-1}, SULFsil = 10.9 kJ mol^{-1}). In fact, the affinity of SULFsil for Li is rather better than might be predicted, as there are literature reports of Li uptake by sulfonic acid strong acid cation ion-exchange resins, where the affinity is very low and a Freundlich type isotherm is produced [40]. However, in this example, the resin was in its Na^+ form (sullfonic acid resins having higher affinity for Na^+ than Li^+) [41], whereas the silicas were supplied in free-base form, which would make for more favourable adsorption. The sulfonic acid group in general is a strong acid cation and this belies its use in non-selective water deionisation applications. Phosphonic acid is a weak acid, chelating functionality and is likely better suited to multivalent cations that can coordinate via two oxygen atoms. This may explain the isotherms observed in this case. However, an aminomethylphosphonic acid polymeric resin was seen to uptake Li strongly, following a Langmuir isotherm [42]. Previous work has suggested that the chemistry of the adsorbent matrix is strongly influential to the performance of a specific functional group [43] and this will be discussed with respect to isotopic enrichment data.

3.2. Three-phase experiments

Several parameters were selected for investigation in three-phase experiments, to probe their effects on the overall Li partitioning. A full dataset is shown in the SI, p8–12. The clearest changes to Li partitioning behaviour were effected by either changing crown ether concentration, or silica mass, akin to changing the sulfonic acid or phosphonic acid concentration (Fig. 3). An interesting feature of the data is that increasing the effective ligand concentration in either the solid or organic phase produced a higher equilibrium Li concentration in this phase (as would be expected). However, it did *not* significantly reduce the Li concentration in the other non-aqueous phase, i.e. the two different Li extraction processes are non-competitive. In the case of changing [B15C5] (Figs. 3a&b), the likely explanation is simply that the overall extraction into organic phase remains quite low, reaching only 14.7% (Table S5). The effect on the concentration gradient is probably just too subtle to be seen in the solid-phase adsorption data. This is likely because the silica isotherm data clearly show that the adsorption is relatively weak and not irreversible. For example, the calculated Langmuir R_L values (Table S4a) are all >0.7.

Previous literature has illustrated that the kinetics of Li mass-transfer into a B15C5-containing organic phase are very rapid, reaching equilibrium in <10 s [13], whereas ion-exchange of metal ions by these organosilicas takes >1 h [29] This may explain why the extraction into the organic phase remains constant, even with large masses of silicas (Figs. 3c&d).

This has implications for design of a potential Li isotope fractionation plant: ligands with low overall Li affinity, but high isotopic selectivity (such as 12-crown-4 ether [16]) could become more favoured, if one can increase their concentration significantly, without greatly affecting Li mass-transfer into the other non-aqueous phase.

Increasing the mass of SULFsil in the system had a far greater effect than for EBPsil (Figs. 3c&d). This can essentially be attributed to the

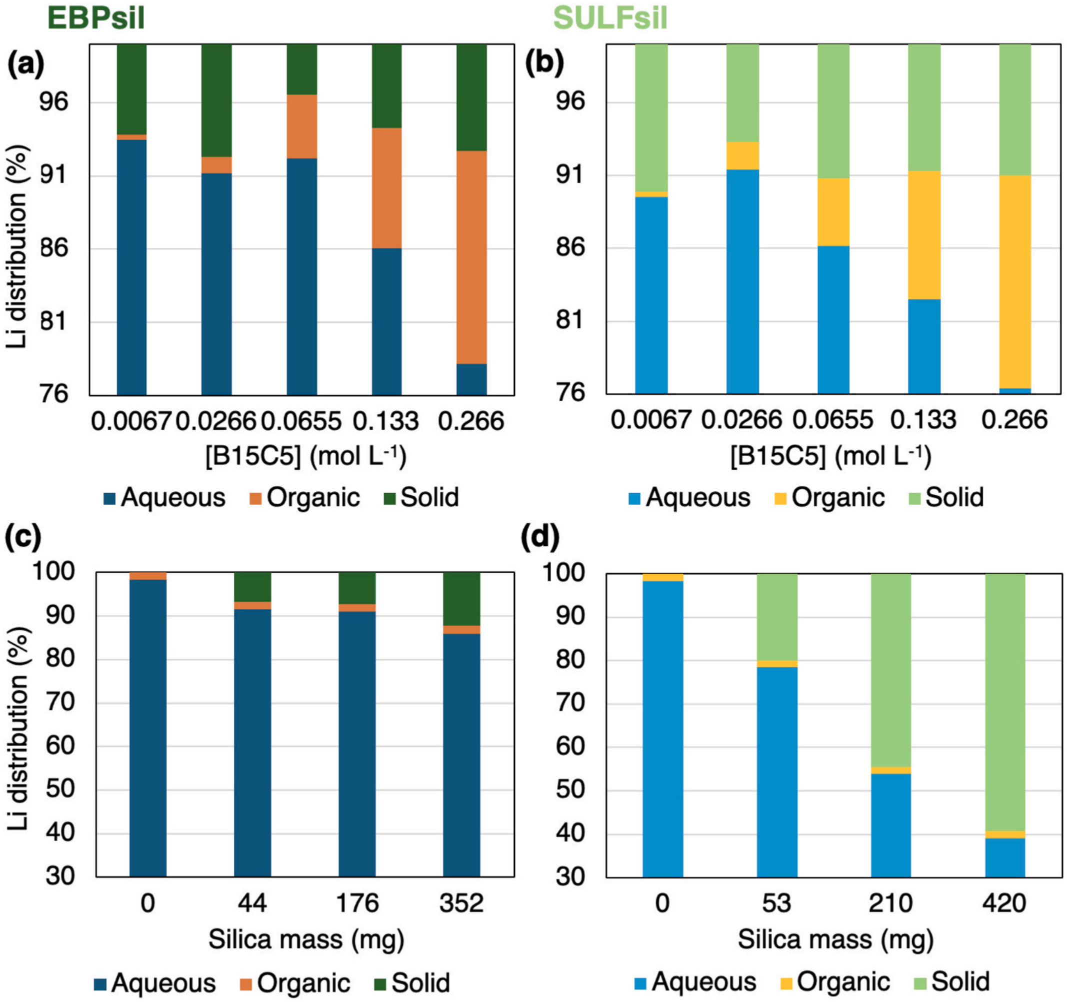


Fig. 3. Li partitioning behaviour in three-phase systems, expressed as overall distribution percentages between the phases. (a) Effect of [B15C5] variation with EBPsil solid phase. (b) Effect of [B15C5] variation with SULFsil solid phase (Initial [Li] = 1000 mg L^{-1}). (c) Effect of silica mass variation with EBPsil solid phase. (d) Effect of silica mass variation with SULFsil solid phase (Initial [Li] = 50 mg L^{-1}).

same characteristics as given in the discussion on two-phase liquid-solid experiments).

Other three-phase system parameters investigated included the organic phase volume, pH, temperature and the addition of a secondary ion (Mg^{2+}), which has a similar hydrated ionic radius to Li^+ and is a potential competitor for binding sites in extraction processes [44].

Increasing organic phase volume (Fig. S1), unlike increasing [B15C5], did adversely affect Li mass-transfer onto the solid phase. This is explainable because aqueous Li^+ ions are strongly solvated and the desolvation energy required for adsorption is considerable [45]. Therefore, the degree of hydrophobicity of the adsorbent particle film layer will be influential. Merely increasing the [B15C5] in the organic phase will not greatly affect the composition of the film layer, but increasing the organic phase volume would likely impact the desolvation energy, because a greater proportion of organic phase is in contact with the adsorbent particle surface, under rapid mixing. A related phenomenon has been observed in two-phase systems where increasing the hydrophobicity of the aqueous phase by DMSO addition improves mass transfer [16].

Variation of initial pH of the aqueous Li solution surprisingly had no clear effect on Li partitioning either to the solid or the organic phase (Fig. S2). Upon checking the equilibrium pH of the aqueous phases post-contact, this was likely because the pH was consistently buffered to ~2–2.5, regardless of initial pH (Table S6). We investigated this by checking post-contact pH in two-phase experiments and it was found that contact with the silicas altered pH by only a small amount (changed from 6.1 to ~5.8), whereas contact with the anisole/IL/B15C5 organic phase produced similar acidification to that seen in the three-phase data. It was also noted that acidification occurred when only deionised water was used, as well as LiCl solution. The IL type used here is known to exhibit some weak acidity, as the imide anion is capable of accepting a Lewis base: the closely related 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imide was investigated for acidity by analysis of a 1% aqueous solution, which was found to reach a pH of only 6.5, although other similar ionic liquids were more acidic [46]. The data are of interest because the favourability of Li mass-transfer is sensitive to pH. Protons can compete for ion-exchange sites on almost all acidic functional groups, especially against low-affinity monovalent ions such as Li^+ [41], while the standard methodology for solvent back-extraction essentially involves contact with an acidified aqueous phase [20,35]. In light of these results, it seems that most crown ether/ionic liquid Li extraction systems reported in the literature may be operating sub-optimally, as there is seldom any attempt to control pH [17,38]. Notably, the SULFsil samples reached a lower pH than EBPsil samples (Table S6). This is likely because contact with the organic phase would have acidified the silica functional groups and these protons would then be exchanged for Li^+ ions, releasing protons into the aqueous phase. SULFsil exchanges more Li^+ ions in total (Figs. 2&3), so this effect would be greater.

The results also show that Na^+ ions also had no significant effect on the Li partitioning between the three phases. This is unsurprising because (a) in the case of the organic phase, 15C5-type ethers are selective for Li ions over Na [47] (b) Even in the case of the organosilicas, where the functional group would not be expected to have such selectivity, the concentration of aqueous Na ions at pH 10 would be ~0.1 mmol L^{-1}, whereas the initial Li concentration would be ~144 mmol L^{-1}. Therefore any interference from Na ions would be insignificant. The pH could not be increased further in our experiments, as this would hydrolyse the silicas.

The effect of Mg^{2+} addition to the system was also interesting, as it significantly decreased Li mass-transfer to the solid phase, but not transfer to the organic phase (Fig. S3). Mg^{2+} would be expected to compete strongly with monovalent ions with common strong acid cation functionalities, simply because of greater charge density [41], while the phosphonic acid group has generally good affinity for alkali earth metals [29]. In contrast, the B15C5 ligand retains selectivity for Li^+, despite the very similar radii of the two ions ($Li^+ = 0.68$ Å, $Mg^{2+} = 0.66$ Å). This was not expected, as both computational and experimental data suggest that Mg^{2+} affinity for the family of 15C5 type ethers is greater than Li^+ [48]. It is probable that the seemingly high affinity of the silicas for Mg^{2+} reduces Mg^{2+} competition with Li^+ ions for B15C5 binding. But this cannot be the full explanation, as the Li partitioning to the organic phase was unaffected even at an Mg concentration of 3500 mg L^{-1} (1.44 mmol per sample), whereas only 0.1 mmol of silica ligand was present per sample. Interestingly, it has been proposed that increasing the positive interfacial charge of a hydrophobic phase enhances Li^+ mass-transfer over Mg^{2+} [49], because the more charge-dense ions are more strongly repelled electrostatically. Therefore, the acidic organic phase in this instance may be causing a similar effect. This suggests an alternate use for a three-phase system for applications where the goal is selective separation of Li only from mixed brines, rather than Li isotopic fractionation.

Finally, increasing the temperature of the system produced an easily-observable trend of decreasing the Li extraction to the organic phase, while no clear trend was observed between temperature change and solid-phase adsorption affinity (Fig. S4). The complexing reaction of Li by crown ethers has negative enthalpy and entropy [16] and therefore the free energy would be expected to decrease in magnitude with increasing temperature. Indeed, we produced Arrhenius plots to calculate the thermodynamic variables (Figs. S5&S6). For the system involving EBPsil, ΔH was -10.9 ± 2 kJ mol^{-1} and ΔS was -73.2 ± 7 J mol^{-1}. For SULFsil, ΔH was -10.5 ± 0.3 kJ mol^{-1} and ΔS was -70.9 ± 1 J mol^{-1}. These data suggest that, contrary to the appearance of Figs. 2c&d, the presence of the different silicas do influence the favourability of Li organic phase partitioning (albeit this is not certain, because of the large uncertainties for the EBPsil values). As a general rule for solid-phase adsorption, increasing temperature increases the kinetics of ion-exchange, but decreases equilibrium uptake capacity [50]. In previous work involving EBPsil, we have observed rapid uptake kinetics, with adsorption essentially complete in <1 h [29,51]. Therefore, kinetics should not be a relevant factor for these data. As such, the substantially better performance of both silicas at 70 °C is unexpected and merits further investigation.

3.3. Li6/7 isotopic fractionation

Isotopic analysis was conducted firstly, to confirm that the ^6Li selectivity of the B15C5 organic phase was in line with previous literature reports on this widely-studied system. Secondly, to investigate whether the addition of the solid phase, and accompanying functionalities, affected isotopic fractionation. As a point of comparison, we also collected fractionation data for experiments in which the [B15C5] was varied, as this parameter is well-known to influence the α value. Figs. 4a&b show that the α values attained in these experiments are in good agreement with those previously reported for crown ether/ionic liquid based methods, which are generally ~1.025–1.035 (Table S1). Our maximum value achieved was 1.035 ± 0.004 and the full range of values is shown in Table S7. It is seen that the optimal molar ratio of Li/B15C5 for high α is ~2–5. A ratio below 2 favours the formation of the less ^6Li-selective sandwich complexes [35]. However, a large molar excess of Li, over B15C5 is evidently also detrimental to α, particularly with the SULFsil system. A similar trend was observed by Demin et al. [52] (although using much higher Li and B15C5 concentrations, the molar ratios are not dissimilar) and was essentially put down to non-selective (independent of crown ether complexation) partitioning of Li into the organic phase, due to an increasingly favourable concentration gradient. We conducted an experiment (Fig. S7) using some solvents frequently seen in Li SX investigations, without crown ether addition, which indeed confirmed some Li transferred to the organic phase, with the co-solvent of [BMIm][NTf_2] and anisole. The α values for Figs. 4c&d are rather lower and reflect the lower initial [Li] (50 vs 1000 mg L^{-1}), meaning the Li/B15C5 molar ratio was <2.

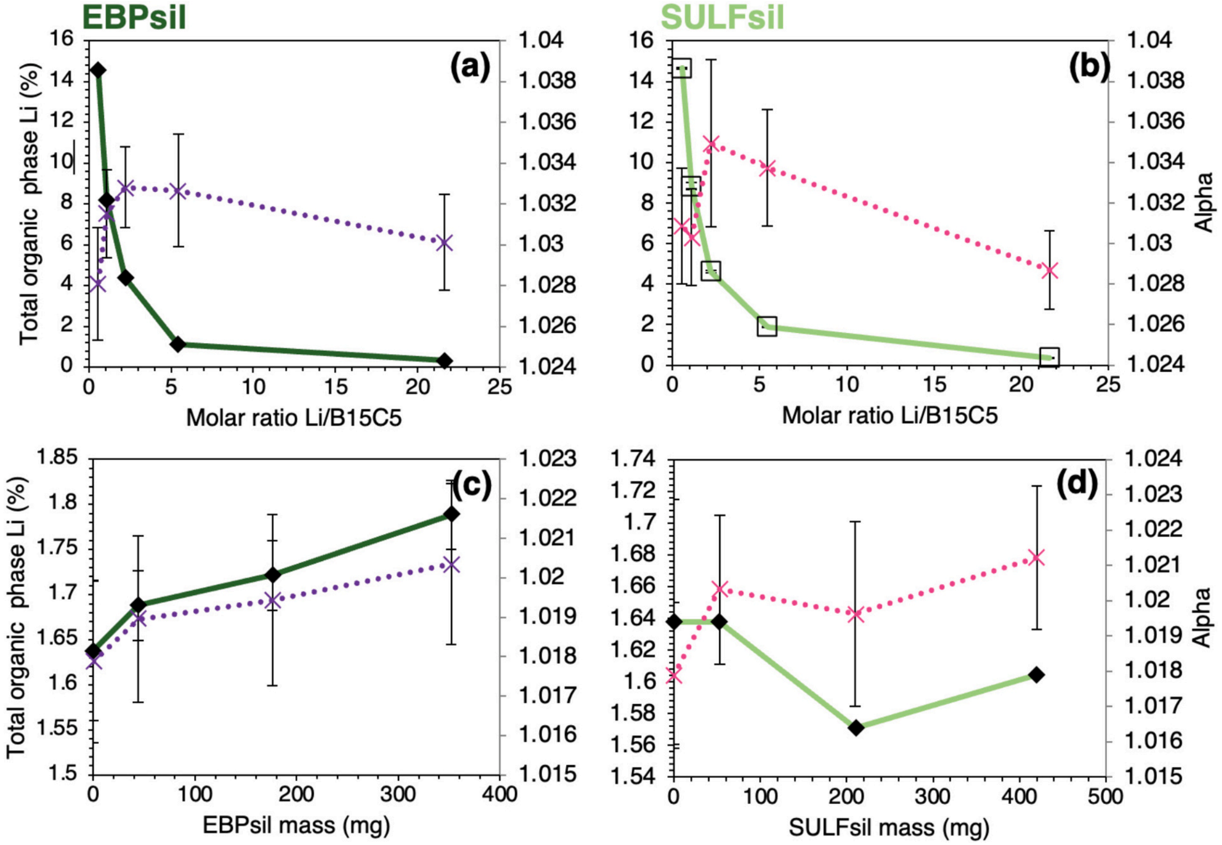


Fig. 4. Li isotopic fractionation data. (a) Effect of changing [B15C5] on both total Li organic phase extraction (diamonds) and enrichment of ^{6}Li in the organic phase (crosses), with EBPsil solid phase. (b) Equivalent data with SULFsil solid phase. (c) Effect of changing solid phase mass on both total Li organic phase extraction (diamonds) and enrichment of ^{6}Li in the organic phase (crosses), with EBPsil solid phase. (d) Equivalent data with SULFsil solid phase. All experimental conditions as per Fig. 3.

A notable feature of these data is that, contrary to expectation, the presence of the two functionalised silicas does in fact impact the α values attained. This can be seen in Figs. 4a&b, where the presence of SULFsil appears to enhance the relationship between increasing Li/B15C5 molar ratio and decreasing α, rather more so than EBPsil (range = 0.0062 vs 0.0047). This distinction is likely due to differing hydrophobicities of the functional groups. The Li isotopic fractionation effect in ion-exchange processes (whether liquid-solid or liquid-liquid) is dependent on differences in solvation energy [45]. Therefore, it follows that the addition of a third phase in constant contact with the two liquid phases could exaggerate or lessen those differences.

Even more remarkably, by increasing the mass of solid phase added, for both silicas, we increased the attained α value by ≤ 0.003; i.e. the silicas exhibited a preference for ^{7}Li uptake and therefore enhanced the isotopic separation observed by analysing the back-extracted organic-phase. This observation is tentative, because of the magnitude of uncertainties in the measured α values. Nonetheless, for EBPsil in particular (Fig. 4c), the trend appears clear.

A thorough review of literature suggests it is very unusual for a solid-phase ion-exchange medium, beyond the 12-metallocrown-3 species previously mentioned [26] to exhibit selectivity for ^{7}Li, whereas studies involving strong acid cation-exchange resins have contrarily found that the materials are ^{6}Li selective [45,53,54]. However, interestingly, a study by Ooi and co-workers [55] investigated ^{6}Li enrichment in a solid-phase, using a titanium phosphate as the active group. When this functionality was embedded in an organic matrix (PVC), the isotopic selectivity for ^{6}Li was significant, but when embedded in an inorganic matrix, the fractionation was not measurable [55]. Furthermore, it was observed that in styrene-based resins, increasing the degree of cross-linking (hydrophobicity) increased the preference of the resin for ^{6}Li [53]. ^{6}Li has the greater hydrated ionic radius. Therefore, its charge density is slightly lower and it is, by nature, more hydrophobic. In the two-phase systems reported in the literature, the organic matrix of the ion-exchange resin solid-phase would, of course, be the more hydrophobic phase and more attractive to ^{6}Li ions. However, in our experimental systems, the ionic lattice of the silica, particularly with the presence of acidic functional groups, not to mention surface silanol groups, would *not* be more hydrophobic than the anisole/[BMIm][NTf$_2$] organic liquid phase and may in fact be sufficiently hydrophilic to prefer ^{7}Li ions. The effect is slightly greater for SULFsil because, as previously mentioned, the strong acid functional group would be fully ionised, rather than partially ionised during phase-contact [41], rendering it more hydrophilic. As such, it is proposed this is the mechanism by which ^{6}Li enrichment in the organic solvent phase is enhanced. We have previously observed how silica-based extractants exhibit very different ion uptake behaviour, compared with analogous ion-exchange resins [51].

Future experiments will be run to explore this hypothesis further. These will include testing for any isotopic fractionation in two-phase only systems (aqueous and silica) and modification of the organic phase to increase or decrease the hydrophobicity, which could be achieved by changing the [BMIm][NTf$_2$] percentage in the solvent. It is also important for future work to progress towards industrially realistic dynamic experiments. These must be executed in such a way as to ensure adequate mixing and residence time for contact of all three-phases, plus a means of separating the phases after contact. Notwithstanding the use of the centrifugal tricanter previously mentioned, a potential setup is shown in Fig. S8, incorporating a simpler agitated tubular reactor (ATR) design. This would immobilise the solid phase within the reactor tube, through which the two liquid phases are pumped. Mixing would be achieved by rapid lateral agitation of the reactor.

Although our conclusions regarding the lithium isotopic separation potential of a three-phase system are made cautiously, the evidence does suggest that a silica-based ion-exchanger is an inherently appropriate adsorbent matrix for design of a three-phase system for Li isotopic separation and this has implications for the future research direction for such systems.

4. Conclusions

We have investigated for the first time a ternary system, with a view to potential fractionation of lithium isotopes, for supply to the nuclear industry. An organic phase, containing B15C5 ether and [BMIm][NTf_2] ionic liquid was assessed alongside two solid-phase organosilicas with phosphonic acid and sulfonic acid functionalities (EBPsil and SULFsil). In comparative two-phase experiments (liquid-liquid and liquid-solid), the organic phase was found to have higher overall affinity for Li, with a maximum distribution coefficient (K_D) of ~0.6. All extractants showed improved Li affinity at a molar ratio of 2 (ligand/Li), attributed to the formation of 2:1 complexes with Li^+ ions coordinated between two crown ethers or functional groups. In modelling of solid-phase adsorption data, both silicas displayed gently sloping isotherms, with SULFsil displaying greater capacity and stronger adsorption behaviour. In three-phase experiments, increasing the effective ligand concentration in the system (for either the solid or organic phase) increased the Li extraction into that phase, though not at the expense of extraction into the other competing phase. The initial solution pH had little effect on the Li partitioning, which was found to be due to buffering towards a mildly acidic pH by the organic phase. In contrast, addition of Mg^{2+} ions was detrimental to solid-phase adsorption, but not on the solvent extraction. Furthermore, it was found that addition of the silica solid phase slightly increased the ^{6}Li isotopic enrichment (α) in the organic phase, to a maximum of 1.035, indicating that the solid phase was ^{7}Li selective. This is extremely rare for a Li ion-exchange process and was believed to be because of the hydrophilic adsorbent matrix, increasing the selective transfer of the more hydrophobic ^{6}Li isotope into the organic phase. As such, we conclude that a silica-based material is an appropriate basis for further investigations into Li isotopic fractionation in three-phase systems.

CRediT authorship contribution statement

Thomas J. Robshaw: Writing – review & editing, Writing – original draft, Project administration, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Magali Goncalves Rego:** Writing – review & editing, Methodology, Investigation, Formal analysis. **Stephen Reid:** Writing – original draft, Validation, Methodology, Investigation, Formal analysis. **Alastair Baker:** Writing – review & editing, Investigation, Funding acquisition. **Timothy Hunter:** Writing – review & editing, Supervision, Resources, Project administration, Funding acquisition. **Kathryn George:** Writing – review & editing, Supervision, Resources, Project administration, Investigation, Funding acquisition, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This project was supported by UK Atomic Energy Authority through the Fusion Industry Programme. The Fusion Industry Programme is stimulating the growth of the UK fusion ecosystem and preparing it for future global fusion powerplant market. More information about the Fusion Industry Programme can be found online: https://ccfe.ukaea.uk/programmes/fusion-industry-programme/. The authors would like to thank Karine Alves-Thorne (School of Chemical and Process Engineering, University of Leeds) for AAS technical advice. We also thank PhosphonicS for their generous donation of the silica adsorbents.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.seppur.2026.136835.

Data availability

The data that has been used is confidential.

References

[1] F. Tsai, et al., Corrosion sensitivity of nickel-based alloy Inconel 600 in pressurized water reactor water chemistry: can KOH replace LiOH? Corros. Sci. 255 (2025) 113052 https://doi.org/10.1016/j.corsci.2025.113052.

[2] D. Zakiryanov, N. Tkachev, High-entropy melt of Lithium, sodium, and potassium fluorides and chlorides as a possible coolant for molten-salt reactors, Radiochemistry 66 (6) (2024) 805–809, https://doi.org/10.1134/S1066362224060031.

[3] J. Park, Enriched lithium and the race for advanced nuclear technologies, Power Technology (2025). https://www.power-technology.com/features/enriched-lithium-and-the-race-for-advanced-nuclear-technologies/.

[4] S.C. Brooks, G.R. Southworth, History of mercury use and environmental contamination at the oak ridge Y-12 plant, Environ. Pollut. 159 (1) (2011) 219–228, https://doi.org/10.1016/j.envpol.2010.09.009.

[5] L. Cui, et al., A novel ion-pair strategy for efficient separation of lithium isotopes using crown ethers, Sep. Purif. Technol. 274 (2021) 118989, https://doi.org/10.1016/j.seppur.2021.118989.

[6] A. Murali, Z. Zhang, M.L. Free, P.K. Sarswat, a comprehensive review of selected major categories of lithium isotope separation techniques, Phys. Status Solidi A 218 (19) (2021) 2100340, https://doi.org/10.1002/pssa.202100340.

[7] J.L. Carrillo, et al., Electrochemical ^{6}Li isotope enrichment based on selective insertion in 1D tunnel-structured V_2O_5, Chem (2025) 102486, https://doi.org/10.1016/j.chempr.2025.102486.

[8] M. Wang, et al., Lithium isotope separation by electromigration, Chem. Phys. Lett. 746 (2020) 137290, https://doi.org/10.1016/j.cplett.2020.137290.

[9] N. Wegrzynowski, T. Martin, T.B. Scott, “Novel Methods of Isotopic Separation of Lithium 6,” Presented at the Nuclear Energy for New Europe, Portoroz, Slovenia, 2024.

[10] C. García-Balboa, P. Martínez-Alesón, V. López-Rodas, E. Costas, M. Díaz, An exploratory study on the possibilities of microalgal biotechnology to obtain the essential ^{6}Li isotope as fusion fuel, Biotechnol. Biofuels Bioprod. 16 (1) (2023) 141, https://doi.org/10.1186/s13068-023-02394-0.

[11] P.S. Dhami, et al., Separation and purification of ^{90}Sr from PUREX HLLW using N, N,N′,N′-tetra(2-ethylhexyl) diglycolamide, J. Radioanal. Nucl. Chem. 296 (3) (2013) 1341–1347, https://doi.org/10.1007/s10967-012-2302-0.

[12] X. Yu, X. Fan, Y. Guo, T. Deng, Recovery of lithium from underground brine by multistage centrifugal extraction using tri-isobutyl phosphate, Sep. Purif. Technol. 211 (2019) 790–798, https://doi.org/10.1016/j.seppur.2018.10.054.

[13] K. Nishizawa, S.-I. Ishino, H. Watanabe, M. Shinagawa, Lithium isotope separation by liquid-liquid extraction using Benzo-15-Crown-5, J. Nucl. Sci. Technol. 21 (9) (1984) 694–701, https://doi.org/10.1080/18811248.1984.9731102.

[14] K. Nishizawa, H. Watanabe, S.-I. Ishino, M. Shinagawa, Lithium isotope separation by cryptand (2B, 2, 1) polymer, J. Nucl. Sci. Technol. 21 (2) (1984) 133–138, https://doi.org/10.1080/18811248.1984.9731024.

[15] K. Nishizawa, H. Watanabe, Intrinsic isotope effect of cryptand (2B,2,1) to Li-6 and Li-7, J. Nucl. Sci. Technol. 23 (9) (1986) 843–845, https://doi.org/10.1080/18811248.1986.9735064.

[16] K. Nishizawa, T. Takano, I. Ikeda, M. Okahara, Extractive separation of Lithium isotopes by crown ethers, Sep. Sci. Technol. 23 (4–5) (1988) 333–345, https://doi.org/10.1080/01496398808060708.

[17] J. Xiao, Y. Jia, C. Shi, X. Wang, Y. Yao, Y. Jing, Liquid-liquid extraction separation of lithium isotopes by using room-temperature ionic liquids-chloroform mixed solvent system contained benzo-15-crown-5, J. Mol. Liq. 223 (2016) 1032–1038, https://doi.org/10.1016/j.molliq.2016.08.078.

[18] H. Sun, et al., Separation of lithium isotopes by using solvent extraction system of crown ether-ionic liquid, Fusion Eng. Design 149 (2019) 111338, https://doi.org/10.1016/j.fusengdes.2019.111338.

[19] X. Zhou, et al., The extraction method for the separation of lithium isotopes using B12C4/B15C5/B18C6-ionic liquid systems, New J. Chem. 47 (2022) 1916–1924, https://doi.org/10.1039/d2nj05369a.

[20] Z. Zhang, Y. Jia, B. Liu, Y. Jing, Y. Yao, Characterization of a novel crown ether system for Lithium isotope separation, Ind. Eng. Chem. Res. 60 (35) (2021) 13031–13039, https://doi.org/10.1021/acs.iecr.1c03245.

[21] Q. Zhang, et al., Lithium isotope separation effect of N-phenylaza-15-crown-5, J. Mol. Liq. 330 (2021) 115467, https://doi.org/10.1016/j.molliq.2021.115467.

[22] Y. Ban, M. Nomura, Y. Fujii, Chromatographic separation of lithium isotopes with silica based monobenzo-15-crown-5 resin, J. Nucl. Sci. Technol. 39 (3) (2002) 279–281, https://doi.org/10.3327/jnst.39.279.

[23] W. Zhou, et al., A green strategy for lithium isotopes separation by using mesoporous silica materials doped with ionic liquids and benzo-15-crown-5, J. Radioanal. Nucl. Chem. 300 (2) (2014) 843–852, https://doi.org/10.1007/s10967-014-3052-y.

[24] F. Yan, et al., Preparation and characterization of Polysulfone-graft-4′-aminobenzo-15-crown-5-ether for Lithium isotope separation, Ind. Eng. Chem. Res. 54 (13) (2015) 3473–3479, https://doi.org/10.1021/acs.iecr.5b00314.

[25] Y. Zeng, et al., "chitosan-graft-benzo-15-crown-5-ether/PVA blend membrane with sponge-like pores for Lithium isotope adsorptive separation," *ACS*, Omega 3 (1) (2018) 554–561, https://doi.org/10.1021/acsomega.7b01625.

[26] Z. Grote, H. Wizemann, R. Scopelliti, K. Severin, Lithium isotope separation by 12-metallacrown-3 complexes, Zeitschrift Fur Anorganische und Allgemeine Chemie 633 (5–6) (2007) 858–864, https://doi.org/10.1002/zaac.200600366.

[27] J. Xiao, et al., Lithium isotopes separation by using benzo-15-crown-5 in eco-friendly extraction system, J. Mol. Liq. 241 (2017) 946–951, https://doi.org/10.1016/j.molliq.2017.06.119.

[28] T. Sugiyama, K. Sugiura, Preparation of Benzo-15-Crown-5 adsorbents for the separation of Lithium isotopes by displacement chromatography, Fusion Sci. Technol. 71 (4) (2017) 473–477, https://doi.org/10.1080/15361055.2017.1293424.

[29] S. Pepper, et al., Adsorption of strontium from aqueous solution using ethyl butyl phosphonate (EBP) silica, Prog. Nucl. Energy 177 (2024) 105458, https://doi.org/10.1016/j.pnucene.2024.105458.

[30] K.Y. Foo, B.H. Hameed, Insights into the modeling of adsorption isotherm systems, Chem. Eng. J. 156 (1) (2010) 2–10, https://doi.org/10.1016/j.cej.2009.09.013.

[31] M. Eriksson, I. Lundstrom, L.G. Ekedahl, A model of the Temkin isotherm behavior for hydrogen adsorption at $Pd\text{-}SiO_2$ interfaces, J. Appl. Phys. 82 (6) (1997) 3143–3146, https://doi.org/10.1063/1.366158.

[32] K. Chu, Revisiting the Temkin isotherm: dimensional inconsistency and approximate forms, Ind. Eng. Chem. Res. 60 (35) (2021) 13140–13147, https://doi.org/10.1021/acs.iecr.1c01788.

[33] A. Ebadi, J. Mohammadzadeh, A. Khudiev, What is the correct form of BET isotherm for modeling liquid phase adsorption? Adsorption-J. Int. Adsorp. Soc. 15 (1) (2009) 65–73, https://doi.org/10.1007/s10450-009-9151-3.

[34] E.J. Billo, Excel for Chemists: A Comprehensive Guide, 3 ed., John Wiley, Hoboken, New Jersey, 2004.

[35] R. Torrejos, et al., Design of lithium selective crown ethers: synthesis, extraction and theoretical binding studies, Chem. Eng. J. 326 (2017) 921–933, https://doi.org/10.1016/j.cej.2017.06.005.

[36] A. Bajaj, N. Poonia, Comprehensive coordination chemistry of alkali and alkaline-earth cations with macrocyclic multidentates - latest position, Coord. Chem. Rev. 87 (1988) 55–213, https://doi.org/10.1016/0010-8545(88)80008-0.

[37] C. Shi, Y. Jia, J. Xiao, X. Wang, Y. Yao, Y. Jing, Lithium isotope separation by liquid-liquid extraction using ionic liquid system containing dibenzo-14-crown-4, J. Mol. Liq. 224 (2016) 662–667, https://doi.org/10.1016/j.molliq.2016.10.081.

[38] P. Zhang, et al., Extraction separation of lithium isotopes with Bromobenzene-15-crown-5/ionic liquids system: experimental and theoretical study, J. Mol. Liq. 364 (2022) 120020, https://doi.org/10.1016/j.molliq.2022.120020.

[39] T.J. Robshaw, et al., Insights into the interaction of iodide and iodine with Cu(II)-loaded bispicolylamine chelating resin and applications for nuclear waste treatment, Chem. Eng. J. 390 (2020) 124647–124659, https://doi.org/10.1016/j.cej.2020.124647.

[40] S. Güneysu, Lithium sorption from aqueous solution with cationic resins, Desalin. Water Treat. 177 (2020) 102–108, https://doi.org/10.5004/dwt.2020.24715.

[41] C.E. Harland, Ion Exchange: Theory and Practice, 2nd ed., Royal Society of Chemistry, Cambridge, 1994.

[42] A. Çiçek, O. Yilmaz, Ö. Arar, Removal of lithium from water by aminomethylphosphonic acid-containing resin, J. Serb. Chem. Soc. 83 (9) (2018) 1059–1069, https://doi.org/10.2298/JSC170930020C.

[43] T.J. Robshaw, A.M. James, D.B. Hammond, J. Reynolds, R. Dawson, M.D. Ogden, Calcium-loaded hydrophilic hypercrosslinked polymers for extremely high defluoridation capacity via multiple uptake mechanisms, J. Mater. Chem. A 8 (2020) 7130–7144, https://doi.org/10.1039/C9TA12285K.

[44] G. Yu, X. Zhang, T. Hubach, B. Chen, C. Held, Highly efficient lithium extraction from magnesium-rich brines with ionic liquid-based collaborative extractants: thermodynamics and molecular insights, Chem. Eng. Sci. 286 (2024) 119682, https://doi.org/10.1016/j.ces.2023.119682.

[45] T. Oi, K. Kawada, M. Hosoe, H. Kakihana, Fractionation of Lithium isotopes in cation-exchange chromatography, Sep. Sci. Technol. 26 (10–11) (1991) 1353–1375, https://doi.org/10.1080/01496399108050537.

[46] A. Beigi, M. Abdouss, M. Yousefi, S. Pourmortazavi, A. Vahid, Investigation on physical and electrochemical properties of three imidazolium based ionic liquids (1-hexyl-3-methylimidazolium tetrafluoroborate, 1-ethyl-3-methylimidazolium bis (trifluoromethylsulfonyl) imide and 1-butyl-3-methylimidazolium methylsulfate), J. Mol. Liq. 177 (2013) 361–368, https://doi.org/10.1016/j.molliq.2012.10.025.

[47] T. Ye, et al., Highly selective Lithium transport through crown ether pillared angstrom channels, Angew. Chem. Int. Ed. 63 (7) (2024) e202316161, https://doi.org/10.1002/anie.202316161.

[48] I. Oral, S. Tamm, C. Herrmann, V. Abetz, Lithium selectivity of crown ethers: the effect of heteroatoms and cavity size, Sep. Purif. Technol. 294 (2022) 121142, https://doi.org/10.1016/j.seppur.2022.121142.

[49] K. Liu, et al., Bilayer crown ether-engineered nanofiltration membranes with dual Li^+ transport channels for ultra-high Mg^{2+}/Li^+ separation from saline lake brines, Water Res. 284 (2025) 123924, https://doi.org/10.1016/j.watres.2025.123924.

[50] T.J. Robshaw, R. Dawson, K. Bonser, M.D. Ogden, Towards the implementation of an ion-exchange system for recovery of fluoride commodity chemicals. Kinetic and dynamic studies, Chem. Eng. J. 367 (2019) 149–159, https://doi.org/10.1016/j.cej.2019.02.135.

[51] S.E. Pepper, K.R. Whittle, L.M. Harwood, J. Cowell, T.S. Lee, M.D. Ogden, Cobalt and nickel uptake by silica-based extractants, Sep. Sci. Technol. 53 (10) (2018) 1552–1562, https://doi.org/10.1080/01496395.2017.1405034.

[52] S.V. Demin, V.I. Zhilov, A.Y. Tsivadze, Lithium and boron isotope effects in extraction systems, Russ. J. Inorg. Chem. 60 (5) (2015) 633–637, https://doi.org/10.1134/s0036023615050046.

[53] T. Suzuki, M. Zhang, M. Nomura, T. Tsukahara, M. Tanaka, Engineering study on lithium isotope separation by ion exchange chromatography, Fusion Eng. Des. 168 (2021) 112478, https://doi.org/10.1016/j.fusengdes.2021.112478.

[54] J. Mikes, J. Durisová, L. Jelínek, Enrichment of lithium isotope ^6Li by ion exchange resin with specific particle size, J. Radioanal. Nucl. Chem. 312 (1) (2017) 13–18, https://doi.org/10.1007/s10967-017-5198-x.

[55] K. Ooi, Y. Miyai, Y. Makita, H. Kanoh, Fractionation of lithium isotopes in ion exchange chromatography with titanium phosphate exchanger, Sep. Sci. Technol. 34 (6–7) (1999) 1133–1144, https://doi.org/10.1080/01496399908951085.