Supplementary material for:

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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DFT computational methods

DFT calculations were performed using the Northwest Computational Chemistry Package (NWChem) [1], with the def2-TZVP basis set [2]. The Becke 97-2 exchange-correlation functional was used in structure optimization and harmonic frequency [3]. In order to study the solvation effect, corresponding to realistic conditions, the geometry structures were optimised using a conductor-like screening model (COSMO)[4, 5], which has been applied to the prediction of copper isotope fractionation [6, 7]. It treats the solvent as a continuum with specific dielectric constants, characterising the ability of the solvent to screen electrostatic interactions. In our study, COSMO was applied to investigate the impact of the organic phase compositions on the isotope fractionation. The dielectric constants were determined by the organic phase compositions, that is 11.6 for pure [BMIM][NTf2][8], and 6.4 for the mixture of [BMIM][NTf2] and anisole with the ratio of 3 to 7.The molecular electrostatic potential (ESP) on van der Waals (vdW) surface with isosurface of $\rho(r)=0.001 e/boh r^3$ was visualized by the Avogadro package[9][10][11].

Structure optimisations

In the two phases, lithium preferentially bonds different numbers of oxygen atoms [9]. Thus, there are different interactions for the lithium ion in water and in the organic phase, evidenced by different Li-O bond strengths. The strengths of the bond depend on the bond distance. It is important for the DFT calculations to optimise the structures of Li-O bonds in both phases first. In the aqueous phase, the average Li-O distance calculated from DFT in the optimized $[Li(H2O)4]^+$ structure was 1.98 Å (structure shown in Figure 6a in the manuscript), which is in good agreement with previous results [11]. In the organic phase, the 1:1 stoichiometric complex $[Li(B5C15)]^+$ forms as found in the experiments above but also in previous studies [10]. The lithium ion is enclosed in the cavity of B15C5 and is coordinated with five oxygen atoms. The calculated bond length for Li-O in the $[Li\text{-}B15C5]^+$ complex is 2.19 Å, indicating a weaker bond strength compared to that in the aqueous solution.

For the lithium isotope exchange reactions, optimised structures of the lithium-reactant complex are also determined, as shown in Figure S1. The complex of Li(B15C5)(H_2O)Cl has a Li-O distance of 1.95 Å (Figure 11), while the Cl^- anion is isolated from Li^+ by a H_2O molecule with Li-Cl distance of 3.91 Å. For Reaction 2 mentioned in the manuscript, NTf2 is a large anionic ligand compared to lithium atom. A H_2O molecule exists in between NTf2 and the extractant. There is a hydrogen bond between one O atom from NTf2 and one H atom from H_2O (H-O 1.75 Å). Here Li^+ is coordinated with six O atoms (five from B15C5, one from H_2O with Li-O distance of 1.98 Å), and NTf2 is isolated from the complex anion with a Li-N distance of 4.62 Å, as shown below in Figure S1.

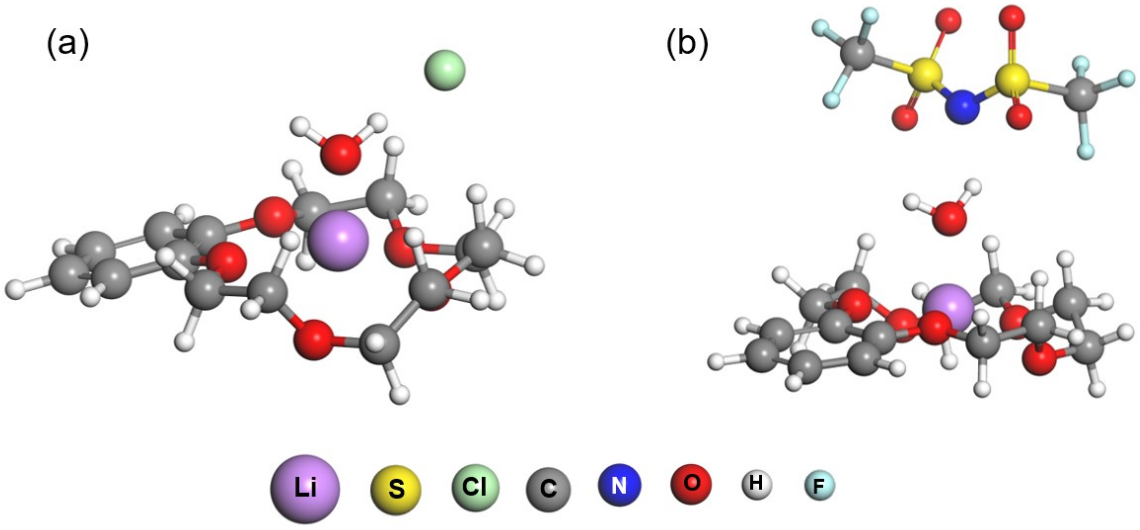

Figure S1. The optimised structures of the (a) Li(B15C5)(H_2O)Cl and (b) Li(B15C5)(H_2O)(NTf2) complexes. Purple, red, white, and grey spheres denote lithium, oxygen, hydrogen, and carbon atoms, respectively. Green, yellow, dark bule and light blue spheres denote chlorine, sulfur, nitrogen, and fluorine atoms, respectively.

Vibrational modes

The vibrational modes B1, B2 and E for Li(H2O)4+, as well as modes A and B for Li(B15C5)+ mentioned in Table 4 are analysed by group theory and represented in Figure S2, respectively.

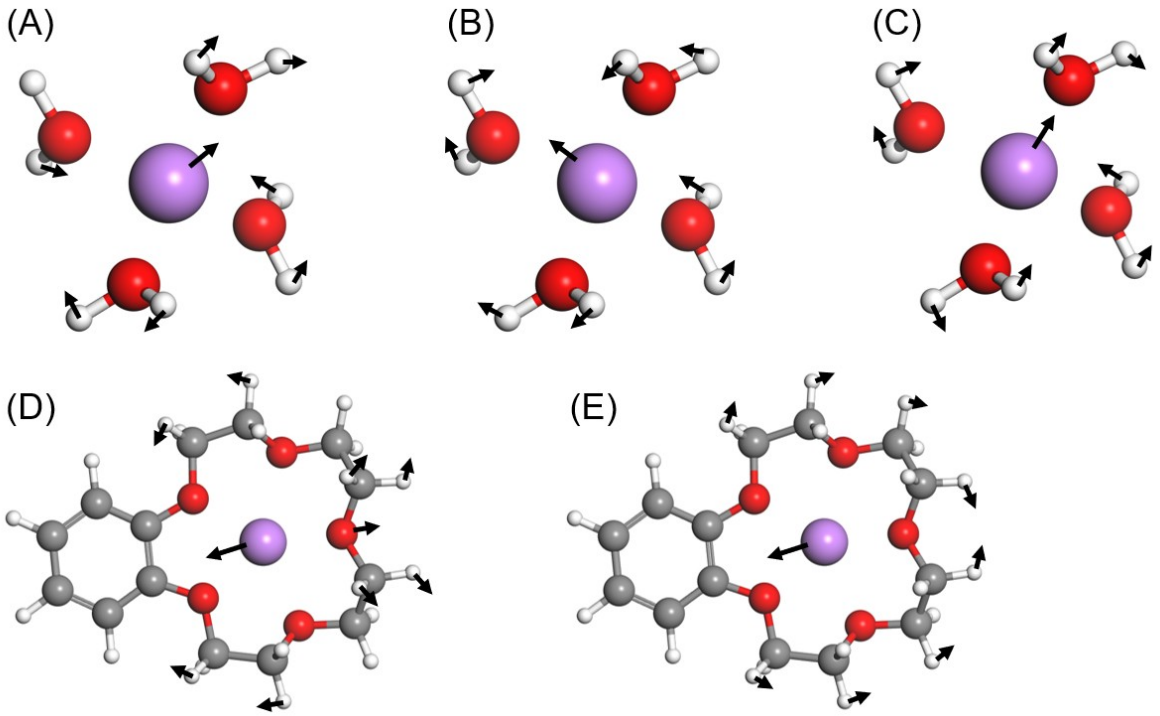

Figure S2. Schematic of vibrational modes for (A) B1 mode of $Li(H_2O)_4^+$, (B) B2 mode of $Li(H_2O)_4^+$,(C) E mode of $Li(H_2O)_4^+$, (D) A mode of $Li(B15C5)^+$,(E) B mode of $Li(B15C5)^+$.

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