

Highly efficient lithium extraction from magnesium-rich brines with ionic liquid-based collaborative extractants.

Thermodynamics and molecular insights.

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Selective extraction of Li^+ from high $\text{Mg}^{2+}/\text{Li}^+$ ratio brines with ionic liquid (IL) based collaborative extractants was investigated by experiments, thermodynamic analyses, and quantum chemical (QC) calculations. The results demonstrated that the system 1-(2-hydroxyethyl)-3-methylimidazolium bis(trifluoromethylsulfonyl)imide + trioctyl phosphate ([HOEMIM][Tf₂N] + TOP) was considered as the best extractant, with the very high extraction efficiency of Li^+ ($E_{\text{Li}^+} \approx 83\%$) and separation selectivity of $\text{Li}^+/\text{Mg}^{2+}$ (≈ 742), which is higher than any known report from the open literature. The thermodynamic model ePC-SAFT was extended to quantitatively predict the phase equilibria of the so-called “organic-inorganic complex strong electrolyte system” presented in this work as well as the related extraction indicator E_{Li^+} . The molecular-level extraction mechanism was explored by QC calculation, indicating that the strong multi-site intermolecular interactions between Li^+ and [HOEMIM][Tf₂N] + TOP break the Li^+ hydration.

The molecular-level Li^+ extraction mechanism from aqueous to organic IL+TOP phase was explored by QC using independent Gradient Model (IGM) analysis. Li^+ and Mg^{2+} are hydrated by strong interaction of “Metal-O-H”, and Li^+ hydration is weaker than Mg^{2+} hydration. Thus, Li^+ can be extracted from the aqueous to organic phases by Li^+ hydration break, producing the complex Li^+ -TOP-[Tf₂N]⁻ dominated by the multi-site interaction consisting of $\text{Li}^+ \rightarrow \text{O}=\text{P}$, $\text{S}-\text{N} \cdots \text{Li}^+$, $\text{S}=\text{O} \cdots \text{Li}^+$, $\text{C}-\text{H} \cdots \text{O}$, and vdW dispersion interactions. In this case, TOP acts as extractant by coordinative interactions ($\text{Li}^+ \rightarrow \text{O}=\text{P}$), and the IL acts a co-extractant stabilizing the Li^+ -TOP-[Tf₂N]⁻ complex in an electrically neutral form.

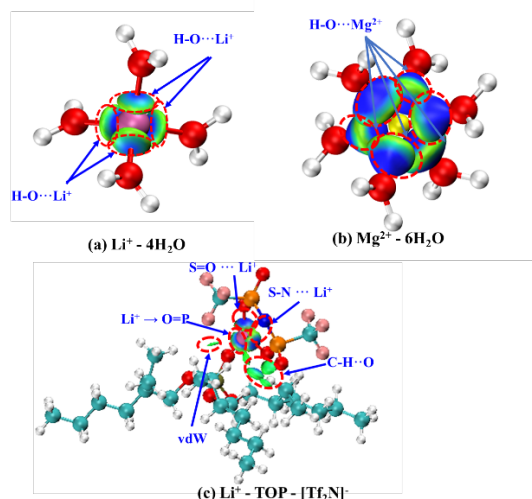


Figure 1. IGM visualization of ion hydration: Li^+ - H_2O (a), Mg^{2+} - H_2O (b) and IGM visualization of the complex Li^+ -TOP-[Tf₂N]⁻ (c).

The extraction indicators for Li^+ extraction were predicted by ePC-SAFT. All the underlying phase equilibria of the subsystems were modeled as well based on the isofugacity criterion. One of the key results was that ePC-SAFT allowed predicting that Li^+ is transferred to the organic phase while Mg^{2+} stays in the aqueous phase, thereby allowing $\text{Li}^+/\text{Mg}^{2+}$ separation. The key method for this was an induced association treatment between Li^+ and TOP in order to mimic the complex formation shown in Fig. 1c, which required only one binary parameter between Li^+ and TOP. Remarkably, $E_{\text{Mg}^{2+}}$ was obtained without any Mg^{2+} -extractant binary parameters. Further, the influence of

organic:aqueous phase ratio (O:A) on E_{Li^+} could be predicted well with ePC-SAFT, and E_{Li^+} finally reaches a limiting value of $\approx 85\%$.

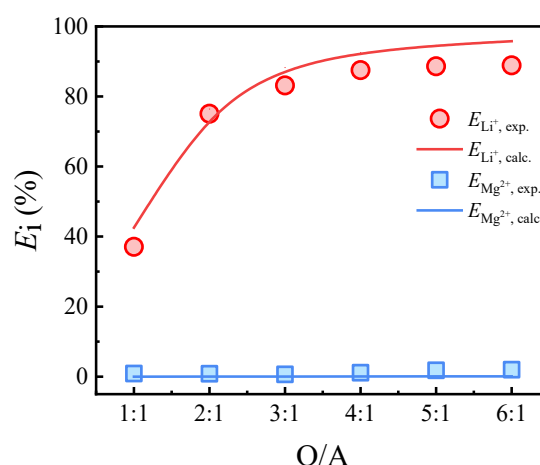


Figure 2. Comparison of the calculated (lines) and experimental (points) on the effects of the volume ratio for the organic to aqueous phase (O/A) on Li^+ and Mg^{2+} extraction efficiency with [HOEMIM][Tf₂N] + TOP as extraction system ($\text{Mg}^{2+}/\text{Li}^+ = 40:1$; and $\text{pH} = 7$ and $C_{\text{IL}} = 0.09 \text{ mol/L}$), and the parameters were fitted to E_{Li^+} at $\text{O/A} = 2:1$ and 298.15 K , i.e., all other modeling lines are predictions.

To conclude, we could demonstrate the powerful prediction capacity of ePC-SAFT and its first successfully extended application to so-called “organic-inorganic complex strong electrolyte system” in $\text{Li}^+/\text{Mg}^{2+}$ extraction separation with ILs.

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