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Theoretical prediction of $^{6}Li/^{7}Li$ separation in solvent extraction system using Urey model

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HIGHLIGHTS

- A method to theoretically estimate the separation factors of $^{6}Li/^{7}Li$ is proposed.
- Urey model can predict the $^{6}Li/^{7}Li$ separation for a solvent extraction system.
- Coordination structure of the Li complex plays a dominant role.
- Weakening Li–O bonding of the Li-crown ether complex favors the separation.
- Lithium isotope exchange is an exothermic reaction.

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ABSTRACT

Separation of lithium isotopes (^{6}Li, ^{7}Li) is a key technology to the development and utilization of nuclear energy. In this work, we present an efficient method to theoretically estimate the separation factors of $^{6}Li/^{7}Li$ in solvent extraction system based on Urey model. The approach was implemented by calculating the equilibrium separation factor of $^{6}Li/^{7}Li$ in the crown ether/Li aqueous solution [15-crown-5 (15C5), Benzo-15-crown-5 (B15C5), 12-crown-4 (12C4), Dicyclohexyl-18-Crown-6 (DH18C6)/LiX-H_2O, X = Cl/I] exchange system utilizing the calculated harmonic vibration frequencies obtained by Density Functional Theory (DFT). The results showed that Urey model can correctly predict the direction of the $^{6}Li/^{7}Li$ separation as observed in the experiments. With this model, the underlying mechanisms driving the equilibrium isotope separation were elucidated further. The coordination structure of the Li complex played a dominant role in the separation of $^{6}Li/^{7}Li$. For the solvent extraction system comprising crown ether phase and LiX aqueous solution, the crown ether with strong ability of excluding the hydrated water of Li gives a higher separation factor. The ways by which Li–O bonding of the Li-crown ether complex can be weakened, such as reducing the coordinated water molecules, applying high polar solvents, performing separation from Li salt with a softer anion, are helpful to improve the separation factor of $^{6}Li/^{7}Li$ at a fixed temperature. The lithium isotopic exchange is an exothermic reaction. Decreasing temperature favors the exchange reaction. This work is expected to provide guidance for the design of the exchanger and screening of the chemical exchange system for the separation of $^{6}Li/^{7}Li$.

1. Introduction

Natural lithium (Li) consists of two stable isotopes, ^{6}Li and ^{7}Li, which have abundance of 7.53% and 92.47%, respectively. Each Li isotope plays an important role in the nuclear industry [1]. ^{6}Li is an indispensable material in nuclear fusion reactors. It has a much higher neutron capture cross-section, so it can absorb neutrons flux to produce tritium, which is very rare on the earth. ^{7}Li can be used as a component of the primary molten salt coolant in thorium-based molten salt reactors. High enriched $^{7}LiOH$ is used to adjust the pH value of primary coolant in pressurized-water reactors. The separation of $^{6}Li/^{7}Li$ is a key technology to the development and utilization of nuclear energy.

For the significant application and increasing demand of lithium isotopes, the separation of $^{6}Li/^{7}Li$ has attracted considerable attentions

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of many researchers worldwide during the past decades. Many techniques for $^{6}Li/^{7}Li$ separation and enrichment have been considered, such as Li amalgam [2], ion-exchange resin chromatography [3], solvent extraction [4,5], laser photo activation [6] etc., among of which, Li amalgam is the only technique that put into industrial use till now. However, the huge employment of mercury is a threat to people and environment [7]. Laser photo activation was approved to be the most effective and highly-isotope selective but may be difficult to produce on a larger scale at present. As the most prospective technique for industrialization, solvent extraction was the most widely investigated method for ^{6}Li enrichment [2,5,8,9]. Isotopic exchange between the Li complexes of two phases is the core of the separation. This process was influenced by many factors including complexing agent, solvent type, lithium salt, temperature etc. It would be complicated and time-consuming if the exchanger and exchange system are screened only through experiments. Moreover, the underlying mechanisms driving the $^{6}Li/^{7}Li$ separation in the chemical exchange process are not clear. Computational approach was proved to be an effective tool to predict many reactions and explain the mechanisms [10–12]. Up to now it is difficult to distinguish ^{6}Li and ^{7}Li by thermodynamic calculation [13]. However, Urey model (or Bigeleisen-Mayer equation) may provide us a feasible way to predict the equilibrium separation of $^{6}Li/^{7}Li$ in light of the mass differences between ^{6}Li and ^{7}Li.

Urey model (or Bigeleisen-Mayer equation) [14,15] is a theoretical model that equilibrium isotope fractions arise from the sensitivity of vibrational frequencies to atomic masses. This model was widely applied to predict the stable isotope fractionations in geochemical field [16–22]. Liu et al. successfully predicted the equilibrium Ge, Se, Si isotopes fraction in various geological system by employing Urey model and quantum chemical approach [16,18,22]. Anbar [17] and Jarzecki [21] investigated the isotopic fraction between ferric species and ferrous species in aqueous solution. Theoretical estimation focused on the equilibrium fractionation of $^{6}Li/^{7}Li$ in aqueous solution or between Li-bearing minerals and aqueous fluids have also been reported [23–25] by means of Urey model and ab initio methods. The Li isotope fractionation at high pressure and temperature was specially discussed for the Earth's crust and mantle purpose [24]. To the best our knowledge, no work has been done in the prediction of the separation factor of $^{6}Li/^{7}Li$ in a solvent extraction process.

Crown ethers are of widespread interest owing to their specific complexation abilities for cations [26,27]. They are cyclic compounds that consist of a ring containing several ether groups (–OCH_2CH_2–). The oxygen atoms of high electronegativity can provide as doner atoms to bind metal ions. It has been reported that oxygen containing functional groups are suitable for chemical reactions and surface adhesion [28]. Crown ethers and their derivatives are the most frequently used and reported complexing agents in $^{6}Li/^{7}Li$ separation. They exhibited comparable separation factor of $^{6}Li/^{7}Li$ with Li amalgam system. In 1980s, Nishizawa's group has done much work in this field [4,29,30]. The B15C5 was found to be the most suitable complexing agent among the investigated crown ethers from the perspective of the separation factor of $^{6}Li/^{7}Li$, the distribution coefficient of Li and the stability of the Li-bearing complex [4]. The maximum single separation factor for $^{6}Li/^{7}Li$ obtained was 1.044 ± 0.003 at 273 K at the optimum operation conditions [29]. In recent years, the studies regarding $^{6}Li/^{7}Li$ separation with crown ethers are still growing [5,8,9]. Although the structures of Li complex with crown ether ligands have been reported [31–33], how the factors such as Li coordination environment, coordination number, bond strengths of Li to the coordinated atoms, etc. manipulate the separation process have not elucidated. The unknown knowledge of the mechanism limited the development of new exchangers.

This work examined Urey model in the prediction of the separation factor of $^{6}Li/^{7}Li$ in solvent extraction system. The crown ether/Li aqueous solution (15C5, B15C5, 12C4, DH18C6/LiX-H_2O, X = Cl/I) chemical exchange systems were used for investigation. The harmonic vibration frequencies were obtained through first-principle calculations. Then the theoretical prediction values were compared with the available experimental results. The crystal structure of lithium iodine (LiI) complexes with B15C5 and 12C4 were prepared and first reported. Meanwhile, the underlying mechanisms driving the equilibrium isotope separation were further elucidated. This model gives us valuable insight into the factors governing the $^{6}Li/^{7}Li$ separation at the atomic scale. This work is expected to provide guidance for the design of the exchanger and screening of the exchange systems for the separation of lithium isotopes, which are meaningful for the practical use.

2. Model and calculation

2.1. Urey model

The isotope separation for a solvent extraction process is based on isotopic exchange reaction. The distribution of the isotopes between the organic phase and aqueous phase is different due to the different thermodynamic properties of isotopic molecules. The separation of the isotopes is the result that the isotopic exchange reaction reaches equilibrium state. The $^{6}Li/^{7}Li$ exchange reaction between Li aqueous species ($Li_{(w)}$) and Li organic species ($Li_{(o)}$) can be expressed as follows:

$$^{6}Li_{(w)} + {}^{7}Li_{(o)} \rightarrow {}^{7}Li_{(w)} + {}^{6}Li_{(o)}$$

The equilibrium constant K is related to the isotope separation factor α ($\alpha = K^{1/n}$), n is the number of the exchanged atom. In this work, K is equivalent to α for all the Li species studied. The equilibrium constant K of the exchange reaction can be expressed as:

$$K = \frac{Q_{^{7}Li_{(w)}} \times Q_{^{6}Li_{(o)}}}{Q_{^{6}Li_{(w)}} \times Q_{^{7}Li_{(o)}}} \tag{1}$$

where Q is the molecular partition function of $Li_{(w)}$ and $Li_{(o)}$. The harmonic quantum molecular partition function of a molecule can be written as a product of translational (Q_{tran}), rotational (Q_{rot}), vibrational (Q_{vib}) and electronic (Q_{elec}) partition functions. Only the vibrational energy plays the central role in controlling the distribution of isotopes between two phases, which is defined by:

$$Q_{vib} = \prod_{i=1}^{3N-6} \frac{e^{-h\nu_i/2kT}}{1-e^{-h\nu_i/kT}} \tag{2}$$

in which h is Planck constant, 6.626×10^{-34} J·s; k is Boltzmann constant, 1.38×10^{-23} J/K; T is temperature in Kelvin (K); N is the atom number of Li species ($3N$-6 is the vibration numbers for non-linear or polyatomic molecules). ν_i is the vibrational frequency (Hz).

Reduced partition function ratio, also referred as β, was introduced in Urey model. By definition, α can be calculated as a function of the reduced partition function ratios:

$$\alpha_{^{6}Li/^{7}Li} = \beta_{^{6}Li/^{7}Li_{(o)}} / \beta_{^{6}Li/^{7}Li(w)} \tag{3}$$

β can be expressed and simplified in terms of the harmonic normal-mode frequencies before and after isotope substitution and the Teller-Redlich product rule:

$$\beta_{^{6}Li/^{7}Li} = \prod_{i=1}^{3N-6} \frac{^{6}Ui}{7Ui} \cdot \frac{^{6}Q_{vib}}{^{7}Q_{vib}} = \prod_{i=1}^{3N-6} \frac{^{6}Ui}{^{7}Ui} \cdot \frac{e^{-^{6}Ui/2}}{e^{-^{7}Ui/2}} \cdot \frac{1-e^{-^{7}Ui}}{1-e^{-6Ui}} \tag{4}$$

where

$$U_i = \frac{h\nu_i}{kT}$$

Therefore, isotope separation in exchange system arises mainly from the differences in molecular vibration energies between the Li isotopic species in the two phases. The determination of the isotope separation factor is related to the change of vibrational frequencies associated to the isotope substitution. More information about Urey model and the derivation of the formulas can be found in the references [15,34].