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Lithium isotope separation with displacement chromatography using crown ether resin immobilized on porous silica beads

Takahiko Sugiyama[a],[*], Kei Sugiura[a], Masahiro Tanaka[b], Youichi Enokida[a]

[a] Nagoya University, Furo-cho, Chikusa-ku, Nagoya 464-8603, Japan
[b] National Institute for Fusion Science, Oroshi-cho 322-6, Toki 509-5292, Japan

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ABSTRACT

A crown ether resin immobilized on porous silica beads was investigated as a chromatographic packing for lithium isotope separation by displacement chromatography. In order to develop an effective chromatographic packing, effects of the diameter of the packing particle on the transport phenomena in the particle were investigated by numerical simulation. Transient change of the concentration profiles in the both solution phase and resin phase were obtained and lithium-6 enrichment in the resin phase was well simulated. A dimensionless coefficient, which represents a ratio of the diffusive mass transfer rate to the adsorption rate, was found in the mass balance equation. The magnitude of the factor was also evaluated for various values of diameter of the packing particle.

1. Introduction

There are two naturally existing isotopes of lithium, lithium-6 at 7.5% and lithium-7 at 92.5% in relative abundance [1]. A technology to enrich lithium-6 over 90 isotopic percent is necessary to establish the fuel cycle for fusion reactors. The displacement chromatography is one of the suitable methods for a large-scale production of the enriched lithium-6, because a scale-up of a process seems easy based on chemical engineering. A wide variety of ion exchange resins has been investigated for a chromatographic enrichment of lithium-6 [2–4]. Recently, a good performance has been reported using a crown ether resin immobilized on porous silica beads [5–7]. An equilibrium separation factor of a crown ether resin is larger than ion exchange resins by an order of magnitude.

On the other hand, the HETP (Height Equivalent to a Theoretical Plate) value of such a crown ether immobilized resin is relatively larger than ion exchange resins. A small HETP value means an effective separation, that is, a short length of column is required for an equilibrium separation. To maximize the merit of large equilibrium separation factor we need to shorten the HETP value of the crown ether immobilized resin. One of the reasons which cause the large HETP value was pointed out as a large mass transfer resistance in intraparticle diffusion. According to the assumption, an overall mass transfer coefficient is used in the model and the concentration profile in the particle is not calculated for separative analyses.

Recently, porous silica beads with small diameter are easily obtained, and such kind of beads can reduce the resistance of intraparticle diffusion. In advance of manufacturing an effective chromatographic packing using porous silica beads as a support matrix, it is very helpful to investigate effects of the diameter on the transport phenomena in the beads. The purpose of the present study is to establish a model applicable to the separative analyses of a chromatographic enrichment of lithium-6 using a crown ether resin immobilized on porous silica beads, where the resistance of intraparticle diffusion is not necessarily large.

2. Simulation procedure

2.1. Mass transfer model in the porous silica beads

The mass transfer process in a chromatographic column is consisted of many steps, such as convection and dispersion in the column, transfer through laminar films, intraparticle diffusion and adsorption or desorption at the local adsorption sites, as shown in Fig. 1. In a present study, we focused on the mass transfer process in the particle. The assumptions in the present model are as follows.

(1) Three kinds of ions, which are lithium-6, lithium-7 and proton, are treated.
(2) The system is adiabatic. The temperature and pressure are constant at a local position in the column.
(3) The chromatographic column is uniformly packed with the adsorbent particles having the same diameter.
(4) The micro pore and adsorption site are uniformly distributed in the adsorbent particle.

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[*] Corresponding author.
E-mail address: t-sugiyama@nucl.nagoya-u.ac.jp (T. Sugiyama).

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Nomenclature

C_i	Concentration of component i in the solution ($\mathrm{mol\,m^{-3}}$)
C_i'	Concentration of component i in the pore of particles ($\mathrm{mol\,m^{-3}}$)
C'^{*}_i	Dimensionless concentration of component i in the pore of particles
C_0'	Concentration at the boundary (characteristic concentration)
$\bar{D}_i$	Effective diffusion coefficient in particles ($\mathrm{m^2\,s^{-1}}$)
dz	Small column length (m)
E	Axial dispersion coefficient ($\mathrm{m^2\,s^{-1}}$)
ε_p	Porosity
ε_v	Void fraction
ka_v	Rate coefficient ($\mathrm{s^{-1}}$)
q_i	Concentration of component i which is adsorbed onto the surface of the pore ($\mathrm{mol\,m^{-3}}$)
q_i^*	Dimensionless concentration of component i which is adsorbed onto the surface of the pore
$q_{i,e}$	Equilibrium concentration of component i ($\mathrm{mol\,m^{-3}}$)
q_0	Exchange capacity ($\mathrm{mol\,m^{-3}}$)
r	Radial distance from particle center (m)
r^*	Dimensionless radial distance from particle center
R_c	Inner radius of a column (m)
R_p	Radius of a particle
r_i	Mass transfer rate between interstitial fluid and resin phase include its pore ($\mathrm{mol\,m^{-3}\,s^{-1}}$)
t	Time (s)
t^*	Dimensionless time
u	Interstitial fluid velocity ($\mathrm{m\,s^{-1}}$)
z	Axial distance from column inlet (m)

(5) The diffusion in the pore and adsorption or desorption at the adsorption site are considered. Mass transfer in laminar films and surface diffusion are not considered.

2.2. Fundamental equations

For the chromatographic process, the material balance equation for component i in an interstitial solution phase in the column is expressed as [8,9]

$$\frac{\partial C_i}{\partial t} + u\frac{\partial C_i}{\partial z} = E\frac{\partial^2 C_i}{\partial z^2} + r_i \tag{1}$$

In the present study we focused on only in the particle, and Eq. (1) was not used. A simultaneous simulation of Eq. (1) with the mass transfer in the particle is future research.

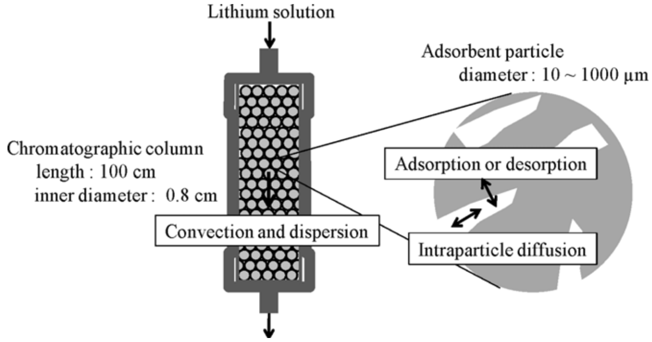

Fig. 1. Illustration of mass transfer process in a chromatographic column.

The material balance equations for component i in a pore (solution phase) and in an adsorption site (resin phase) are expressed as

$$\frac{\partial C_i'}{\partial t} = \bar{D}_i\left(\frac{\partial^2 C_i'}{\partial r^2} + \frac{2}{r}\frac{\partial C_i'}{\partial r}\right) - \frac{ka_v}{\varepsilon_p(1-\varepsilon_v)}(q_{i,e} - q_i) \tag{2}$$

$$\frac{\partial q_i}{\partial t} = ka_v(q_{i,e} - q_i) \tag{3}$$

The second term on the right hand side of Eq. (2) shows the adsorption rate. A linear driving force was assumed to represent the adsorption rate. In the present study the electrochemical valence of each component is unity. The exchange capacity q_0 is, then, expressed as

$$q_0 = \sum_{i=1}^{M} q_i \tag{4}$$

This relationship is also established at the equilibrium.

$$q_0 = \sum_{i=1}^{M} q_{i,e} \tag{5}$$

The selectivity constant of component i to j is defined by

$$K_j^i = \frac{q_{i,e}/q_{j,e}}{C_i'/C_j'} \tag{6}$$

so that

$$q_{i,e} = \frac{q_{j,e}K_j^i C_i'}{C_j'} \tag{7}$$

By substituting Eq. (7) into Eq. (5), we obtain

$$q_{j,e} = \frac{q_0 C_j'}{\sum_{m=1}^{M}(K_j^m C_m')} \tag{8}$$

Substitution Eq. (8) into Eq. (7) gives

$$q_{i,e} = \frac{q_0 K_j^i C_i'}{\sum_{m=1}^{M}(K_j^m C_m')} \tag{9}$$

Therefore, the material balance equations for component i in the pore and in the adsorption site are rearranged as

$$\frac{\partial C_i'}{\partial t} = \bar{D}_i\left(\frac{\partial^2 C_i'}{\partial r^2} + \frac{2}{r}\frac{\partial C_i'}{\partial r}\right) - \frac{ka_v}{\varepsilon_p(1-\varepsilon_v)}\left\{\frac{q_0 K_j^i C_i'}{\sum_{m=1}^{M}(K_j^m C_m')} - q_i\right\} \tag{10}$$

and

$$\frac{\partial q_i}{\partial t} = ka_v\left\{\frac{q_0 K_j^i C'_i}{\sum_{m=1}^{M}(K_j^m C'_m)} - q_i\right\} \tag{11}$$

respectively.

The second term of the right hand side of Eq. (1) shows the mass transfer rate between interstitial fluid and resin phase including its pore. The rate which one particle absorbs or desorbs is calculated using Eqs. (10) and (11) as

$$\int_0^{R_p}\left\{\frac{\partial C_i'}{\partial t} + \frac{1}{\varepsilon_p(1-\varepsilon_v)}\frac{\partial q_i}{\partial t}\right\}\varepsilon_p(4\pi r^2)dr \tag{12}$$

The number of particles in the small column volume $\pi Rc^2 dz$ is

$$n = \frac{3}{4\pi R_p^3}(1-\varepsilon_v)\pi R_C^2\,dz \tag{13}$$