Lithium Isotope Fractionation during Transport through Liquid Membrane with Oligomethylene-bridged Bisphenanthroline Derivatives

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Lithium transport through a liquid membrane with bisphenanthroline derivatives resulted in the isotope fractionation with separation factors between 1.008 and 1.020. The lithium isotope fractionation depended on the length of the oligomethylene bridge between two phenanthroline units. The isotope separation factor was the highest for the sample bridged by heptamethylene groups.

The study of lithium isotope effects is important in the fields not only of industrial nuclear science but also of fundamental and geological sciences. Lithium isotope fractionation by two-phase chemical exchanges have been studied extensively in various systems.[1] The membrane permeation process is one of the most promising methods for separating the lithium isotopes economically. Benzo-15-crown-5 is known to have a high separation factor for lithium isotope in a liquid membrane system.[2]

Oligomethylene-bridged bis-1,10-phenanthroline (Figure 1) has been found to transport lithium ions selectively through a chloroform liquid membrane.[3] The bisphenanthroline derivatives are suitable for the study of the isotope fractionation mechanism, since the rate of lithium ion transport as well as the ion selectivity depends largely on the length of the oligomethylene chain between two phenanthroline units. The present paper describes their isotope fractionation properties for lithium isotope in the liquid membrane system and discusses the fractionation mechanism.

Bisphenanthroline derivatives with different length methylene bridges were prepared as reported previously.[3] We denote them as Bisphen-C5, Bisphen-C6, etc. where the numbers correspond to those of the methylene group. The monomer sample 2,9-dibuthyl-1,10-phenanthroline (which we denote as Di-buphen) was used as a reference.

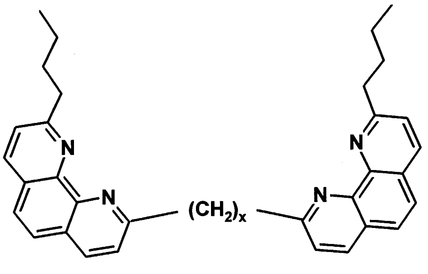

Figure 1. Bis (1,10-phenanthroline) derivatives.

Lithium ion transport studies were carried out using a U-shaped glass tube at 298 K, under the conditions described in Table 1. Each phase was mechanically agitated at 200 rpm. After 48 hours of transport experiment, the lithium concentration of the aqueous receiving-phase was determined by atomic absorption spectrometry. The ^{7}Li/^{6}Li isotopic ratio was determined by a surface ionization technique on a VG 336 mass spectrometer with a wide flight tube. The internal precision was less than 0.005% and the external precision was less than 0.2%. Details of the analytical method are given in our previous paper.[4] The isotopic separation factor (S) is defined as, $S = (^7Li/^6Li)_0 / (^7Li/^6Li)_R$, where $(^7Li/^6Li)_0$ is the lithium isotope ratio (12.35) of the original LiI solution and $(^7Li/^6Li)_R$ that of the aqueous receiving-phase.

Table 1. The values of isotope separation factors(S)

Sample	$[Li]_R$ / mmol dm^{-3}	$(^7Li/^6Li)_R$	S
Di-buphen	43	12.35	1.000
Bisphen-C4	72	12.25	1.008
Bisphen-C5	55	12.12	1.019
Bisphen-C6	75	12.20	1.012
Bisphen-C7	49	12.11	1.020
Bisphen-C8	32	12.25	1.008

Initial conditions: source phase, 15 cm^3 of 3.0 mol dm^{-3} LiI aqueous solution / organic phase, 30 cm^3 of $CHCl_3$ with 0.30 mmol dm^{-3} carrier (0.60 mmol dm^{-3} for Di-buphen) / receiving phase, 15 cm^3 of H_2O.

The results of lithium transport and isotope fractionation are summarized in Table 1. The rates of lithium transport are higher for the samples (Bisphen-C6 and -C4) with even methylene groups than for those with odd methylene groups. This result agrees well with the previous one in which Bisphene-C6 has shown the highest rate of lithium transport among the bisphenanthroline derivatives studied.[3] It also showed the highest selectivity for lithium ions among alkali metal ions (Li^+, Na^+, and K^+). The rate of lithium transport correlates with the stability of the lithium complex in the organic phase. Therefore, the present result suggests that the bisphenanthroline derivative with even methylene groups has a structure sterically suitable to form a stable 1 : 1 complex with lithium ions. The low rate of transport on Bisphen-C8 can be explained by the difficulty in forming the 1 : 1 complex with lithium ions. The methylene chain is so long that Bisphen-C8 may behave partly like a phenanthoroline monomer.

The isotope fractionation property does not correlate with the rate of lithium transport. The monomer type Di-buphen does not show lithium isotope fractionation at all. The separation factor increases in the order Di-buphen < Bisphen-C8, Bisphen-C4 < Bisphen-C6 < Bisphen-C5 < Bisphen-C7. The S values above 1 indicate that the lighter isotope, ^{6}Li, is preferentially fractionated into the receiving-phase and the heavier isotope, ^{7}Li, is enriched in the source-phase. The separation factor on Bisphen-C7 is lower than that on benzo-15-crown-5, but it is comparable to that (S = 1.024) by ion exchange with cubic antimonic acid.[4,5] It is interesting that the samples (Bisphen-C5 and -C7) with slightly low rates of lithium transport give high separation factors for the lithium isotope. This suggests that the ionophore forming a slightly distorted (or unstable) lithium complex shows a preference for lithium isotope fractionation over that in which lithium ions are stably fixed. These results show that lithium isotope fractionation is not simply correlated with the stability of the lithium complex in the organic phase.

The fractionation behaviors were analyzed in terms of membrane transport process and isotope exchange reaction. The present lithium transport belongs to the system of facilitated diffusion of an ion pair. The rate of transport in this system can be expressed as follows,[6]

$$J = DKC_0(C_S^2 - C_R^2) / L(1 + KC_S^2)(1 + KC_R^2) \qquad (1)$$

where D is the diffusion coefficient of the lithium complex in the organic phase, K is the extraction equilibrium constant, C_0 is the concentration of the ligand in the organic phase, C_S is the lithium concentration in the aqueous source-phase, C_R that of the aqueous receiving-phase, and L the thickness of the membrane. Since the lithium transport is slow (up to only 3% transport after 48 h) in the present case, we can assume $1 >> KC_S^2$ and $1 >> KC_R^2$. Then eq. 1 becomes $J = DKC_0(C_S^2 - C_R^2) / L$. This equation indicates that the rate of lithium transport is proportional to the extraction equilibrium constant (K) and the diffusion coefficient (D) of the lithium complex. This equation holds also for lithium isotope transport. Since the diffusion coefficient of the lithium complex is independent of the lithium isotope, we can conclude that the fractionation of the isotope is caused by the difference in the extraction equilibrium constant between the two isotopes.

The equilibrium isotope exchange reaction and equilibrium separation factor (S_{eq}) are given as follows;

$$^{7}\mathrm{Li(aq)} + {}^{6}\mathrm{LiBisphen} \rightleftarrows {}^{6}\mathrm{Li(aq)} + {}^{7}\mathrm{LiBisphen} \qquad (2)$$

$$S_{eq} = (^{7}\mathrm{Li}/^{6}\mathrm{Li})_{aq} / (^{7}\mathrm{Li}/^{6}\mathrm{Li})_{\mathrm{Bisphen}} \qquad (3)$$

The equilibrium separation factor can be written using a reduced partition function ratio (RPFR) as follows,

$$ln\, S_{eq} = ln\, f_{\mathrm{Li(aq)}} - ln\, f_{\mathrm{LiBisphen}} \qquad (4)$$

where $ln\, f_{\mathrm{Li(aq)}}$ is the RPFR of hydrated lithium ions in the aqueous phase and $ln\, f_{\mathrm{LiBisphen}}$ is the RPFR of the lithium complex in the organic phase. The RPFR can be evaluated roughly from the knowledge of the totally symmetric stretching frequency of the bond between the lithium ions and coordination atom, based on Bigeleisen-Mayer's simplifying formula,[7,8]

$$ln\, f \fallingdotseq \Delta M m u^2 n / (24MM') \qquad (5)$$

$$\fallingdotseq (h / 2\pi kT)^2 (\Delta M k_A n / 24MM') \qquad (5')$$

where M and M' are the masses of the heavier and lighter isotopes of lithium, m the mass of the surrounding atom, $\Delta M = M - M'$, n the number of surrounding atoms, $u = hcw/kT$ and w is the total symmetric stretching frequency. Notations *h* and *k* are Planck and Boltzmann constants, respectively, T is temperature, and k_A the force constant for vibration. The RPFR of hydrated lithium ions has been calculated as 1.063 using the results of Raman spectroscopy.[5] Then eq. 4 becomes, by assuming the coordination number of four for the lithium complex;

$$ln\, S_{eq} \fallingdotseq 1.063 - \mathrm{const.} \cdot k_A \qquad (4')$$

Equation 4' shows that the equilibrium separation factor decreases with the increase of force constant (k_A) of the total symmetric stretching vibration of the lithium complex. This suggests that the ionophore with a higher selectivity for lithium ions gives a lower isotope separation factor. This may be the reason for the lower S values on Bisphen-C6 and -C4 than on Bisphen-C5 and -C7. The low S value on Bisphen-C8 can be explained by the difficulty in forming a 1:1 complex with lithium ions. The S value may approach to that (1.000) of Di-buphen with an increase in the length of methylene bridge.

The present results will create a new approach to design ionophores effective for lithium isotope separation.

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