Temperature Dependence of Lithium Isotope Effects in Ion Exchange Electromigration

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The isotope separation coefficient of lithium electromigration through a cation exchange membrane is determined at 6, 11, 20 and 40 °C. It is found that this coefficient increases with temperature while the slope of the isotope distribution in the band decreases with increasing temperature. These tendencies are opposite to those usually observed in ion exchange chromatography.

Introduction

Isotope separation by ion exchange electromigration is a combination of chromatography and electromigration in aqueous solution. As to the latter process, Brewer, Madrosky and Straus accomplished isotope separation of potassium, chlorine and copper [1–3], Chemla and Bonnin of boron, lithium, sodium and rubidium [4–7], and Bakulin, Fiks, Konstantinov et al. of lithium [8–11]. Martin and Lübke used diaphragm tubes [12, 13], and Behne, Bilal and Wagener capillary tubes [14–16]. In experiments using wetted paper strips the isotope effects were found to increase with temperature [5, 6]. A review on the isotope effects in electromigration was given by Klemm and Heinzinger [17].

In previous studies the present authors have measured isotope effects in electromigration using a cation exchange membrane as migration medium [18–21]. The chemical characteristics of the cation exchange membrane resemble those of gel type spherical cation exchange resins. The ion exchange resin contains usually 40 to 50% of water and fixed ions at a concentration of approximately 2 equivalents per liter. Thereby the ion exchange resin is frequently regarded as a concentrated electrolyte solution of $4 - 6$ M (mole/dm^3). The anions, however, are fixed in a cation exchange membrane. This may prohibit the formation of higher order complexes between the movable cations and fixed anions. Also the fixation of the anions reduces the diffusivity of the cations.

In the present work we have studied the temperature dependency of the isotope effect of lithium electromigration through a cation exchange membrane.

Experimental

Materials

The cation exchange membrane Aciplex CK-1, a homogeneous, strongly acidic type stylene divinylbenzen copolymer resin, was supplied by Asahi Chemical Industry Co. Prior to use the membrane was converted to the H$^+$ form and cut into strips (2 cm wide and 60 cm long). Other chemicals were of reagent grade.

Procedure

A pretreated cation exchange membrane was set in the electromigration cell immersed in a thermostated water bath, cf. Figure 1. The anode compartment was filled with 1 M LiNO$_3$ containing a small amount of LiCO$_3$ powder which worked as a pH buffer preventing the anode solution from lowering its pH. The cathode compartment was filled with a 0.1 M HNO$_3$ solution. The electromigration of the lithium ions towards the cathode was performed at constant current. A sharp band boundary was forming at the front. The experimental conditions of four runs are listed in Table 1.

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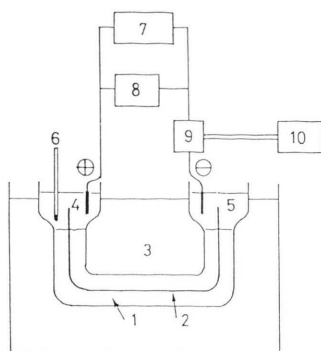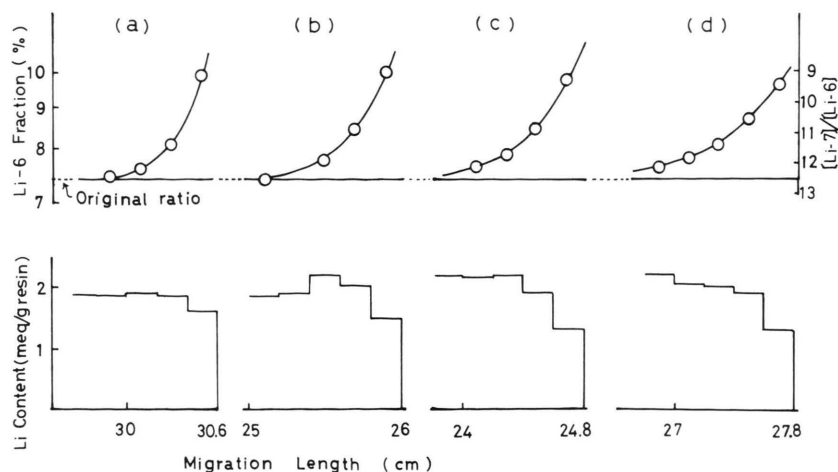
Fig. 1.

Fig. 2.

Fig. 1. The experimental arrangement. 1. Carbontetrachloride. 2. Cation exchange membrane. 3. Thermostated water bath. 4. Anode solution. 5. Cathode solution. 6. Thermometer. 7. DC power supply. 8. Voltmeter. 9. Ammeter. 10. Recorder.

Fig. 2. Lithium contents and isotopic ratios in the frontal segments of the band. a) Run 1 (6 °C), b) Run 2 (11 °C), c) Run 3 (20 °C), d) Run 4 (40 °C).

After the migration the membrane was taken out of the cell and the front part of the lithium band was cut into segments of 2 mm width. The lithium in the segments was leached by 1 M HNO_3 and the concentration of the lithium in the solutions was measured by flame photometry at 673 nm. The rest of the leaching solution was dried and the lithium in it was converted to LiI for mass spectrometry by repeatedly adding drops of an HI solution. The $^6Li/^7Li$ ratios in the samples were determined with a mass-spectrometer MAT CH-5.

Results and Discussion

The results of the isotope analyses and the concentration measurements are plotted in Figure 2. The isotope separation coefficient ε, which indicates the relative mobility difference, is calculated from the isotope analysis data presented in Fig. 2 by using the equation

$$\varepsilon = \Sigma_j f_j (R_j - R_0)/Q R_0 (1 - R_0), \qquad (1)$$

where f is the contents of lithium in a segment, R the atomic fraction of the isotope ^6Li, Q the total amount of lithium in the migration band, and the

Table 1. Experimental conditions and result of electro-migration.

Run	1	2	3	4
Temperature (°C)	6	11	20	40
Current density (mA/cm²)	130	125	120	120
Final voltage* (V)	670	390	280	180
Migration length (cm)	30.6	26	24.8	27.8
Velocity (cm/h)	2.2	2.2	2.1	2.0
$\varepsilon \times 10^3$**	2.3	3.2	3.8	4.5
k_s (cm^{-1})	5.8	4.8	4.1	2.7

* at the end of the migration.
** The error of each ε is estimated as $\pm 3 \times 10^{-4}$.

subscripts 0 and j indicate the original solution and the j-th segment. The calculated ε's are given in Table 1 and plotted in Figure 3.

The obtained ε at 20 °C agrees well with the previously reported values of 3.6×10^{-3} and 3.8×10^{-3} at the band velocities of 3.2 and 3.7 cm/hr, respectively [18]. These values also coincide with the data reported by Bonnin and Chemla [4]. They obtained $\varepsilon = 3.8 \times 10^{-3}$ for the lithium isotopes using wetted filter paper at room temperature. Bakulin et al. [8] and Konstantinov et al. [10] obtained larger values of ε: $7-12 \times 10^{-3}$ for an aqueous solution of 5 M Li_2SO_4.
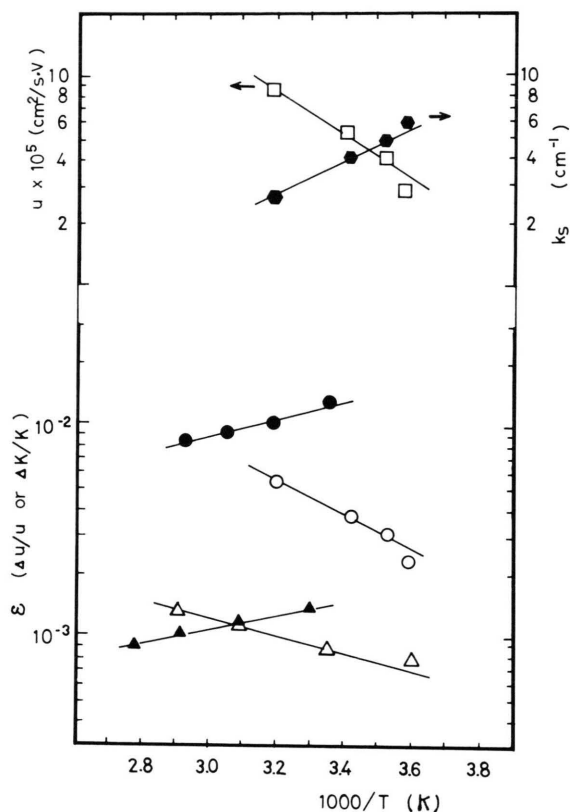
Fig. 3. Arrhenius plots of separation coefficients (ε), apparent mobilities (u) and slope coefficients (k_s). ε's of ion exchange electromigration; lithium in this work: $\circ$ and rubidium [21]: $\triangle$. ε's of chemical exchange systems; boron by using anion exchange resin [23]: $\bullet$ and $U\,(\text{IV}) - U\,(\text{VI})$ [24]: $\blacktriangle$. Here K is the chemical exchange constant.

The apparent mobility of the lithium ions, u, is defined as the velocity of the front of the band, multiplied with the length of the band and divided by the voltage applied to the band. In the final stage of the experiment the voltage applied to the band is practically identical with the voltage between anode and cathode. The apparent mobilities of the lithium ions calculated that way are plotted in Figure 3.

Separation Coefficient

In Table 1 and Fig. 3 it is seen that the separation coefficient ε for lithium increases with increasing temperature. This tendency has also been found for

rubidium electromigration in the same cation exchange membrane [21], cf. Figure 3. Chemical exchange systems, on the other hand, show usually the opposite tendency. The reported separation coefficients of a boron chemical exchange system using anion exchange chromatography [23] and a uranium chemical exchange system between $U\,(\text{IV})$ and $U\,(\text{VI})$ [24] are also plotted in Figure 3. Therefore the results of the present work indicate that chemical exchange reactions were not playing a major role in the isotope effects.

On the other hand, the residence time of the water molecules near the Li^+ ions decreases with increasing temperature, and consequently the effective relative mean difference between the isotopes becomes larger at higher temperatures. This would explain why ε increases with increasing temperature. It should be noted, however, that the isotope effect of lithium ion migration was reported to have a minimum at 60 °C for aqueous Li_2SO_4 [8] and a minimum at 40 °C for aqueous CH_3COOLi [14]. This indicates that classical kinetic effects as well as chemical effects may be involved in the migration of light ions such as Li^+.

Slope Coefficient

The isotope enrichment curves in Fig. 2 are the steeper the lower the temperature. To quantitatively discuss the steepness, the slope coefficient k_s was introduced [22]:

$$r - r_0 = (r_{\max} - r_0) \exp\left(-k_s x\right), \qquad (2)$$

where r is the isotopic ratio ($[^6\text{Li}]/[^7\text{Li}]$) and x the distance from the front of the band. The calculated slope coefficients are listed in Table 1.

The decrease of k_s with increasing temperature was also observed in the rubidium ion exchange electromigration experiments: $k_s = 5.73$, 4.77, 3.79 cm^{-1} for 5, 25, 50 °C, respectively. Evidently the increase of diffusion coefficients with temperature is the reason for this behaviour. Usually chemical exchange isotope enrichment systems show the opposite tendency. Since the reaction rates between the two phases are enhanced at elevated temperatures, the chemical equilibrium is more rapidly attained at high temperatures and therefore the en-

richment curves become sharper with increasing temperature. In a forthcoming paper the Hight of an Equivalent Theoretical Plate (HETP) in these and other experiments shall be evaluated and discussed.

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