

Rubidium Isotope Separation by Constant Current Electromigration in a Cation-exchange Membrane

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Separation of rubidium isotopes (^{85}Rb , ^{87}Rb) by electromigration in a cation exchange membrane has successfully been carried out in a band operation manner at 25 °C. The migration velocity has been varied from 2.5 to 12.1 cm/h. There existed a wide non-isotope-fractionated zone between the ^{85}Rb enriched zone at the front and the ^{85}Rb depleted zone at the rear of the band. The single stage separation factor was about 1.0009 and was independent of the migration velocity, migration length and operation technique at a given temperature. The steepness of the ^{85}Rb accumulation curves, increased with increasing migration velocity.

Key words: Isotope separation, isotope effect, electromigration, rubidium isotope, ion-exchange membrane.

I. Introduction

The methods of isotope separation by electromigration may be classified into two groups, depending on whether the electrolyte contains water (wet method) or is free from it (dry method). As to Rb isotope separation, wet electrolytes have been used by Ramirez [1], Bonnin and Chemla [2], Fiks [3], and Wagener [4], and dry electrolytes (molten salts) by Jordan and Klemm [5], Mamgalo, Arnikaar and Chemla [6], Lundén, Floberg and Mattsson [7], Okada [8], and Kanno [9]. In general, in dry systems the isotope effects are larger than in wet systems.

Electromigration in an ion-exchange membrane is a wet method. Nevertheless the magnitude of the isotope effect for the Li isotopes observed there is in between those of the dry and other wet methods.

A cation-exchange membrane is an appropriate supporting medium for isotope separation by electromigration [10]. Cations are selectively adsorbed by a cation-exchange membrane and migrate in it while anions do not enter the wet membrane. The adsorbed cations are not subject to convective mixing of their isotopes, which is a great advantage of electromigration in a cation-exchange membrane.

The cation-exchange membrane preserves its intrinsic properties as a cation exchanger, which was demonstrated by experiments on the mutual separation of alkali metal ions [11].

In [12] we did show that the relative mobility difference between the ^{85}Rb and ^{87}Rb ions in a cation-exchange membrane increases with increasing temperature, which is attributable to the dehydration of the Rb ions at higher temperatures. In the present paper, we report on the migration velocity effect on the Rb isotope enrichment. The experiments were carried out in a band operation manner, so that ^{85}Rb enrichment at the front and ^{87}Rb enrichment at the rear could be studied.

II. Experimental

A) Cation-exchange Membrane

The cation-exchange membrane was a non-reinforced, homogeneous, strongly acidic (exchange group: $-\text{RSO}_3^-$) cation-exchange membrane, Aciplex CK-1. It was used in the form of a strip with 2 cm \times 0.25 mm cross section and was conditioned to the H-form before the migration experiments.

B) Migration Procedure

First the membrane was set into the migration apparatus shown in Figure 1. Then the migration tube was filled up to the anolyte and catholyte out-

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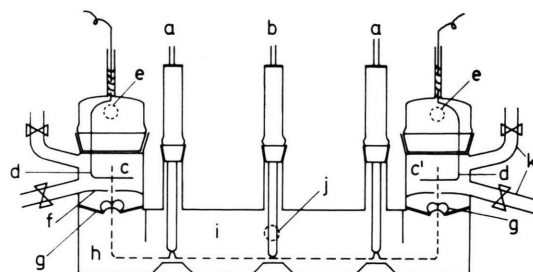


Fig. 1. Apparatus for electromigration. a) Detectors for the potential difference; b) Thermister; c) Catholyte, HCl; c') Anolyte (RbCl + RbOH) or (LiCl + Li₂CO₃); d) Pt electrodes; e) Outlet for gas; f) Boundary between electrolyte solution and synthetic oil; g) Magnetic clip covered with teflon; h) Cation-exchange membrane (Ashiplex CK-1); i) Synthetic oil (flonlube FL-500; $(-\text{CF}_2 - \text{CFCI}-)_n$; j) Inlet of synthetic oil; k) Inlet and outlet of electrolyte solutions.

lets with synthetic oil, Flonlube FL-500 ($d=1.8$), which is a good insulator and used as coolant. The anolyte was a 1:1 mixture of a 0.1 M (1 M = 1 mol/dm³) RbCl and a 0.1 M RbOH solution. The catholyte was 1 M HCl. The whole assembly was put into a water bath whose temperature was kept at 25.0 ± 0.1 °C.

By applying direct electric current, the Rb ions in the anolyte were introduced into the membrane and migrated towards the cathode. When the Rb adsorption zone had grown to ca. 5 cm, the current was suspended for a short while, during which the anolyte was replaced by a 1:1 mixture of a 0.5 M LiCl solution and a 0.1 M Li₂CO₃ solution and the membrane in the anolyte was conditioned to the Li-form batchwise. On resuming the current supply, the band operation manner commenced. When the migration distance had reached ca. 20 cm, the current was stopped and the strip was taken out and cut into fractions with widths of ca. 2–5 mm.

C) Analysis

The Rb and Li contents of each fraction were determined by the previously reported method [12]. The ⁸⁵Rb/⁸⁷Rb isotopic ratios in the fractions were determined using a MAT 261 mass spectrometer with the thermal ionization technique.

Five experiments were carried out. The experimental conditions are summarized in Table 1. The first 4 experiments (Run Nos. 201, 202, 203, and 204) were made as similar as possible except for the

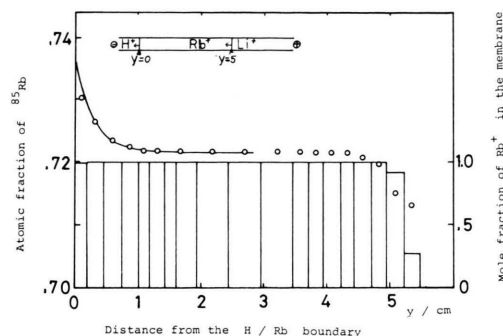


Fig. 2. Chromatogram and ⁸⁵Rb atomic fractions of Run No. 201.

current density to see the effect of the migration velocity on the isotope enrichment. Experiments with current densities > 0.54 A/cm² were not possible because of the thermal deterioration of the membrane. In the last experiment (Run No. 211), the membrane was pulled back towards the anode in a countercurrent manner.

III. Results and Discussion

Figures 2 through 5 show the chromatograms and the atomic fractions of ⁸⁵Rb of experiments No. 201, 202, 203, and 204, respectively. The configuration of the migration system and the definition of the coordinate system are shown in the inset of Figure 2. The histograms show the mole fractions of Rb ions relative to the exchange capacity of the membrane, and the open circles are ⁸⁵Rb atomic fractions. The migration velocities obtained at the current densities in Table 1 are tabulated in the second column of Table 2.

In Fig. 2 it is seen that the H/Rb boundary is very sharp while the Rb/Li boundary is diffuse. This is because the difference in the mobilities of H⁺ and Rb⁺ is much larger than that in those of Rb⁺ and Li⁺; the mobilities of H⁺, Rb⁺ and Li⁺ in the membrane relative to that of K⁺ are 3.78, 0.972 and 0.431, respectively [11]. It is also seen in Fig. 2 that the ranges of isotope fractionation at the front and the rear of the band amount to ca. 1 cm and that there is a long non-isotope-fractionated zone between them. This makes it possible to discuss the two ranges separately.

Table 1. Experimental conditions.

Run No.	Temp. (°C)	Migration length (cm)	Migrating ions in the membrane	Current density (A · cm ⁻²)	Applied voltage (V)
201	25	20.5	⊖ Pt: H ⁺ Rb ⁺ (5.2 cm) Li ⁺ : Pt ⊕	0.09	35–131
202	25	19.5	⊖ Pt: H ⁺ Rb ⁺ (5.0 cm) Li ⁺ : Pt ⊕	0.18	68–264
203	25	20.3	⊖ Pt: H ⁺ Rb ⁺ (5.5 cm) Li ⁺ : Pt ⊕	0.36	115–400
204	25	20.5	⊖ Pt: H ⁺ Rb ⁺ (5.5 cm) Li ⁺ : Pt ⊕	0.54	165–510
211	25	43.5	⊖ Pt: H ⁺ Rb ⁺ (5.0 cm) Li ⁺ : Pt ⊕	0.36	150–500

Table 2. Observed migration velocities and accumulation-curve parameters.

Run No.	Migration velocity	Obtained parameter			
	(cm · h ⁻¹)	<i>k'</i> (cm ⁻¹)	<i>R</i> _{<i>t</i>0}	<i>A</i>	
201	2.46	3.77	0.72169 ± 0.00002	0.01576 ± 0.00016	Frontal part of Rb band
202	4.54	4.95	0.72162 ± 0.00005	0.01889 ± 0.00062	Frontal part of Rb band
203	8.08	5.31	0.72156 ± 0.00002	0.02186 ± 0.00021	Frontal part of Rb band
204	12.1	5.73	0.72171 ± 0.00002	0.02838 ± 0.00029	Frontal part of Rb band
211	8.56	3.28	0.72172 ± 0.00003	0.03646 ± 0.00032	Frontal part of Rb band
F2*	8.94	4.77	0.72188 ± 0.00010	0.02103 ± 0.00031	Breakthrough

* Reference [12].

The observations made in the experiments No. 202, 203, and 204, corroborate those made in the experiment No. 201.

In all experiments, the broad Rb/Li boundaries gave irregular ⁸⁵Rb curves and the maximum enrichment is not necessarily found in the rearmost fraction. When the boundary is diffuse, one needs to consider the ternary system consisting of the two Rb isotopes and Li. A numerical analysis of such systems has been given in [13, 14].

Contrary to the Rb/Li boundaries, the H/Rb boundaries are very sharp. In the following we limit our discussion to the ⁸⁵Rb accumulation in the frontal region.

In [12] we proposed an empirical equation that expresses the ⁸⁵Rb accumulation curve when the enrichment is not high,

$$R_i = A \cdot \exp(k' \cdot y) + R_{i0}, \quad (1)$$

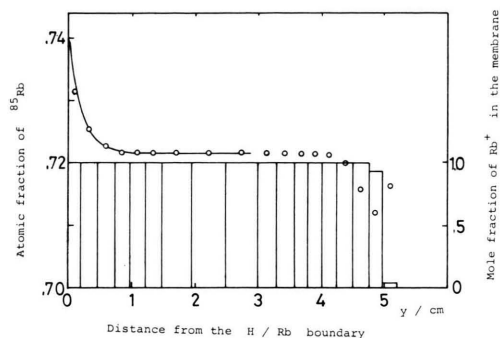
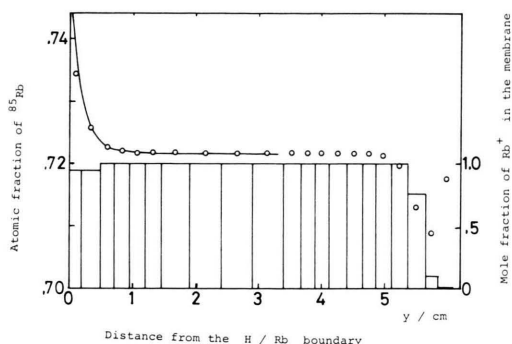
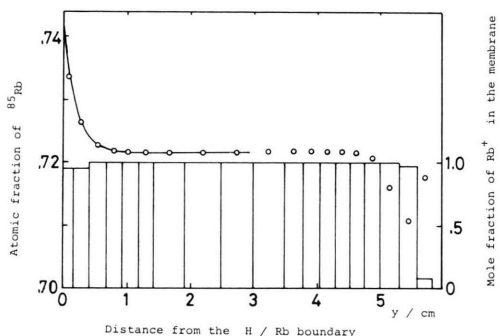
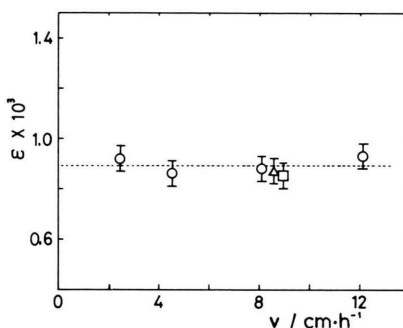
where *R_i* is the atomic fraction of ⁸⁵Rb at the distance *y* from the Rb/H boundary at the time *t* (*R_i* = *R_{i0}* at *t* = 0), *A* is a function of *t* (*A* = 0 at *t* = 0) and *k'* is a function of the migration velocity of Rb⁺ and the interdiffusion coefficient of its isotopes. The exact analytical ⁸⁵Rb curve can be obtained from a publication of Klemm [15].

Our data except for the most frontal points have been least-squares fitted to (1) and the obtained parameter values are summarized in Table 2. Comparing Runs No. 201, 202, 203, and 204, it is seen that *k'* increases with the migration velocity. Figures 2–5 show that also the depletion curves of ⁸⁵Rb at the rear of the bands are the sharper the larger the migration velocity. Comparison of Runs No. 203 and 211 indicates that *k'* decreases with increasing migration length. This observation from a single experiment should be checked, however. The solid lines in Figures 2–5 are drawn using the parameter values in Table 2. The agreement of the experimental and calculated results is excellent, showing that (1) is a good expression of the ⁸⁵Rb accumulation curve.

The migration velocity ratio of ⁸⁵Rb and ⁸⁷Rb, *S* can be calculated by the equation

$$S = v_{85}/v_{87} = 1 + \left[\sum_i \{(R_i - R_{i0}) f_i\} / [Q R_{i0} (1 - R_{i0})] \right], \quad (2)$$

where *v_j* (*j* = 85, 87) is the migration velocity of the isotope *j*, *Q* the total exchange capacity of the membrane strip used for the Rb migration, *f_i* and *R_i* are the Rb content and the atomic fraction of ⁸⁵Rb in the *i*-th fraction, respectively, and the summation is

Fig. 3. Chromatogram and ^{85}Rb atomic fractions of Run No. 202.Fig. 5. Chromatogram and ^{85}Rb atomic fractions of Run No. 204.Fig. 4. Chromatogram and ^{85}Rb atomic fractions of Run No. 203.Fig. 6. $\varepsilon (= S - 1)$ vs. v (migration velocity) plots. \circ 's: results of 20 cm migration in band operation (present work); \triangle : the result of 43.5 cm migration in band operation (present work); \square : the result of 20 cm migration in breakthrough operation (Ref. [12]), all at 25 °C.

taken over the entire ^{85}Rb enriched zone. Equation (2) is applicable not only to electromigration in various media such as molten salts and ion-exchange membranes but also to ion-exchange chromatography.

In the Aciplex CK-1 membrane the RSO_3^- anion, which is the counterion of the Rb^+ cation, is fixed to the skeleton of the membrane. Other anions present in the system, i.e., Cl^- and OH^- , can hardly enter the membrane. Thus the transport number of Rb^+ in the membrane is practically unity [11] and there is no difference between external and internal mobilities in our case. The separation factors obtained in this work, together with the results of our earlier work [12] and those of electromigration in molten salts [5–9] are listed in Table 3. In some papers, the Rb isotope effect is expressed in terms of the mass effect, $-\mu$. The S -values in these cases are

calculated by the relation

$$S = 1 - (2/86) \mu. \quad (3)$$

Table 3 shows that there is no substantial difference in the S -values for electromigration in the cation-exchange membrane and in molten salts, which is contrary to the results obtained for Li isotope separation. In Li isotope separation, electromigration in molten salts given much larger separation factors than electromigration in the cation-exchange membrane. In the case of Rb migration, the residence time of the water molecules near the Rb^+ ions decreases with increasing temperature and consequently the effective relative mass difference between the two isotopes becomes larger at higher temperatures. Thus, the value of the separation factor increases with increasing temperature. In migration at room temperature there is a small but ap-

Table 3. Comparison of the separation factors obtained in some electromigration systems. Only the system that gives the largest separation factors is cited from each reference.

Type	System	Temp. (°C)	Migration time (h)	Single stage separation factor	Reference
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	8.3	1.00092	No. 201 (this work)
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	4.3	1.00086	No. 202 (this work)
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	2.5	1.00088	No. 203 (this work)
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	1.7	1.00093	No. 204 (this work)
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	5.1	1.00087	No. 211 (this work)
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	25	2.3	1.00085	Ref. [12]
Wet method	Rb ⁺ : - SO ₃ ⁻ (fixed group in medium)	70	2.3	1.00136	Ref. [12]
Wet method	RbCl (3 M, aqueous solution)	20		1.00108	Ref. [3]
Dry method	RbNO ₃ (fused): NO ₃ ⁻ (counter current)	445	23	1.00142	Ref. [7]
Dry method	RbBr (fused): Br ⁻ (counter current)	852		1.00184	Ref. [5]
Dry method	RbNO ₃ (fused): NO ₃ ⁻ (counter current)	360	46	1.00093	Ref. [8]
Dry method	RbI (fused): I ⁻ (counter current)	730	26.5	1.0020	Ref. [9]

preciable hydration effect which reduces the effective relative mass difference of the Rb isotopes and thus makes the *S*-values smaller than those obtained in molten salt migration. This disadvantage of electromigration in the membrane is, however, compensated by the fact that the system can be operated at room temperature. Thus, electromigration in the cation-exchange membrane may be a promising method for Rb isotope separation.

In Fig. 6, $\varepsilon = S - 1$ is plotted against the migration velocity of the Rb ions. It is clearly seen that the Rb separation factor is independent of the migration velocity, the migration length and the operational technique (breakthrough or band operation) at 25 °C.

IV. Conclusion

The main findings of the present work are as follows.

In our system the separation factor, *S*, is about 1.0009 at 25 °C, and is independent of the migration velocity and migration length.

The *k'*-value, which is an indicator of the steepness of the isotope accumulation, increases with increasing migration velocity. The thermal deterioration of the membrane sets a limit to the migration velocity.

The present method is simple and effective for Rb isotope separation.

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