On the Distribution of Isotopes in a Separation Column in Countercurrent Electromigration of Molten Binary Mixtures

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Z. Naturforsch. **38 a,** 97 – 105 (1983); received September 29, 1982

Dedicated to Professor Alfred Klemm on the occasion of his 70th birthday

In countercurrent electromigration of molten binary mixtures with a common anion in which each cation is composed of two isotopes, the less mobile cation is enriched toward the anode, and, at the same time, the isotopes of this cation become distributed in a complicated way. Thus, the zone next to the anode where the heavy isotope is enriched is immediately followed by a region where a slight enrichment of the light isotope occurs, while for the more mobile cation the heavy isotope is enriched in both these regions. This phenomenon has been observed in experiments with the systems $(Li-K)NO_3$ and $(Li-K)Cl$ and it has also been reproduced by analyzing the flow equations for the constituent components numerically with a computer. It is verified that the existing formulation for the calculation of the elementary separation factor holds independent of whether there is such an anomaly in the isotope distribution for the less mobile cation.

Introduction

In countercurrent electromigration of molten salts, which was invented by Klemm [1, 2], the light cationic isotope is usually enriched toward the cathode and the heavy one toward the anode. In pure salt systems such as $LiNO_3$ [3] and KNO_3 [4], however, an anomaly in the isotope distribution has been observed around the mouth of a separation column which opens into a large cathode compartment; light isotopes such as ^6Li and ^{39}K are slightly enriched in this part of the column, while the isotopic composition in the large cathode compartment remained unchanged. The interpretation of this phenomenon is still under consideration.

Apart from this, in a molten mixture of $(Li-K)_2SO_4$, a clear enrichment of the light isotope ^{39}K was found in some runs in a region between the zone near the anode with the expected enrichment of ^{41}K and one in which the initial composition remained [5]. This phenomenon could not, however, be interpreted at that time.

The purpose of the present paper is to show experimentally that the latter phenomenon is a very common one in such binary mixtures and also to demonstrate that the profile of the apparently anomalous distribution of isotopes can be reproduced by solving numerically the differential equations for the flow of isotopic ions.

It will also be shown that even in such a case the elementary separation factor, or the mass effect, can be calculated from a formula that is well established for the case in which the isotopes are "normally" distributed.

Experimental Results

A large number of electromigration experiments have been carried out with approximately eutectic mixtures of $(Li-K)Cl$ and of $(Li-K)NO_3$. The electromigration cells were similar to those employed in previous experiments [6]. Thus, a separation column densely packed with silica powder of 100 – 150 mesh was held in a large cathode compartment. Depending on the type of the melt either chlorine or a mixture of nitrogen dioxide and oxygen was introduced at the cathode. The entire results will be published in the near future. We will show here only the results for the distribution of the chemical species and isotopes for a couple of typical examples.

In the case of the chloride, K^+ migrated faster than Li^+ at all accessible temperatures at the eutectic mixture, about 60 mol% LiCl. Therefore, Li^+

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Table 1. Distribution of isotopes after electromigration of molten (Li−K)Cl. Electromigration condition, Voltage: 55 V, Electric current: 100−120 mA, Duration: 16.3 h, Transported charge: 6275 C, Temperature: 553−556 °C, Separation column: Int. diam.: 4 mm, Length: 191 mm, Diaphragm material: Quartz powder (100−150 mesh), Initial composition: $p_{\mathrm{Li}}^{0} = 0.595 \pm 0.005$, $^{7}\mathrm{Li}/^{6}\mathrm{Li} = 12.193 + 0.054$, $^{41}\mathrm{K}/^{39}\mathrm{K} = 0.07130 \pm 0.00015$.

Fr.No.	Length (mm)	LiCl (millimole)	KCl (millimole)	p_{Li}	$^{7}\mathrm{Li}/^{6}\mathrm{Li}$	$^{41}\mathrm{K}/^{39}\mathrm{K}$
1	13	2.386 ± 0.012	0.791 ± 0.014	0.751 ± 0.006	16.345 ± 0.028	0.07609 ± 0.00018
2	13	1.443 ± 0.008	0.424 ± 0.013	0.773 ± 0.008	13.048 ± 0.029	0.07387 ± 0.00028
3	18	1.986 ± 0.010	0.662 ± 0.013	0.750 ± 0.006	11.927 ± 0.024	0.07219 ± 0.00015
4	23	2.272 ± 0.012	0.860 ± 0.015	0.725 ± 0.006	11.808 ± 0.027	0.07173 ± 0.00022
5	18	1.729 ± 0.009	0.719 ± 0.013	0.706 ± 0.006	11.912 ± 0.017	0.07214 ± 0.00021
6	19	1.615 ± 0.009	0.816 ± 0.015	0.664 ± 0.006	12.041 ± 0.016	0.07176 ± 0.00020
7	20	1.543 ± 0.008	0.924 ± 0.016	0.625 ± 0.006	12.056 ± 0.020	0.07182 ± 0.00024
8	22	1.801 ± 0.009	1.153 ± 0.021	0.610 ± 0.006	12.146 ± 0.024	0.07104 ± 0.00009
9	17	1.415 ± 0.008	0.924 ± 0.016	0.605 ± 0.006	12.161 ± 0.037	0.07155 ± 0.00011
10	15	1.372 ± 0.008	0.863 ± 0.015	0.614 ± 0.006	12.236 ± 0.056	0.07130 ± 0.00018
11	13	1.472 ± 0.008	0.886 ± 0.016	0.624 ± 0.006	12.096 ± 0.029	0.07183 ± 0.00016

The values of ε_c, $\varepsilon_{\mathrm{Li}}$, and ε_{K} are calculated to be − 0.138 ± 0.005, 0.0141 ± 0.0003, and 0.0036 ± 0.0002, respectively, from Fractions No. 1 to No. 7.

Table 2. Distribution of isotopes after electromigration of molten (Li−K)NO_3. Electromigration condition; Voltage: 135−160 V, Electric current: 60−80 mA, Duration: 27.7 h, Transported charge: 6823 C, Temperature: 188−196 °C, Separation column: Int. diam.: 4 mm, Length: 142 mm, Diaphragm material: Quartz powder (100−150 mesh), Initial composition: $p_{\mathrm{Li}}^{0} = 0.415 \pm 0.004$, $^{7}\mathrm{Li}/^{6}\mathrm{Li} = 12.477 \pm 0.027$, $^{41}\mathrm{K}/^{39}\mathrm{K} = 0.07084 \pm 0.00020$.

Fr.No.	Length (mm)	$LiNO_3$ (millimole)	KNO_3 (millimole)	p_{Li}	$^{7}\mathrm{Li}/^{6}\mathrm{Li}$	$^{41}\mathrm{K}/^{39}\mathrm{K}$
1	9	0.025 ± 0.001	0.774 ± 0.016	0.031 ± 0.001	24.257 ± 0.050	0.07325 ± 0.00020
2	16	0.084 ± 0.002	1.533 ± 0.019	0.052 ± 0.001	15.468 ± 0.132	0.07083 ± 0.00025
3	18	0.684 ± 0.015	1.312 ± 0.018	0.343 ± 0.006	15.261 ± 0.067	0.06976 ± 0.00017
4	14	0.717 ± 0.015	0.984 ± 0.013	0.422 ± 0.006	12.860 ± 0.024	0.07074 ± 0.00020
5	18	0.865 ± 0.016	1.154 ± 0.014	0.428 ± 0.005	12.522 ± 0.040	0.07094 ± 0.00046
6	18	1.025 ± 0.018	1.263 ± 0.018	0.448 ± 0.006	12.461 ± 0.023	0.07088 ± 0.00051
7	26	1.471 ± 0.022	1.880 ± 0.021	0.439 ± 0.005	12.451 ± 0.017	0.07058 ± 0.00014
8	23	1.107 ± 0.018	1.780 ± 0.024	0.383 ± 0.005[a]	12.327 ± 0.042	0.07107 ± 0.00019

The values of ε_c, $\varepsilon_{\mathrm{Li}}$, and ε_{K} are calculated to be 0.0025 ± 0.0004, 0.0060 ± 0.0002, and 0.00011 ± 0.00015, respectively, from Fractions No. 1 to No. 4.

[a] The separation column was left in open air for a few weeks after electromigration and the part near the bottom became wet; thus, it is likely that more $LiNO_3$ than KNO_3 was lost which would account for the low p_{Li} of sample 8.

was enriched and K^+ was depleted toward the anode in the separation column. In all the runs, the heavier isotopes ^{7}Li and ^{41}K were enriched in the zone next to the anode and there followed a zone where the isotope enrichments went in opposite directions. Thus while there still was a detectable enrichment of the heavy ^{41}K there was a change for lithium, so that the light isotope ^{6}Li was enriched instead, see Table 1, samples 3−7.

For nearly eutectic mixtures of (Li−K)NO_3 (about 41 mol% $LiNO_3$), it was found that the mobility of Li^+ was greater than that of K^+ below about 250 °C and vice versa above this temperature [7, 8]. In the former case there were some indications, but not clear evidence of an anomalous distribution for the K^+ isotopes. An example of the isotope distribution is given in Table 2. In the latter case an anomalous distribution of Li^+ isotopes was clearly observed in all the runs. The results of such an experiment is shown in Figure 1.

Numerical Calculations

For binary systems with a common anion, in which each cation is composed of two isotopes, the distributions of the cations and their isotopes can be estimated by means of a computer. Since all the required data are available for the (Li−K)NO_3 system, this will be chosen as an example for the cal-

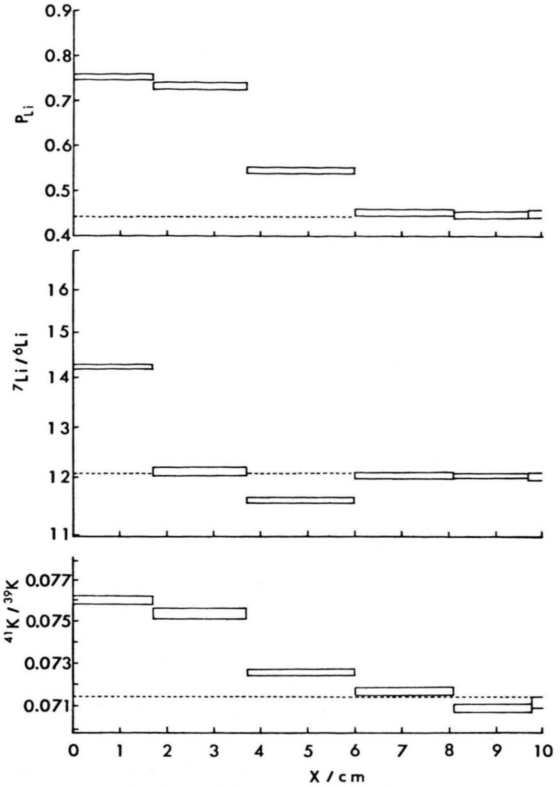

Fig. 1. Distribution of the chemical and isotopic compositions in a separation column for electromigration of (Li–K)NO_3. Voltage: 90–92 V, Electric current: 125 mA, Duration: 15.5 h, Transported charge: 6875 C, Temperature: 378–382 °C, Separation column: Int. diam.: 4 mm, Length: 202 mm, Diaphragm material: Quartz powder (100–150 mesh), Initial composition: $p^0_{Li} = 0.427 \pm 0.007$, $^7Li/^6Li = 12.139 \pm 0.053$, $^{41}K/^{39}K = 0.07141 \pm 0.00009$. The dotted lines correspond to the initial compositions. The length of the bars shows that of the fractions. The width corresponds to twice the standard deviation of errors. The composition of the salt surrounding the anode, i.e. above the separation column, is omitted in this figure. Calculations including that sample and three from the separation column (up to $x = 6$ cm) give $\varepsilon_c = -0.107 \pm 0.004$, $\varepsilon_{Li} = 0.0085 \pm 0.0012$ and $\varepsilon_K = 0.0023 \pm 0.0010$.

culation. A similar discussion holds, of course, for other similar systems as well.

In a separation column, the flows J per cross sectional area in the direction from the anode to the cathode are expressed for the ions specified by the subscripts by [1, 9]

$$J_{Li} = (u_{Li} - \bar{u})\, c_{Li} - D_{Li}(\partial c_{Li}/\partial x)\,, \tag{1}$$

$$J_K = (u_K - \bar{u})\, c_K - D_K(\partial c_K/\partial x)\,, \tag{2}$$

$$J_{NO_3} = (-u_{NO_3} - \bar{u})\, c_{NO_3} - D_{NO_3}(\partial c_{NO_3}/\partial x)\,, \tag{3}$$

where u is the scalar component of the external velocity, $\bar{u}$ the velocity of the countercurrent flow, c the concentration and D the effective diffusion coefficients.

From the condition of the electrical neutrality,

$$z_{Li}\, c_{Li} + z_K c_K + z_{NO_3} c_{NO_3} = 0\,, \tag{4}$$

where z is the charge number, and therefore $z_{Li} = z_K = +1$ and $z_{NO_3} = -1$.
In countercurrent electromigration of molten salts, there is generally no volume flow in the separation column:

$$J_{Li} V_{LiNO_3} + J_K V_{KNO_3} = 0\,, \tag{5}$$

where V is the molar volume. The additivity of the molar volume for the mixture holds in this case [10] as well as many other cases.

The electrical current density I_d is expressed by

$$I_d = F(z_{Li} J_{Li} + z_K J_K + z_{NO_3} J_{NO_3})\,, \tag{6}$$

where F is the Faraday constant.

For the isotopes ^6Li, ^7Li, ^{39}K and ^{41}K, relations quite similar to (1) and (2) hold:

$$J_6 = (u_6 - \bar{u})\, c_6 - D_{Li}(\partial c_6/\partial x)\,, \tag{7}$$

$$J_7 = (u_7 - \bar{u})\, c_7 - D_{Li}(\partial c_7/\partial x)\,, \tag{8}$$

$$J_{39} = (u_{39} - \bar{u})\, c_{39} - D_K(\partial c_{39}/\partial x)\,, \tag{9}$$

$$J_{41} = (u_{41} - \bar{u})\, c_{41} - D_K(\partial c_{41}/\partial x)\,, \tag{10}$$

where the subscripts 6, 7, 39 and 41 denote $^6Li^+$, $^7Li^+$, $^{39}K^+$ and $^{41}K^+$, respectively, and it is assumed that $D_6 \simeq D_7 \simeq D_{Li}$ and $D_{39} \simeq D_{41} \simeq D_K$.

$$c_6 + c_7 = c_{Li}\,, \tag{11}$$

$$c_{39} + c_{41} = c_K\,, \tag{12}$$

$$J_6 + J_7 = J_{Li}\,, \tag{13}$$

$$J_{39} + J_{41} = J_K\,, \tag{14}$$

where the abundance of ^{40}K is neglected, since it is very small ($\simeq 0.00012$).

The relative difference in internal electromigration velocities* of the two cations is defined as

$$\varepsilon_c \equiv \frac{(u_{Li} - u_K)\,(c_{Li} + c_K)}{(u_{Li} + u_{NO_3})\, c_{Li} + (u_K + u_{NO_3})\, c_K}\,. \tag{15}$$

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* In several of our previous publications we have written $\Delta b/b$ instead of ε, where b = internal ionic mobility.

For the Li and K isotopes, the elementary separation factors* are defined as

$$\varepsilon_{\mathrm{Li}} \equiv \frac{(u_6 - u_7)\, c_{\mathrm{Li}}}{(u_6 + u_{\mathrm{NO_3}})\, c_6 + (u_7 + u_{\mathrm{NO_3}})\, c_7}\,, \tag{16}$$

$$\varepsilon_{\mathrm{K}} \equiv \frac{(u_{39} - u_{41})\, c_{\mathrm{K}}}{(u_{39} + u_{\mathrm{NO_3}})\, c_{39} + (u_{41} + u_{\mathrm{NO_3}})\, c_{41}}\,. \tag{17}$$

From Eqs. (1) to (17), it follows (see the appendix)

$$\begin{aligned} J_i = \left(\frac{I_d}{F}\right) \frac{c_i A_i}{c_{\mathrm{Li}} + c_{\mathrm{K}}} &+ \left\{ \frac{c_i A_i}{c_{\mathrm{Li}} + c_{\mathrm{K}}} (D_{\mathrm{Li}} - D_{\mathrm{NO_3}}) \right. \\ &\left. + \frac{c_i V_{\mathrm{LiNO_3}}}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} D_{\mathrm{Li}} \right\} \left(\frac{\partial c_{\mathrm{Li}}}{\partial x} \right) \\ &+ \left\{ \frac{c_i A_i}{c_{\mathrm{Li}} + c_{\mathrm{K}}} (D_{\mathrm{K}} - D_{\mathrm{NO_3}}) \right. \\ &\left. + \frac{c_i V_{\mathrm{KNO_3}}}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} D_{\mathrm{K}} \right\} \left(\frac{\partial c_{\mathrm{K}}}{\partial x} \right) \\ &- D_i \left(\frac{\partial c_i}{\partial x} \right), \end{aligned} \tag{18}$$

where $i = {}^6\mathrm{Li}$, ${}^7\mathrm{Li}$, ${}^{39}\mathrm{K}$ and ${}^{41}\mathrm{K}$, and

$$A_6 = \frac{\varepsilon_c\, p_{\mathrm{K}} V_{\mathrm{KNO_3}}}{p_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + p_{\mathrm{K}} V_{\mathrm{KNO_3}}} + \varepsilon_{\mathrm{Li}}\, p_7 (1 + \varepsilon_c\, p_{\mathrm{K}})\,, \tag{19}$$

$$A_7 = \frac{\varepsilon_c\, p_{\mathrm{K}} V_{\mathrm{KNO_3}}}{p_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + p_{\mathrm{K}} V_{\mathrm{KNO_3}}} - \varepsilon_{\mathrm{Li}}\, p_6 (1 + \varepsilon_c\, p_{\mathrm{K}})\,, \tag{20}$$

$$A_{39} = -\frac{\varepsilon_c\, p_{\mathrm{Li}} V_{\mathrm{LiNO_3}}}{p_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + p_{\mathrm{K}} V_{\mathrm{KNO_3}}} + \varepsilon_{\mathrm{K}}\, p_{41} (1 - \varepsilon_c\, p_{\mathrm{Li}})\,, \tag{21}$$

$$A_{41} = -\frac{\varepsilon_c\, p_{\mathrm{Li}} V_{\mathrm{LiNO_3}}}{p_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + p_{\mathrm{K}} V_{\mathrm{KNO_3}}} - \varepsilon_{\mathrm{K}}\, p_{39} (1 - \varepsilon_c\, p_{\mathrm{Li}})\,. \tag{22}$$

Here, $p_{\mathrm{Li}} = c_{\mathrm{Li}}/(c_{\mathrm{Li}} + c_{\mathrm{K}})$, $p_{\mathrm{K}} = c_{\mathrm{K}}/(c_{\mathrm{Li}} + c_{\mathrm{K}})$, $p_6 = c_6/c_{\mathrm{Li}}$, $p_7 = c_7/c_{\mathrm{Li}}$, $p_{39} = c_{39}/c_{\mathrm{K}}$, and $p_{41} = c_{41}/c_{\mathrm{K}}$.

The variation of the distribution of each isotope in the separation column can be calculated by solving the equation of continuity with a finite difference method. That is, the concentration of isotopic species i in the N-th fraction at time $t = t + \Delta t$ is expressed in the explicit form by

$$\begin{aligned} c_i(N, t + \Delta t) &= c_i(N, t) \\ &+ \{J_i(N, t) - J_i(N + 1, t)\}\, (\Delta t / \Delta x)\,. \end{aligned} \tag{23}$$

The fractions were numbered from the anode side, the length of each one, Δx, being 1 mm. The value of Δt was 60 s. These values of the parameters meet the condition $D\, \Delta t / (\Delta x)^2 \leqq 0.5$ (D is the effective diffusion coefficients appearing in the calculation), which is required for the "stability" of the calculation in the explicit form [11]. The initial condition was $c_i(N, 0) = c_i^0$, and the boundary condition was $J_i(1, t) = 0$ and $c_i(N', t) = c_i^0$, where c^0 is the initial concentration of the corresponding species and N' refers to the fraction in the large cathode compartment to which the mouth of the separation column was open.

An example of the calculated profile of the distribution of the cations and their isotopes is shown in Figure 2. The input parameters used in this calculation (Table 3) are similar to those of the experiment reported in Figure 1. The effective diffusion coefficients are unknown. They were tentatively assumed to be 1.5 times the self-diffusion coefficients in the same system, which were interpolated or extrapolated from the experimental data [8] with respect to concentrations and temperatures. The anomaly in the isotopic ratio of ${}^7\mathrm{Li}/{}^6\mathrm{Li}$ is distinctly observed, while there is no anomaly in

Table 3. The values for the parameters used in the calculation.

Duration: 15.5 h = 5.58×10^4 s Temperature: 380 °C
$V_{\mathrm{LiNO_3}} = 4.030 \times 10^{-5}\ \mathrm{m^3/mol}$ $V_{\mathrm{KNO_3}} = 5.501 \times 10^{-5}\ \mathrm{m^3/mol}$
$\varepsilon_c = 0.1854\, p_{\mathrm{Li}} - 0.1867$ $(0.427 \leqq p_{\mathrm{Li}} < 1)$ [7]
$\varepsilon_{\mathrm{Li}} = 0.0085$ $\varepsilon_{\mathrm{K}} = 0.0023$
$I_{\mathrm{d}} = 2.0 \times 10^4\ \mathrm{A/m^2}$ $D = 1.5\, D_{\mathrm{self}}$
$D_{\mathrm{Li\,self}} = -9.919 \times 10^{-10}\, p_{\mathrm{Li}}^2 + 2.049 \times 10^{-9}\, p_{\mathrm{Li}} + 2.141 \times 10^{-9}\ (\mathrm{m^2/s})$, [8]
$D_{\mathrm{K\,self}} = -8.298 \times 10^{-10}\, p_{\mathrm{Li}}^2 + 1.304 \times 10^{-9}\, p_{\mathrm{Li}} + 1.846 \times 10^{-9}\ (\mathrm{m^2/s})$, [8]
$D_{\mathrm{NO_3\,self}} = -7.178 \times 10^{-10}\, p_{\mathrm{Li}}^2 + 4.752 \times 10^{-9}\, p_{\mathrm{Li}} + 1.683 \times 10^{-9}\ (\mathrm{m^2/s})$. [8]

Length of separation column: 20 cm
Initial chemical and isotopic composition;

$p_{\mathrm{Li}}^0 = 0.427$; ${}^7\mathrm{Li}/{}^6\mathrm{Li} = 12.150$; ${}^{41}\mathrm{K}/{}^{39}\mathrm{K} = 0.071429$.

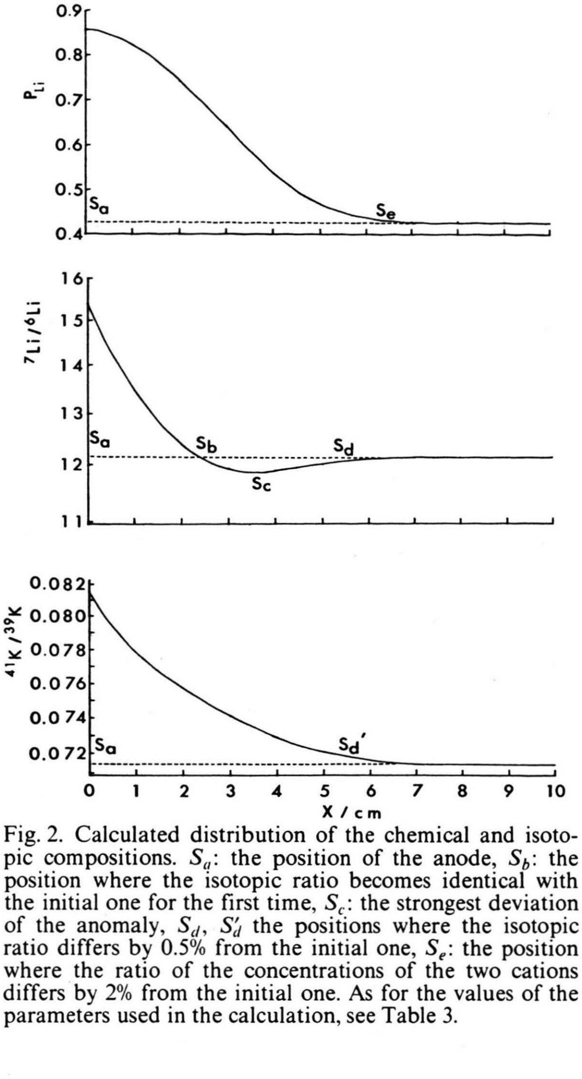

Fig. 2. Calculated distribution of the chemical and isotopic compositions. S_a: the position of the anode, S_b: the position where the isotopic ratio becomes identical with the initial one for the first time, S_c: the strongest deviation of the anomaly, S_d, S_d' the positions where the isotopic ratio differs by 0.5% from the initial one, S_e: the position where the ratio of the concentrations of the two cations differs by 2% from the initial one. As for the values of the parameters used in the calculation, see Table 3.

that of $^{41}K/^{39}K$. If the effective diffusion coefficients are assumed to be larger, the region in which the chemical composition and the isotopic ratios change becomes longer and the amplitude of the anomaly decreases.

All five velocities u_6, u_7, u_{39}, u_{41} and u_{NO_3} depend on the composition of the melt, and we can expect this to be the case also for the relative velocity differences ε_c, ε_{Li} and ε_K. In an electromigration experiment as well as in the numerical calculations, composition changes are obtained in a region between the anode and some point S_f beyond which all compositions remain constant. (S_f corresponds to approximately $x = 7$ cm in Figure 2.) These composition changes will have some influence on the details of the distributions but not on the integrated deviation from the initial composition. Thus, an electromigration experiment gives the relative velocity differences corresponding to the initial composition at S_f. In the present calculations the composition dependences are taken into account for ε_c as well as for the diffusion coefficients (Table 3). The elementary separation factors ε_{Li} and ε_K are assumed to be constant, since their concentration dependence is still under evaluation from our experiments. Anyhow, the dependence of u_{Li} and u_K is mainly related with ε_c and not with ε_{Li} and ε_K.

Discussion

The cause of the anomaly can be analyzed by use of formulae. From the equation of continuity, Eq. (24) is derived:

$$\partial p_7(x,t)/\partial t = L(x,t)/c_{Li}(x,t)\,, \tag{24}$$

where

$$L(x,t) = p_7(x,t)\,(\partial J_6(x,t)/\partial x) - p_6(x,t)\,(\partial J_7(x,t)/\partial x)\,. \tag{25}$$

When $L(x,t)$ is negative at $x = x$ and $t = t$, ^{6}Li is being enriched with reference to ^{7}Li at this position at this moment.

Around the region S_b to S_d (see Fig. 2), diffusion contributes much less than electromigration to the total flux. That is, the main contribution to J and also to $\partial J/\partial x$ is made by the first term of the right-hand side of (18). Thus, for $L(x,t)$ only the electromigration term is considered:

$$L_{el}(x,t) = (B_A + B_B)(\partial p_6/\partial x) + B_C(\partial p_{Li}/\partial x) + B_D(\partial \varepsilon_c/\partial x)\,, \tag{26}$$

where

$$B_A = \left(\frac{I_d}{F}\right)\frac{\varepsilon_c\, p_{Li}(1-p_{Li})\,V_{KNO_3}}{p_{Li}\,V_{LiNO_3} + (1-p_{Li})\,V_{KNO_3}}\,, \tag{27}$$

$$B_B = \left(\frac{I_d}{F}\right)\varepsilon_{Li}(1-2p_6)\,p_{Li}\{1+\varepsilon_c(1-p_{Li})\}, \tag{28}$$

$$B_C = \left(\frac{I_d}{F}\right)\varepsilon_{Li}\,p_6(1-p_6)\,\{1+\varepsilon_c(1-2p_{Li})\}, \tag{29}$$

$$B_D = \left(\frac{I_d}{F}\right)\varepsilon_{Li}\,p_6(1-p_6)\,p_{Li}(1-p_{Li})\,. \tag{30}$$

Further, for the present case where ε_c can be approximated by a linear function of p_{Li} with a slope a, L_{el} is rewritten as

$$\begin{aligned} L_{\text{el}}(x, t) = {} & (B_{\text{A}} + B_{\text{B}})(\partial p_6/\partial x) \\ & + (B_{\text{C}} + a\, B_{\text{D}})(\partial p_{\text{Li}}/\partial x)\,. \end{aligned} \tag{31}$$

At the chosen temperature and concentration ε_c is negative, see Table 3, and its absolute value is always much smaller than unity. Hence B_{A} is negative and B_{B} is positive, while $B_{\text{A}} + B_{\text{B}}$ is negative. Since $(\partial p_6/\partial x)$ goes from positive to negative at S_c, the first term on the right-hand side of (31) is negative between S_a and S_c but positive between S_c and S_d. The second term is negative in the whole region between S_a and S_d, since $(\partial p_{\text{Li}}/\partial x)$ is negative and both B_c and $a\, B_{\text{D}}$ are positive. The absolute value of the second term is larger than that of the first one in the region S_c to S_d where the two terms have opposite signs mainly because $|\partial p_6/\partial x| \ll |p_{\text{Li}}/\partial x|$ in this region.

Incidentally, in the region S_a to S_b, the term of diffusion flux, that is $D_{\text{Li}}(\partial c_6/\partial x)$ or $D_{\text{Li}}(\partial c_7/\partial x)$ in (18) becomes larger than the electromigration term and the diffusion term contributes to an enrichment of ^{7}Li against ^{6}Li. Therefore, enrichment of ^{7}Li takes place there in spite of the negative value of L_{el}.

On the other hand, for the more mobile cation, that is potassium ions in this case, the entity corresponding to $L_{\text{el}}(x, t)$ is positive over the whole region from S_a to S_e, and therefore the heavier isotope ^{41}K is being enriched there.

Thus, in this kind of binary systems, an anomaly in the distribution of isotopes always occurs for the cation which is less mobile. Since the isotope effect of lithium ions is large, the anomaly is easily detectable experimentally. It should be mentioned, however, that this phenomenon is not limited to lithium isotopes. Our calculations for the binary system (Li−Rb)NO$_3$, gave a small, but significant, anomaly for the rubidium isotopes, when the rubidium ion is less mobile than lithium. The isotope separation factor of pure rubidium nitrate is so small, $\varepsilon_{\text{Rb}} = 0.00074$ for pure rubidium nitrate at 350 °C [12], that one cannot hope to detect the anomaly in any laboratory experiment with molten (Li−Rb)NO$_3$. It is, however, not surprising that the anomaly was not detected even for lithium isotopes in a number of previous experiments with binary systems. The anomalies could often have been beyond the limit of accuracy of the mass spectrometric measurement owing to rather small elementary separation factors combined with large effective diffusion coefficients.

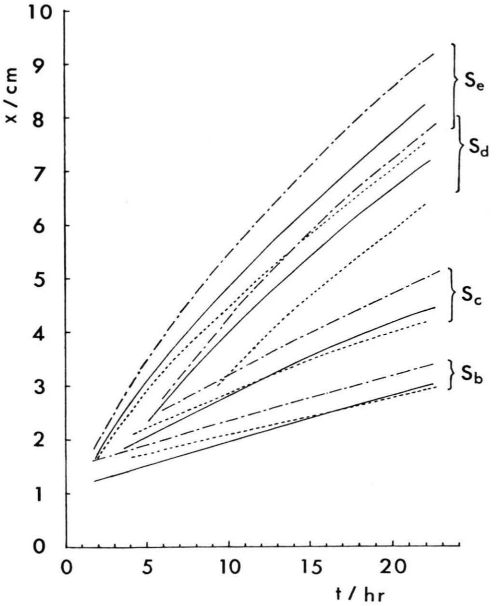

Fig. 3. The calculated lengths of the regions within which changes of the chemical and isotopic compositions are detected. ----: $D = 1.5 \times D_{\text{self}}$, $I_{\text{d}} = 1.5 \times 10^4$ A/m^2, ——: $D = 1.5 \times D_{\text{self}}$, $I_d = 2.0 \times 10^4$ A/m^2, —·—·—: $D = 2.0 \times D_{\text{self}}$ $I_d = 2.0 \times 10^4$ A/m^2. As for the values of other parameters, see Table 3.

The length of the region where the change of the chemical composition is detectable depends on the precision of chemical analysis. Here, we assume tentatively that, when the ratio of the concentrations of the two cations differs by 2% from that of the initial one, the change would be detectable. The length between S_a and S_e is longer than is expected from the diffusion coefficients alone, since in binary systems a flux in addition to the diffusion flux occurs from the restriction that there should be no volume flow along the separation column. Figure 3 also indicates that this length depends not only on the diffusion coefficients but also on the strength of the electric field.

The length of the region where the isotopic ratios change, which corresponds to that between S_a and S_d (or S'_d), is shorter than that between S_a and S_e, as seen from Figures 2 and 3. This is probably because the change of the isotopic compositions around S_d and S'_d is caused mainly by the concentration gradient of the chemical compositions and further because $\varepsilon_{\mathrm{Li}}$ and ε_{K} are much smaller than $|\varepsilon_c|$ in the present case. In a pure salt the length of enrichment is theoretically given by $l \simeq \sqrt{\pi D t}$ [1, 13]. As is expected, this length is much shorter than in binary salts; for example, $l = 2.9$ cm for $D_{\mathrm{Li}} = 4.80 \times 10^{-9}$ m^2/s and $t = 930 \times 60$ s, while the value of x for S_d is 5.5 cm for a smaller average diffusion coefficient in the present case (see Figures 2 and 3).

Although $\varepsilon_{\mathrm{Li}}$ is considerably greater than ε_{K}, S'_d is a little more distant from S_a than S_d is; for example, S_d and S'_d are 5.5 cm and 5.6 cm distant, respectively, in the case shown in Figure 2.

The reason would be that for lithium ions the gradient of the chemical composition there conduces to enrichment of the lighter isotope ^{6}Li, which compensates for enrichment of the heavier isotope at the anode, while for potassium ions it is helpful also for that of the heavier isotope ^{41}K.

In Fig. 4, the total separation factor at S_c in the present case is given as a function of time for a few combinations of diffusion coefficients and current densities. It follows, as is expected, that the total separation factors deviate more from unity, as the current densities become larger and the diffusion coefficients become smaller.

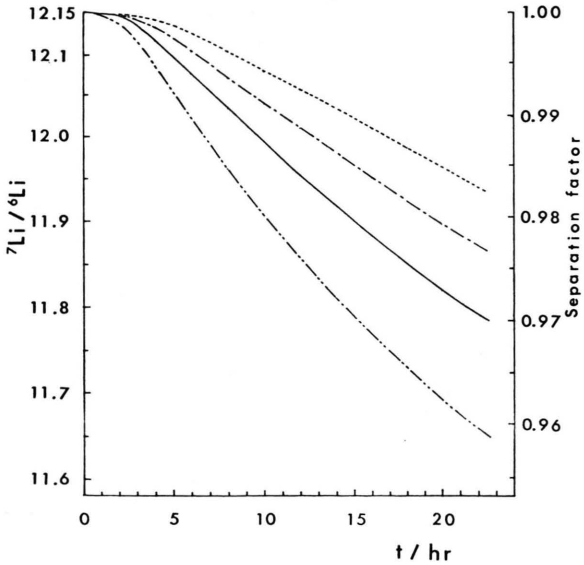

Fig. 4. The total separation factor for the strongest deviation of the anomaly of the isotopic ratio ^{7}Li/^{6}Li. ---: $D = 1.5 \times D_{\mathrm{self}}$, $I_d = 1.5 \times 10^4$ A/m^2, —--—--: $D = D_{\mathrm{self}}$, $I_{\mathrm{d}} = 2.0 \times 10^4$ A/m^2, ——: $D = 1.5 \times D_{\mathrm{self}}$, $I_{\mathrm{d}} = 2.0 \times 10^4$ A/m^2, —·—·—: $D = 2.0 \times D_{\mathrm{self}}$, $I_d = 2.0 \times 10^4$ A/m^2. The values of other parameters are the same as those given in Table 3.

Finally, in order to check the validity of the relations used for determining the relative differences in internal mobilities and the elementary separation factors in binary systems, we have calculated ε_c, $\varepsilon_{\mathrm{Li}}$, and ε_{K} for the distribution of the chemical elements and the isotopes yielded by the present numerical calculations.

As regards ε_c, the formula is [1, 5]

$$\varepsilon_c = -\left(\frac{F}{Q}\right)\left(\frac{\sum_j c_{\mathrm{Li}j}}{p^0_{\mathrm{Li}}} - \frac{\sum_j c_{\mathrm{K}j}}{p^0_{\mathrm{K}}}\right), \tag{32}$$

where Q is the transported charge, and p^0 refers to the initial composition; the summation is taken over the part where the change of the initial composition is observed.

As for $\varepsilon_{\mathrm{Li}}$, the formula is given by [5]

$$\varepsilon_{\mathrm{Li}} = -\left(\frac{F}{Q\, t^0_{\mathrm{Li}}}\right)\left(\frac{\sum_j c_{6j}}{p^0_6} - \frac{\sum_j c_{7j}}{p^0_7}\right), \tag{33}$$

where t^0_{Li} is the internal transport number of lithium ions at the initial chemical composition, that is

$$t^0_{\mathrm{Li}} = p^0_{\mathrm{Li}} + \varepsilon_c\, p^0_{\mathrm{Li}}(1 - p^0_{\mathrm{Li}})\,. \tag{34}$$

For ε_{K}, a quite similar formula is given.

From the distribution of the chemical and isotopic compositions produced by the numerical calculations, the input values of ε_c, $\varepsilon_{\mathrm{Li}}$ and ε_{K} can be exactly obtained by using (32) and (33). This proves that (32) and (33) are valid also when an anomaly appears. Incidentally, if in the calculation of ε_c, $\varepsilon_{\mathrm{Li}}$, and ε_{K} the summation is truncated at S_e, S_d, and S'_d, respectively, the obtained values of $|\varepsilon_c|$, $\varepsilon_{\mathrm{Li}}$, and ε_{K} are lower by 0.2%, higher by 0.8% and lower by 2.7% under the condition given in Table 3. The errors become larger if the duration is shorter, current densities are lower, and the effective diffusion coefficients are larger. For accurate experimental determination of ε_c etc., therefore, electromigration under the conditions of long duration, large current densities and small effective diffusion coefficients is desirable.

If one is not aware of the possibility of anomalous isotope distributions for electromigration experiments with mixtures, there is a risk that too large isotope effects are reported for the element for which the anomaly occurs. This is specially the case when the facilities for mass analyses are restricted.

Thus either if the analyses are stopped when the normal isotope ratio is obtained (position S_b of Figure 2) or when the isotope composition becomes the same for two adjacent samples (region near S_c), calculations according to (33) give a too large isotope effect. Thus there is a possibility that the very large isotope effect found by Klemm, Hintenberger and Hoernes [2] for potassium in a LiCl–KCl mixture with a low concentration of KCl can be affected by an anomaly in the separation column.

In conclusion, in countercurrent electromigration of binary molten system with a common anion, an anomaly appears in the isotopic ratio of a less mobile cation in a separation column on the anode side; an anomaly in the opposite direction would be observed for a more mobile cation on the cathode side. The anomaly is caused mainly by the concentration gradients of the cations. Numerical calculations by means of a computer are useful for analysis of the flow of several components containing diffusion terms as in the present case.

The calculations were performed with FACOM M-160 computer at Tokyo Institute of Technology. We are grateful to Mr. M. Lövenby for mass spectrometric analysis. The experiments at Chalmers University of Technology were supported by the Swedish Natural Sciences Research Council.

Appendix

It follows from (6) that

$$\frac{I_\mathrm{d}}{F} = J_\mathrm{Li} + J_\mathrm{K} - J_{\mathrm{NO}_3}. \tag{A1}$$

Substituting (1)–(3) into (A 1), we have

$$\frac{I_\mathrm{d}}{F} = (u_\mathrm{Li}\, c_\mathrm{Li} + u_\mathrm{K}\, c_\mathrm{K} + u_{\mathrm{NO}_3}\, c_{\mathrm{NO}_3}) - \bar{u}\,(c_\mathrm{Li} + c_\mathrm{K} - c_{\mathrm{NO}_3}) - \left(D_\mathrm{Li}\frac{\partial c_\mathrm{Li}}{\partial x} + D_\mathrm{K}\frac{\partial c_\mathrm{K}}{\partial x} - D_{\mathrm{NO}_3}\frac{\partial c_{\mathrm{NO}_3}}{\partial x}\right). \tag{A2}$$

Sustituting (4) and (15) into (A 2), we obtain

$$\frac{I_\mathrm{d}}{F} = \frac{1}{\varepsilon_c}\,(u_\mathrm{Li} - u_\mathrm{K})\,(c_\mathrm{Li} + c_\mathrm{K}) - \left\{(D_\mathrm{Li} - D_{\mathrm{NO}_3})\frac{\partial c_\mathrm{Li}}{\partial x} + (D_\mathrm{K} - D_{\mathrm{NO}_3})\frac{\partial c_\mathrm{K}}{\partial x}\right\}. \tag{A3}$$

It follows from (15) that

$$(c_{\mathrm{NO}_3} - \varepsilon_c\, c_\mathrm{Li})\, u_\mathrm{Li} - (c_{\mathrm{NO}_3} + \varepsilon_c\, c_\mathrm{K})\, u_\mathrm{K} = \varepsilon_c\, c_{\mathrm{NO}_3}\, u_{\mathrm{NO}_3}. \tag{A4}$$

From (A 3) and (A 4), we obtain

$$u_\mathrm{Li} = \frac{(1 + \varepsilon_c\, c_\mathrm{K}/c_{\mathrm{NO}_3}}{c_{\mathrm{NO}_3}}\, X - u_{\mathrm{NO}_3}, \tag{A5}$$

$$u_\mathrm{K} = \frac{(1 - \varepsilon_c\, c_\mathrm{Li}/c_{\mathrm{NO}_3})}{c_{\mathrm{NO}_3}}\, X - u_{\mathrm{NO}_3}, \tag{A6}$$

where

$$X \equiv \frac{I_\mathrm{d}}{F} + D_\mathrm{Li}\frac{\partial c_\mathrm{Li}}{\partial x} + D_\mathrm{K}\frac{\partial c_\mathrm{K}}{\partial x} - D_{\mathrm{NO}_3}\frac{\partial c_{\mathrm{NO}_3}}{\partial x}.$$

From (16) and the following relation

$$c_6\, u_6 + c_7\, u_7 = c_\mathrm{Li}\, u_\mathrm{Li}, \tag{A7}$$

we find that

$$u_6 = (1 + \varepsilon_\mathrm{Li}\, c_7/c_\mathrm{Li})\,(u_\mathrm{Li} + u_{\mathrm{NO}_3}) - u_{\mathrm{NO}_3}. \tag{A8}$$

Further, combining (A 5) and (A 8), we recover

$$u_6 = (X/c_{\mathrm{NO}_3})\,(1 + \varepsilon_c\, c_\mathrm{K}/c_{\mathrm{NO}_3})\,(1 + \varepsilon_\mathrm{Li}\, c_7/c_\mathrm{Li}) - u_{\mathrm{NO}_3}. \tag{A9}$$

On the other hand, combining (1), (2) and (5), we obtain

$$\bar{u} = \frac{1}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} \left\{ u_{\mathrm{Li}} c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + u_{\mathrm{K}} c_{\mathrm{K}} V_{\mathrm{KNO_3}} - V_{\mathrm{LiNO_3}} D_{\mathrm{Li}} \frac{\partial c_{\mathrm{Li}}}{\partial x} - V_{\mathrm{KNO_3}} D_{\mathrm{K}} \frac{\partial c_{\mathrm{K}}}{\partial x} \right\}. \qquad (\mathrm{A\,10})$$

Substituting (A 5) and (A 6) into (A 10), we find

$$\bar{u} = \frac{1}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} \left[\left\{ \frac{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}}{c_{\mathrm{NO_3}}} + \frac{\varepsilon_c c_{\mathrm{Li}} c_{\mathrm{K}}}{c_{\mathrm{NO_3}}^2} (V_{\mathrm{LiNO_3}} - V_{\mathrm{KNO_3}}) \right\} X - V_{\mathrm{LiNO_3}} D_{\mathrm{Li}} \frac{\partial c_{\mathrm{Li}}}{\partial x} - V_{\mathrm{KNO_3}} D_{\mathrm{K}} \frac{\partial c_{\mathrm{K}}}{\partial x} \right] - u_{\mathrm{NO_3}}. \qquad (\mathrm{A\,11})$$

Substitution of (A 9) and (A 11) into (7) by use of (4) leads to (A 12), which is the case for ^{6}Li in (18).

$$J_6 = \frac{c_6}{c_{\mathrm{Li}} + c_{\mathrm{K}}} \left(\frac{I_{\mathrm{d}}}{F} \right) A_6 + \left[\frac{c_6}{c_{\mathrm{Li}} + c_{\mathrm{K}}} (D_{\mathrm{Li}} - D_{\mathrm{NO_3}}) A_6 + \frac{c_6 V_{\mathrm{LiNO_3}} D_{\mathrm{Li}}}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} \right] \left(\frac{\partial c_{\mathrm{Li}}}{\partial x} \right) + \left[\frac{c_6}{c_{\mathrm{Li}} + c_{\mathrm{K}}} (D_{\mathrm{K}} - D_{\mathrm{NO_3}}) A_6 + \frac{c_6 V_{\mathrm{KNO_3}} D_{\mathrm{K}}}{c_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + c_{\mathrm{K}} V_{\mathrm{KNO_3}}} \right] \left(\frac{\partial c_{\mathrm{K}}}{\partial x} \right) - D_{\mathrm{Li}} \frac{\partial c_6}{\partial x}, \qquad (\mathrm{A\,12})$$

where

$$A_6 \equiv \frac{\varepsilon_c p_{\mathrm{K}} V_{\mathrm{KNO_3}}}{p_{\mathrm{Li}} V_{\mathrm{LiNO_3}} + p_{\mathrm{K}} V_{\mathrm{KNO_3}}} + \varepsilon_{\mathrm{Li}} p_7 (1 + \varepsilon_c p_{\mathrm{K}}).$$

Similarly, J_7, J_{39} and J_{41} can be derived from (1) to (17).

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