The Isotope Effect of Li$^+$ Ions in Electromigration of Molten LiNO$_3$

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The relative difference in internal mobilities of ^{6}Li and ^{7}Li, ε, in molten LiNO$_3$ has been remeasured in the temperature range from 559 K to 726 K by countercurrent electromigration (Klemm's method). As temperature increases, the isotope effect increases, although the increasing rate decreases; it is practically constant above 650 K. The ε values are lower than those measured by Lundén and Ekhed [5] by 15–25%. The effective diffusion coefficients have been estimated from the distribution of the isotopes in the separation tube by numerical simulation.

Introduction

Measurements of isotope effects on ionic mobilities in molten salts yield useful information not only for performing isotope separation by the countercurrent electromigration method invented by Klemm [1–3] but also for interpreting the mechanism of the ionic transport. Molten LiNO$_3$ is a potential salt for enrichment of Li isotopes. Some 20 years ago the relative difference in the internal mobilities, ε, of ^{6}Li and ^{7}Li in molten LiNO$_3$ was measured at several temperatures by Okada [4], and Lundén and Ekhed [5]. The obtained ε values were 10–15% lower in [4] than in [5] and slightly decreased with temperature in [4] while they were nearly constant in [5].

Recently Klemm and Lundén [6] have argued that the anomalous distribution of isotopes in countercurrent electromigration of neat melts such as LiNO$_3$ [5] and KNO$_3$ [7] is attributable to ε increasing with temperature. Thus a positive dependence of ε on temperature in LiNO$_3$ would confirm their argument.

Presently a more accurate mass spectrometer for isotope abundance measurements is available for us. Also an apparatus for temperature control of the electromigration cell has been developed. We thus were in a position to remeasure these ε values and their temperature dependence.

Experimental

Lithium nitrate of reagent grade was vacuum-dried at about 400 K overnight. Ammonium nitrate of reagent grade was used without special dehydration.

The electromigration cell used was the same as the one devised for enrichment of ^{6}Li and shown in Fig. 1 of [8]. The cathode compartment contained molten NH$_4$NO$_3$ and the rest of the cell molten LiNO$_3$. The separation tube for enrichment of ^{7}Li had 4 mm internal diameter and ca. 160 mm length. It was packed as densely as possible with alumina powder of ca. 50 µm grain size. For every experiment the diaphragm part of the separation tube was filled with fresh LiNO$_3$ because the old LiNO$_3$ in the cell could have been contaminated during the previous runs.

The temperature of the melt was kept within ± 2 K with a temperature controller (Model DSM made by Shimaden Electric Co. Ltd., Tokyo). Constant direct current was supplied with a DC supplier Model PAD 500-0.6 made by Kikusui Electric Co. Ltd., Tokyo. After electromigration, the separation tube was taken out and cut into pieces.

Table 1. Experimental conditions and results.

Exp. no.	Temp.	Electric current	Duration	Transported charge	ε_{Li}	D_{eff} (I) $(10^{-9}\,\mathrm{m^2\,s^{-1}})$	(II)
	(K)	(mA)	(hrs)	(C)			
1	559	150	18.0	9 538	0.0091 ± 0.0001	2.8	2.5
2	561	145	44.2	23 237	0.0096 ± 0.0001	1.9	1.5
3	561	300	24.0	23 555	0.0099 ± 0.0001	1.7	1.9
4	610	150	48.0	25 103	0.0114 ± 0.0001	2.2	1.8
5	610	300	24.0	24 797	0.0110 ± 0.0001	2.9	2.7
6	660	150	48.0	25 116	0.0115 ± 0.0002	2.8	2.5
7	660	300	24.5	25 458	0.0118 ± 0.0001	2.6	3.3
8	725	150	30.0	15 074	0.0118 ± 0.0002	3.3	2.9
9	725	220	24.0	17 852	0.0119 ± 0.0001	4.1	4.4
10	726	300	24.0	24 856	0.0117 ± 0.0001	4.2	4.0

The amount of Li in the pieces was determined by flame spectrophotometry and the isotope ratio ^{7}Li/^{6}Li was measured by surface ionisation with a Varian MAT CH5 mass spectrometer. For obtaining good reproducibility, always the same amount of Li (ca. 1 μg) as LiI was put on the side filament and the rising rate of the heating current and the waiting time before the measurement were the same for each sample. The reproducibility for the ratio ^{7}Li/^{6}Li was better than 0.2%.

Results

The main experimental conditions and the results are given in Table 1.

The relative difference in internal mobilities of ^{6}Li and ^{7}Li, ε, is calculated by [2, 4]

$$\varepsilon = (b_6 - b_7)/b \tag{1}$$
$$= -(F/Q)[(1 + r_0)/r_0] \sum_i [n_i(r_0 - r_i)/(1 + r_i)],$$

where b is the internal mobility of Li ($b = y_6 b_6 + y_7 b_7$, y = isotope abundance, $y_6 + y_7 = 1$), F the Faraday constant, Q the transported charge, n the quantity of Li and r the isotope ratio ($r = {}^7$Li/^{6}Li). The suffixes 0 and i refer to the samples before electromigration and the i-th sample thereafter, respectively. The summation is taken from the fraction nearest to the anode up to the one where the isotope ratio was practically unchanged.

From the obtained ε values and the distribution of the isotopes in the separation tube after electromigration, the effective diffusion coefficients are estimated as follows.

The cross section of the melt in the diaphragm is assumed to be uniform. The net flow of ^{6}Li per cross section in the diaphragm part is expressed by

$$J_6 = \varepsilon I_d\, c_6\, c_7/F\, c^2 - D_{eff}(dc_6/dx) , \tag{2}$$

where I_d is the current density; c, c_6 and c_7 are the concentrations of Li$^+$, ^{6}Li$^+$, ^{7}Li$^+$ ions, respectively; D_{eff} is the effective interdiffusion coefficient of Li-isotopes. This equation is derived from (18) in [9] for the system consisting of one kind of cation with two isotopes. A similar equation holds for ^{7}Li.

Combining (2) with the equation of continuity, one obtains

$$c_6(x, t + \Delta t)$$
$$= c_6(x, t) + (\Delta t/\Delta x)[(\varepsilon I_d/F c^2) \tag{3}$$
$$\cdot \{c_6(x, t)\, c_7(x, t) - c_6(x + \Delta x, t)\, c_7(x + \Delta x, t)\}$$
$$- (D_{eff}/\Delta x)\{2c_6(x, t) - c_6(x - \Delta x, t) - c_6(x + \Delta x, t)\}].$$

The evolution of the distribution of the isotopes can be calculated using (3); a combination of $\Delta x = 1$ mm and $\Delta t = 60$ s is chosen for the calculation. The calculation of D_{eff} has been done with a trial and error method, that is, the D_{eff} value with which the experimentally obtained distribution can be well reproduced has been finally chosen and given in column (I) in Table 1. In Fig. 1 it is shown for an example how the experimentally obtained distribution is reproduced by such a calculation.

The existence of an anomalous distribution of the isotopes near the separation tube opening to the large vessel, which was discovered in the experiments on pure LiNO$_3$ [5] and KNO$_3$ [7] by Lundén and Ekhed, could not be affirmed nor denied in the present experiments.

Discussion

Temperature Dependence of ε

The temperature gradient in the vertical direction in the separation tube, which is estimated to have been less than 0.2 K/cm, does not affect the obtained ε value because (1) is based on the material and transported charge balance in a cross sectional area in the separation tube where the isotope ratio remains unchanged during electromigration. Thus only the temperature at this place affects the ε value.

The ε values are plotted against the temperature in Figure 2. The previously obtained values by Okada [4] and Lundén and Ekhed [5] are also given for comparison. Figure 2 shows that the reproducibility of the present results is very good and that they are independent of the current density in the investigated range, as expected. As the temperature increases, ε increases but becomes practically constant above 650 K. The temperature dependence agrees well with that obtained by Lundén and Ekhed [5] but their values are systematically larger. The difference between the results of [4] and the present ones is partly due to the better temperature control and mainly to more precise mass spectrometry.

The present ε values and the temperature dependence agree well with those obtained for the nearly eutectic (Li, K)NO$_3$ melt [10].

The temperature dependence can be interpreted as follows.

The positive temperature dependence of the isotope effect in the case of molten LiCl has been interpreted in terms of the self-exchange velocities (SEV) obtained by molecular dynamics simulation [11]. The SEV refers to separating motion of neighbouring unlike ion pairs and has been found to be strongly related with internal mobilities for molten alkali chlorides [11].

The separating motion of each pair can be classified into four processes, that is, the oscillating process (O-process), the leaving process (L-process), the wandering process (W-process) and the coming-back process (C-process) [11, 12]. In the L-process the SEV is dependent only on the masses of the cation and anion of interest and on the temperature, and therefore its isotope effect is relatively large. The O-process is the process during which the distance between neighbouring unlike ions is changing in an oscillatory way, and its duration is determined mainly by the motion of the surrounding ions of the unlike ion pair of interest and therefore the isotope effect of its duration is relatively small. As temperature increases, the occurrence of the L-process becomes more frequent and therefore the isotope effect increases.

The increasing rate becomes, however, smaller with increasing temperature. As temperature increases, the distance between neighbouring like ions becomes greater, i.e. a cation is more attracted by the neighbouring anion with less interaction from other neighbouring anions. In other words, association increases with temperature [13] and the shortening rate of the O-process with temperature increase slows down. Thus, the increase of ε becomes smaller with increasing temperature.

The C-process reduces the isotope effect of the SEV, since the lighter isotope comes back more readily than the heavier one. The occurrence of the C-process is expected to decrease with increasing temperature; this also favours the increase of the isotope effect. However, it remains to be known by molecular dynamics simulation how much the decrease of the C-process contributes to the increase of the isotope effect of the SEV in LiNO$_3$.

Effective Diffusion Coefficient

Information on effective diffusion coefficients D_{eff} is of practical use for design and analysis of isotope separation experiments. In Fig. 3, the temperature dependence of D_{eff} for Li$^+$ ions calculated from (3) is shown, in which the dashed line denotes the self-diffusion coefficients D_{self} of Li$^+$ ions determined by Dworkin et al. [14].

Another way for calculating D_{eff} is to use the relation [1, 2]:

$$D_{eff} = l^2/\pi t, \tag{4}$$

where l is the length of the enriched region of ^{7}Li from the anode during the time t of the electromigration. The calculated values are given on column (II) in Table 1. Estimation of l from the distribution contains some errors due to disturbance of the distribution near the anode, and calculation by use of (3) probably yields more accurate values.

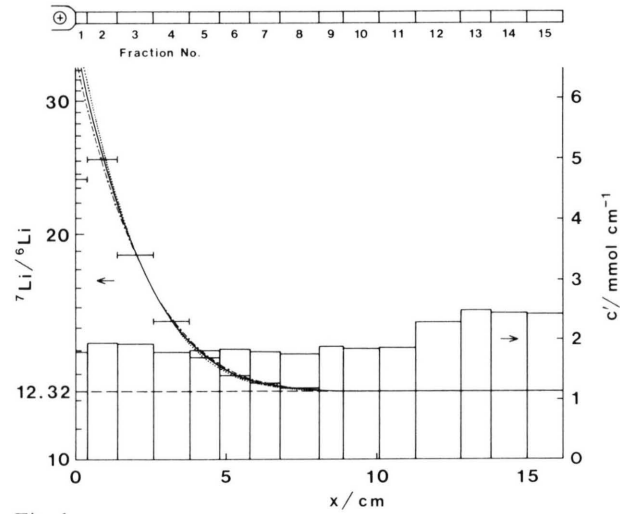D_{eff} can be smaller than D_{self} (see Figure 3). This is because the labyrinth factor of the diaphragm is

Fig. 1

Fig. 2

Fig. 1. Distribution of Li isotopes in the separation tube (Exp. no. 4); the ratio $^7Li/^6Li$ and the quantity of Li, c', per cm are shown. The solid curve shows the ratio $^7Li/^6Li$ calculated on the assumption of $D_{eff} = 2.2 \times 10^{-9} \, m^2 \, s^{-1}$. For comparison, the cases $D_{eff} = 2.0 \times 10^{-9} \, m^2 \, s^{-1}$ (········) and $2.4 \times 10^{-9} \, m^2 \, s^{-1}$ (–·–·–) are also shown.

Fig. 2. The ε value vs. temperature. ●, □, △: this work, ×: [4], ––––: the estimated curve from 11 measured points in the range 586–761 K [5].

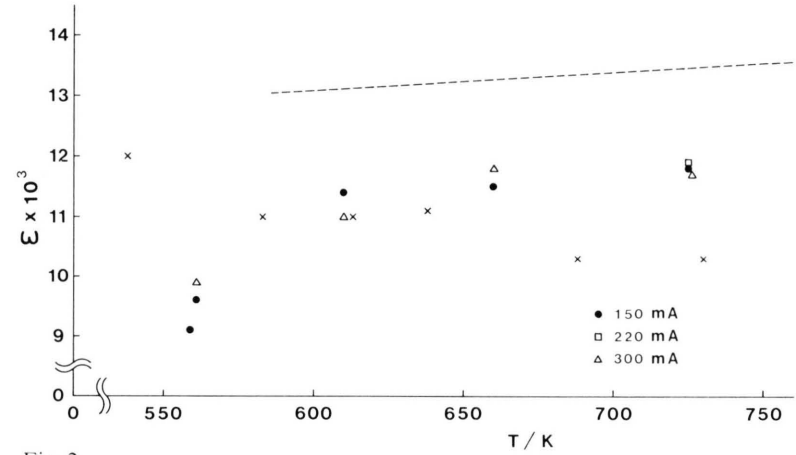Fig. 3. The D_{eff} values vs. temperature. The broken line shows D_{self} [14]. ⊙: D_{self} calculated by MD simulation [15].
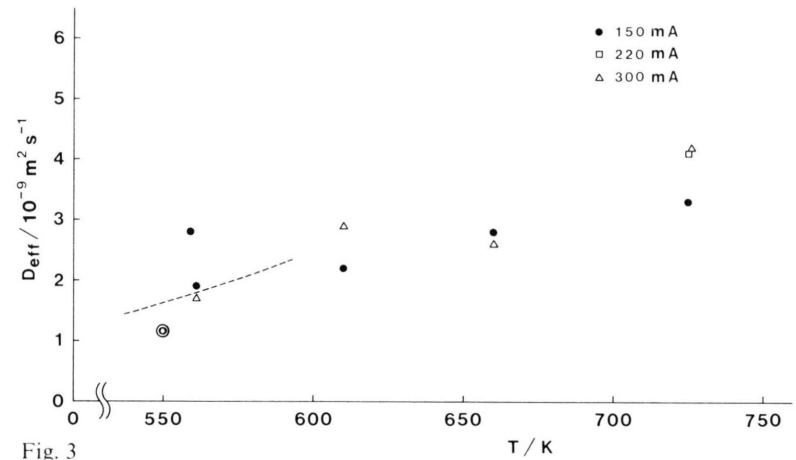

Fig. 3

greater than unity and thus the real diffusion path is longer than the apparent one. The obtained values of D_{eff} seem to be independent of the electric current and dependent on temperature, as expected. If the packing of the diaphragm were equal at every run, the obtained values of D_{eff} should have been the same at the same temperature. As seen from Fig. 3, the values scatter only little.

In conclusion, the ε value is ascertained to be independent of the electric current density within the investigated range; ε increases with increasing temperature, although the increasing rate decreases. This temperature dependence is qualitatively accounted for in terms of the SEV in melts such as LiCl and consistent with the argument presented by

Klemm and Lundén [6] for the anomalous distribution of isotopes in neat $LiNO_3$ melt [5].

The effective diffusion coefficients are estimated in two different ways, one of which seeming to be new and preferable.

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