The Isotope Effect of Li-Ions in Countercurrent Electromigration of Molten LiOH

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The relative difference, ε, in the internal mobilities of ^{6}Li and ^{7}Li ions in molten LiOH has been measured with the Klemm method. In the investigated range of temperature from 763 K to 873 K, ε has been determined to be 0.0068–0.0080 and seems to increase slightly with temperature.

Introduction

The isotope effect on the mobility of Li ions has been measured for pure molten salts such as LiCl [1], LiBr [2], LiI [2] and $LiNO_3$ [3, 4] but not for LiOH, mainly because of its corrosivity. In the present study this has been made up for at various temperatures using Klemm's countercurrent electromigration method [5].

Experimental

LiOH produced by Merck Co. Ltd. (containing 98% LiOH and max. 2% Li_2CO_3) was used without further purification, Klemm's countercurrent electromigration method being rather insensitive to low concentration impurities, and also because there is no conventional method to remove CO_3^{2-} ions from LiOH. The melt was stored in a small alumina vessel and bubbled for more than 12 hr with dry nitrogen gas which had passed through conc. sulphuric acid and molecular sieve 4 A.

The electromigration cell was similar to that used for internal mobility ratio measurements of the molten systems $(Li, K)_2CO_3$ [6] and (Na, K)OH [7]. The main container was made of alumina. Two tubes with different diameters (i. d.: 4 mm and 10 mm; material: SSA-S made by Nihon Kagaku Togyo Co. Ltd.) were connected with alumina cement (Aron ceramic D made by Toagosei Chem. Co. Ltd.) and used as the separation tube. The bottom end of the tube was installed with alumina wool without using a binding reagent. In the narrower part the tube was packed over 15 cm with alumina powder of 150–180 μm grain size.

The separation tube was put into the small vessel which contained the LiOH melt under investigation. After the diaphragm part was filled with the melt by capillarity, it was transferred into the electromigration cell containing LiOH melt as a catholyte. this LiOH, made by Kanto Chem. Co. Ltd., is labeled min. 95% LiOH H_2O containing max. 0.5% Li_2CO_3. It had been dehydrated beforehand in the same vessel by heating at about 730 K for more than 24 hr. The separation tube was placed in the catholyte melt so that the cement connection was positioned ca. 2 cm above the level of the melt.

Electromigration was performed with constant current of 160–170 mA. Platinum wire of 1 mm ϕ was used as the anode and silver wire of 0.5 mm ϕ as the cathode. A mixed gas of O_2 and hot water vapour was bubbled around the cathode during the electromigration to convert otherwise electrodeposited metal into the original melt. Meanwhile, dry nitrogen gas was passed through the catholyte melt to remove excess water. The furnace was a "gold furnace" made by Trans. Temp. Co., U.S.A.; the temperature of the melt could be kept at a prescribed temperature within ± 2 K during electromigration.

After electromigration of 20–22 hr, the separation tube was taken out, cleaned on the outside wall and cut into several pieces for determination of the Li content and the isotope ratio. The content was determined by flame spectrophotometry, and the isotope ratio of ^{7}Li/^{6}Li with a Varian MAT CH5 mass spectrometer.

Results and Discussion

The relative difference in internal mobilities of $^6Li^+$ and $^7Li^+$ ions is calculated by [4, 5]

$$\begin{aligned} \varepsilon &= (b_6 - b_7)/b_{\mathrm{Li}} \qquad (1) \\ &= -(F/Q)\,[(1+r_0)/r_0] \sum_i [n_i(r_0 - r_i)/(1+r_i)], \end{aligned}$$

where b_{Li} is the internal mobility of Li^+ ions: $b_{\mathrm{Li}} = y_6 b_6 + y_7 b_7$ (y_6 and y_7 are the abundances of ^{6}Li and ^{7}Li, respectively, before electromigration; F is the Faraday constant, Q the transported charge, $r = {}^7\mathrm{Li}/{}^6\mathrm{Li}$ (suffixes 0 and i refer to the samples before electromigration and in the i-th fraction, respectively; $r_0 = 12.40 \pm 0.02$) and n_i is the quantity of Li in the i-th fraction. The summation is taken from the fraction nearest to the anode to the one where the initial isotope ratio remains unchanged.

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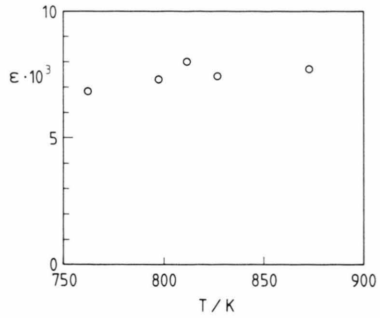

Fig. 1. The isotope effect of Li internal mobility in LiOH melt vs. temperature.

Table 1. Experimental conditions and results.

Run No.	*T*/K	Current/mA	*t*/hr	*Q*/C	ε^{a}
1	763	160	22.0	11 197	0.0068 ± 0.0001
2	798	160	21.0	12 150	0.0073 ± 0.0001
3	813	160	20.5	10 845	0.0080 ± 0.0001
4	828	170	20.0	10 866	0.0074 ± 0.0001
5	873	170	21.5	10 286	0.0077 ± 0.0001

[a] The given error results from the isotope ratio measurement and chemical analysis.

Table 2. Isotope effect in the internal mobilities of Li^+ ions in some pure melts.

Salt	ε	Temp. range (K)	Ref.
LiCl	0.0194 – 0.0292	996 – 1168	[1]
LiBr	0.0202 – 0.0242	853 – 888	[2]
LiI	0.023	773	[2]
$LiNO_3$	0.0091 – 0.0119	559 – 726	[4]
LiOH	0.0068 – 0.0080	763 – 873	This work

The lowest and highest values of ε do not necessarily correspond to the ones obtained at the lowest and highest temperatures, respectively.

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

In Fig. 1 the ε values are plotted against temperature. It seems that ε slightly increases with temperature in the investigated range. A positive temperature dependence had been found in other melts such as LiCl [1], $LiNO_3$ [3, 4] and their mixtures with K^+ ions [8, 9]. Our interpretation in terms of the self-exchange velocity has already been given in previous papers [10, 11].

some other pure Li salts in Table 2. The values are smaller in the present system than in the other systems. This is presumably because the contribution of the motion of Li^+ ions to the self-exchange velocity of the unlike ion pairs would not be so great in the present system; in other words, this may be because the external transport number of Li^+ ions would not be so great in LiOH.

Shvedov and Ivanov [12] have reported that the external transport numbers of Na^+ and K^+ ions are 0.10 ± 0.03 and 0.03 ± 0.03 in molten NaOH and KOH, respectively, at 653–773 K. If the transport number of Li^+ in LiOH were so small as in NaOH and KOH, the isotope effect of Li^+ ions would be much smaller than obtained here; thus, the transport number of Li^+ is expected to be not so small as those of the cations in NaOH and KOH, nor so large as those in LiCl and $LiNO_3$. The inference of the relatively large transport number of OH^- ions in LiOH leads to the assumption that clustering of OH^- ions due to hydrogen bonding does not occur in the melt.

It would be interesting to know in which direction the H atoms are oriented in neighbouring Li^+ and OH^- ions in the melt. Studies on hydroxide melts by molecular dynamics simulation as well as neutron diffraction are now under progress, which would make it possible to interpret the present data more quantitatively.

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