Anomalous Distribution of K-Isotopes During Countercurrent Electromigration in Molten (Li, K) NO_3

Isao Okada, Teruo Haibara, Osamu Odawara
Department of Electronic Chemistry, Tokyo Institute of Technology, Nagatsuta, Midori-ku, Yokohama 227, Japan

Masao Nomura, and Makoto Okamoto
Research Laboratory for Nuclear Reactors, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 156, Japan

Z. Naturforsch. **43a,** 1005–1006 (1988);
received August 28, 1988

The previously presented theory that, in countercurrent electromigration of molten common anion binary mixtures, the lighter isotope of the less mobile cation should anomalously enrich in a zone next to the anode, has been substantiated for the K isotopes in molten (Li, K) NO_3.

Until Lundén and Ljubimov's discovery of 'non-ideal behaviour' some twenty years ago [1, 2], it had generally been believed that, in countercurrent electromigration of pure or mixture melts with an initially uniform distribution along a separation tube, the lighter and heavier isotopes of the cation enrich only at the cathode and anode, respectively. They discovered in countercurrent electromigration of molten (Li, K) $(SO_4)_{0.5}$ that on the anode side of the separation tube the gradient of $^{41}K/^{39}K$ is slightly positive before it becomes zero.

In a previous paper [3] we have argued that in electromigration of molten systems consisting of two cations A and B and a common anion, enrichment of the lighter isotope of the less mobile cation B should occur in the region where $dc_B/dz < 0$, where c_B is concentration of B, and z is the distance taken from the anode towards the cathode. For more general cases, including temperature gradients, the reasons for such changes in composition in countercurrent electromigration have been discussed by Klemm and Lundén [4] with essentially the same conclusion for the above mentioned case.

Our argument was experimentally substantiated by enrichment of ^6Li in the range where $dc_{Li}/dz < 0$ in electromigration of molten binary mixtures (Li, K) Cl and (Li, K) NO_3; the condition $dc_{Li}/dz < 0$ was realized, if the Li^+ ions were less mobile than the K^+ ions. In case where at low temperature the K^+ ions were less mobile, however, enrichment of ^{39}K was not clearly detected (see Table 2 in [3]). This is presumably because the precision of the used mass spectrometer was not good enough.

Thus, the purpose of the present work is to substantiate our theoretical equations in [3] by showing experimentally that an anomalous enrichment of ^{39}K actually occurs at the place where $dc_K/dz < 0$; in the present work we have used a mass spectrometer with much better accuracy and precision.

(Li, K) NO_3 of the eutectic composition (mole fraction of $LiNO_3$, $x_{Li} = 0.58$) was chosen. Since $b_{Li} > b_K$ below ca. 520 K [5], at lower temperatures K^+ ions are expected to enrich with respect to Li^+ ions on the anode side in a separation tube, and there the condition of $dc_K/dz < 0$ (and therefore $dx_K/dz < 0$) being realized, ^{39}K should enrich in this region. Thus, electromigrations were performed at 450 K. The experimental procedures were similar to those in the previous study [5]. The separation tube was inserted into a large vessel containing catholytes of a mixture of (Li, K) NO_3 of the eutectic composition + NH_4NO_3 (about 50 mol% of the total mixture); since the temperature of the electromigration was relatively low, NH_4NO_3 could be used as one of the catholytes serving also as a heat bath for the separation tube. Alumina powder of 100–150 µm was used as diaphragm. The diaphragm part was ca. 4 mm in diameter and ca. 20 cm in length. After electromigration the separation tube was cut into several pieces for the chemical and isotope analyses. The quantities of Li^+, K^+ and NH_4^+ ions in each fraction were measured with an ion chromatographic analyser (IC 500S made by Yokogawa Electric Co. Ltd., Tokyo). A Varian MAT 261 mass spectrometer was used for the measurement of the isotope ratios $^7Li/^6Li$ and $^{41}K/^{39}K$. The reproducibility of the isotope ratio measurements was nearly within the experimental errors of each measurement.

The main experimental conditions and the results are given in Table 1. The fractions are numbered from the top (anode side) to the bottom of the separation tube. The ε_c values defined as $\varepsilon_c = (b_{Li} - b_K)/\bar{b}$ ($\bar{b} = x_{Li} b_{Li} + x_K b_K$) are in good agreement with the previously obtained ones (the extrapolated value of ε_c was ca. 0.080 [5]).

Reprint requests to Prof. Isao Okada, Department of Electronic Chemistry, Tokyo Institute of Technology at Nagatsuta, Midori-ku, Yokohama.

0932-0784 / 88 / 1100-1005 $ 01.30/0. – Please order a reprint rather than making your own copy.

Table 1. The main experimental conditions and the results. x^0_{Li}: initial concentration of $\mathrm{LiNO_3}$, Q: transported charge, t: duration of electromigration, $\varepsilon_c = (b_{\mathrm{Li}} - b_{\mathrm{K}})/\bar{b}$, $\varepsilon_{\mathrm{Li}} = (b_6 - b_7)/b_{\mathrm{Li}}$, $\varepsilon_{\mathrm{K}} = (b_{39} - b_{41})/b_{\mathrm{K}}$ (b_6, b_7, b_{39} and b_{41} are the internal mobilities of $^6\mathrm{Li}^+$, $^7\mathrm{Li}^+$, $^{39}\mathrm{K}^+$ and $^{41}\mathrm{K}^+$ ions, respectively).

Exp. No.	T/K	x^0_{Li}	Q/C	t/hr	ε_c	$\varepsilon_{\mathrm{Li}}$	ε_{K}
1	450	0.414	6649	37.6	0.0882 ± 0.0007	0.0074 ± 0.0001	0.0010 ± 0.0001
2	450	0.414	6092	38.8	0.0778 ± 0.0008	0.0061 ± 0.0001	0.0007 ± 0.0002
3	450	0.414	6618	32.4	0.0866 ± 0.0008	0.0079 ± 0.0001	0.0010 ± 0.0002

Table 2. The distribution of the isotopes and the cations after electromigration (Exp. No. 3). Initial values: $x^0_{\mathrm{Li}} = 0.414 \pm 0.001$, $^7\mathrm{Li}/^6\mathrm{Li} = 12.166 \pm 0.029$, $^{41}\mathrm{K}/^{39}\mathrm{K} = 0.07172 \pm 0.00012$. The total length of the diaphragm part was 22.2 cm. The values from Fr. Nos. 9 to 14 are not given here, in which $\mathrm{NH_4^+}$ ions were also contained.

Fr. No.	Length/mm	$N_{\mathrm{Li}}/\mathrm{mmol}$	$N_{\mathrm{K}}/\mathrm{mmol}$	x_{Li}	$^7\mathrm{Li}/^6\mathrm{Li}$	$^{41}\mathrm{K}/^{39}\mathrm{K}$
1	–	0.240 ± 0.002	0.857 ± 0.009	0.219 ± 0.007	15.326 ± 0.099	0.07423 ± 0.00014
2	14	0.079 ± 0.001	0.697 ± 0.007	0.102 ± 0.008	17.738 ± 0.014	0.07272 ± 0.00013
3	16	0.085 ± 0.001	1.157 ± 0.012	0.068 ± 0.009	16.073 ± 0.082	0.07192 ± 0.00012
4	16	0.185 ± 0.002	1.214 ± 0.012	0.132 ± 0.008	14.942 ± 0.067	0.07141 ± 0.00012
5	16	0.419 ± 0.004	0.944 ± 0.009	0.307 ± 0.005	13.886 ± 0.033	0.07156 ± 0.00006
6	16	0.535 ± 0.005	0.803 ± 0.008	0.400 ± 0.004	12.911 ± 0.014	0.07165 ± 0.00009
7	16	0.533 ± 0.005	0.741 ± 0.007	0.418 ± 0.004	12.472 ± 0.014	0.07185 ± 0.00008
8	16	0.588 ± 0.006	0.840 ± 0.008	0.412 ± 0.004	12.309 ± 0.010	0.07180 ± 0.00007

In all the runs anomalous enrichment of $^{39}\mathrm{K}$ has been observed. As an example, distributions of the cations and the isotope ratios in one experiment are given in Table 2. Around the region corresponding to Fr. Nos. 4 and 5, it can be assumed that $\mathrm{d}x_{\mathrm{K}}/\mathrm{d}z < 0$ during most of electromigration, and thereby $^{39}\mathrm{K}$ was anomalously enriched. In Fr. No. 4 $^{39}\mathrm{K}$ was enriched by ca. 4.5% with reference to the initial salt, which is distinctively above the limit of the errors of the used mass spectrometer. Even if in Fr. No. 3 $\mathrm{d}x_{\mathrm{K}}/\mathrm{d}z$ may have been negative during most of electromigration, the $^{39}\mathrm{K}$ enriched there may have been overcompensated by $^{41}\mathrm{K}$ enriched at the anode and diffusing into this region.

Similar distributions have been found in the other two runs.

Thus, as previously predicted by the equations and the numerical calculations based on them, this kind of anomaly generally occurs for the isotopes of the less mobile cation in countercurrent electromigration of a common anion binary mixture. It was probably ascribable to the insufficient precision of the mass spectrometer that in the previous study [3] the anomaly of the K isotopes could not apparently be detected.

[1] V. Ljubimov and A. Lundén, Z. Naturforsch. **21 a,** 1592 (1966).

[2] A. Lundén and V. Ljubimov, Z. Naturforsch. **23 a,** 1558 (1968).

[3] I. Okada and A. Lundén, Z. Naturforsch. **38 a,** 97 (1983).

[4] A. Klemm and A. Lundén, Z. Naturforsch. **41 a,** 935 (1986).

[5] A. Lundén, J. Habasaki, and I. Okada, Z. Naturforsch. **42 a,** 683 (1987).