BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 394—397 (1970)

Isotope Effect of Molten Thallous Nitrate in Countercurrent Electromigration

Isao OKADA and Nobufusa SAITO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo

(Received July 8, 1969)

The isotope effect of the thallous ion in the countercurrent electromigration of molten thallous nitrate has been measured at 219°C. The relative internal mobility difference between $^{203}Tl^+$ and $^{205}Tl^+$, $\Delta V/V_{Tl}$, has been determined to be 0.00035 ± 0.00002. The mass effect $\mu_{Tl}=(\Delta V/V_{Tl})/(\Delta M/M_{Tl})$, has been calculated to be -0.035 ± 0.002, and this value has been compared with those of alkali nitrates previously determined.

Several studies have been made of the mass effects[*1] of internal mobilities[1)] in countercurrent electromigration with a variety of molten alkali nitrates.[2—7)] However, no data on the mass effects have been published for other molten nitrates. This report will be concerned with the mass effect of the internal mobilities of thallous nitrate in a molten state.

Experimental

The experiments were performed in the cell shown in Fig. 1. A mixture of desiccated lithium and potassium nitrates was poured into a quartz beaker and melted by electric heating. On the other hand, a separation tube made of Vycor glass was packed with quartz powder (100—150 mesh size) and placed into a vessel containing molten thallous nitrate. After the molten nitrate had been soaked up to the upper end of the diaphragm of quartz powder in the separation tube, it was transferred into the quartz beaker. Then electromigration was immediately started. A platinum wire and an aluminum tube were used as the anode and the cathode of the electromigration respectively. The temperature of the separation tube was kept at 219±3°C,[*2] and a mixture of nitrogen dioxide and oxygen was introduced into the cathode compartment at a constant rate throughout the electromigration. When the electromigration had terminated, the separation tube was taken out from the quartz beaker. After cooling, the surface of the tube was thoroughly cleaned, and the tube was cut into several fractions. The salt in each fraction was leached out with water. In order to determine the thallium content of each fraction, aliquots of the fractions were poured on a column of an anion exchange resin, Dowex-1 (100—200 mesh), of the OH-form. The thallium ion was eluted with distilled water. The thallium in the the effluent was then determined by means of Andrew's titration.

Sodium iodide was added to another aliquot of each fraction. After the resulting precipitate of TlI had been filtered, the potassium in the filtrate was determined gravimetrically as potassium tetraphenylborate. The lithium content of each fraction was determined by spectrophotometry.

The isotopic ratio of thallium in each fraction was measured with an Atlas CH-4 mass spectrometer equipped with a double-filament ion source for surface ionization. The ionizing and vaporizing filaments were made of rhenium ribbons. The distance between these filaments was about 2 mm. Background and memory effects were eliminated by boiling the ionization box in distilled water for 20 min and by then heating *in vacuo* both ionizing and vaporizing filaments at about 2500°C with a current of 5A for 30 min. The sample (about 10 μg as thallium) was painted on the vaporizing filament in the form of thallous nitrate. After the ionization box had been placed in the ion-source compartment of the mass spectrometer, the ionizing filament was slowly heated electrically up to about 1200°C. The ion current of thallium was found to be stable after about 30—50 min. The ion current of ^{205}Tl was controlled to about 3×10^{-12} A at the collector by adjusting the temperature of the ionizing filament.

[*1] Mass effect, μ, is defined as the ratio of relative mobility difference, $\Delta V/V$, to relative mass difference, $\Delta M/M$, of two isotopes. It is expressed as $\mu=(\Delta V/V)/(\Delta M/M)$.

1) A. Klemm, "Molten Salt Chemistry," ed. by M. Blander, Interscience Publishers, New York, London (1963) p. 538.

2) A. Lundén and A. Ekhed, *Z. Naturforsch.*, *A*, **24**, 892 (1969).

3) N. Saito, I. Tomita and I. Okada, unpublished.

4) N. Saito, I. Tomita and I. Okada, *J. Nucl. Sci. Technol. (Tokyo)*, **3**, 140 (1966).

5) A. Lundén and A. Ekhed, *Z. Naturforsch.*, *A*, **23**, 1779 (1968).

6) A. Lundén, C. Reutersward and N. G. Sjöberg, *ibid.*, *A*, **10**, 279 (1955).

7) A. Lundén, *ibid.*, *A*, **21**, 1510 (1966).

[*2] The thermogravimetric analysis of thallous nitrate has indicated that no thermal decomposition of the nitrate takes place below 300°C with a heating rate of 2°C/min.

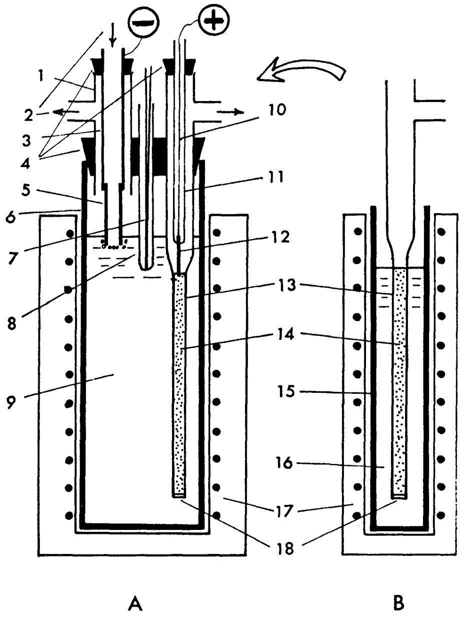

Fig. 1. Electromigration cell.

A: Electromigration cell.
B: Vessel for filling molten $TlNO_3$ into the separation tube.
1: Pyrex glass tube
2: Mixture of NO_2 and O_2
3: Stainless steel tube
4: Silicone stopper
5: Aluminum tube
6: Quartz beaker
7: Thermocouple (Alumel-chromel)
8: Pyrex sheath for thermocouple
9: Mixture of molten $LiNO_3$ and KNO_3
10: Stainless steel lead
11: Pyrex glass tube
12: Platinum wire
13: Separation tube (Vycor glass)
14: Quartz powder of diaphragm
15: Pyrex glass vessel
16: Molten $TlNO_3$
17: Electric oven
18: Quartz frit

Results and Discussion

Four runs of electromigration were carried out. The results of these experiments are summarized in Table 1. For one of these experiments, the detailed experimental conditions and the results obtained are given in Table 2.

For the calculation of the relative internal mobility difference of isotopic ions of thallium, $^{203}Tl^+$ and $^{205}Tl^+$, a formula presented by Klemm[8] can be reformed as follows:

$$\begin{aligned}\varepsilon &= (V_{203}-V_{205})/V_{Tl}\\ &= (\boldsymbol{F}/Q)\{(x_0+1)/x_0\}\sum_i (x_i-x_0)N_i/(x_i+1) \qquad (1)\end{aligned}$$

where V_{203}, V_{205}, and V_{Tl} are the internal mobilities of $^{203}Tl^+$, $^{205}Tl^+$, and the thallous ion; where x_i and x_0 are the isotopic ratios of ^{205}Tl to ^{203}Tl in the ith fraction of thallium salt in the separation tube after and before electromigration respectively; where N_i is the equivalent quantity of the thallous ion in the ith fraction; where Q is the transported charge, and where $\boldsymbol{F}$ is the Faraday constant.

The mean square error of the relative internal mobility difference, σ_ε^2, is expressed as:

$$\begin{aligned}\sigma_\varepsilon^2 &= (\partial\varepsilon/\partial x_0)^2\sigma_{x_0}^2 + \sum_i (\partial\varepsilon/\partial x_i)^2\sigma_{x_i}^2 + \sum_i (\partial\varepsilon/\partial N_i)^2\sigma_{N_i}^2\\ &= (\boldsymbol{F}/Qx_0)^2\sum_i [\{x_i+x_0^2)N_i/(x_i+1)^2\}(\sigma_{x_0}^2/x_0^2)\\ &\quad + (x_0+1)^4N_i^2\sigma_{x_i}^2/(x_i+1)^4\\ &\quad + (x_0+1)^2(x_i-x_0)^2\sigma_{N_i}^2/(x_i+1)^2] \qquad (2)\end{aligned}$$

where σ_{x_i} and σ_{x_0} are the standard deviation of the isotopic ratio in the ith fraction of the thallium in the separation tube after and before electromigration respectively, and where σ_{N_i} is the mean deviation of the equivalent quantity of thallous ion in the ith fraction. The values of ε are calculated by Eq. (1) only for the fractions in which ^{205}Tl is enriched. If Eq. (1) is applied to the region of the separation tube where the contents of lithium and potassium nitrates are negligibly small as compared with thallium, the calculated value of ε can be regarded as that of pure thallous nitrate.

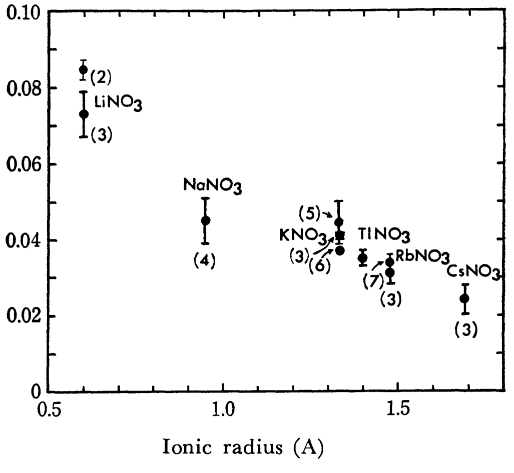

Fig. 2. Relationship between the cationic radius and the internal mass effect of molten nitrates. Figures in parentheses stand for the reference number.

Salt	mp (°C)	Ref.	Temp. (°C)
$LiNO_3$	261	(2)	313—488
		(3)	265—460
$NaNO_3$	308	(4)	340—380
KNO_3	333	(3)	380
		(5)	354—454
		(6)	360
$RbNO_3$	316	(3)	360
		(7)	354
$CsNO_3$	414	(3)	450
$TlNO_3$	206.5	This work	219

---

[8] A. Klemm, *Z. Naturforsch.*, **1**, 252 (1946).

TABLE 1. RESULTS OF THE ELECTROMIGRATION

Experiment No.	1	2	3	4
Electric current (mA)	100—105	60—80	80—100	80—100
Voltage (V)	100	125—130	90	115—120
Duration (hr)	100	74.5	50	50
Transported charge (Coulomb)	37380	16930	15570	15890
Temperature (°C)	219±3	219±3	219±3	219±3
Separation tube				
Length (mm)	99+33	105+29	95+25	143
Int. diam. (mm)	4 5	4 5	4 5	4
Relative internal mobility difference $\{\varepsilon=(\Delta V/V)\}$	0.00031 ±0.00003	0.00031 ±0.00003	0.00037 ±0.00003	0.00037 ±0.00004
Internal mass effect $(-\mu_i)$	0.032 ±0.003	0.032 ±0.003	0.038 ±0.003	0.038 ±0.004

TABLE 2. EXPERIMENTAL CONDITION FOR THE ELECTROMIGRATION

(Exp. No. 3)
Electric current: 80—100 mA,
Voltage: 90 V,
Duration: 50 hr,
Transported charge: 15570 Coulomb,
Temperature: 219±3°C,
Separation tube: 95 mm (int. diam. 4 mm; upper part)
+25 mm (int. diam. 5 mm; lower part).

Fr. No.	Length (mm)	$TlNO_3$ (mM)	$^{205}Tl/^{203}Tl$	$LiNO_3$ (mM)	KNO_3 (mM)	Quartz (mg)
1	—	0.020±0.002	2.470±0.007	0.01	0.03	0
2	12	0.284±0.002	2.540±0.006	0.09	0.02	120
3	16	1.144±0.001	2.451±0.006	0.09	0.05	254
4	18	1.746±0.001	2.392±0.005	0.09	0.09	276
5	10	0.514±0.002	2.378±0.005	0.05	0.03	151
6	14	0.863±0.002	2.371±0.004	0.09	0.04	234
7	17	1.093±0.001	2.374±0.004	0.19	0.39	248
8	18	3.540±0.016	2.363±0.006	0.24	0.11	521
9	15	0.629±0.002	2.346±0.003	—	0.87	397

The isotopic ratio before electromigration: 2.381±0.006

The calculations based on the results of Experiments Nos. 1, 2, 3, and 4 have shown that the mean values of the relative internal mobility difference between ^{203}Tl and ^{205}Tl and of the internal mass effect,[1] μ_{Tl}, for thallous nitrate are 0.00035±0.00002 and −0.035±0.002 respectively.

In order to compare the mass effect of thallous nitrate with those of the alkali nitrates so far measured, the mass effects of these cations are plotted as a function of the cationic radius[9] in Fig. 2. Figure 2 clearly demonstrates that, the larger the cationic radius, the lower the internal mass effect of molten nitrates.

It is of interest that the linear relationship between the cationic radius and the internal mass effect which is observed for alkali nitrates also holds for thallous nitrate.

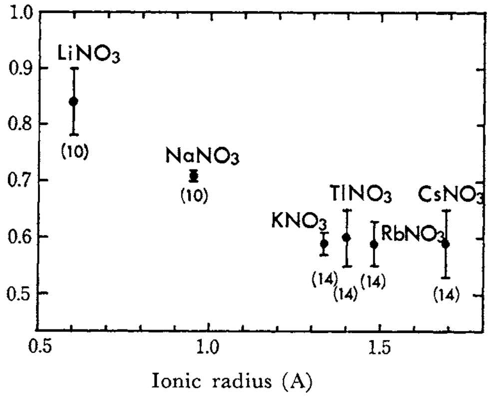

Fig. 3. Relationship between the cationic radius and the transport number of cation in the molten nitrates.
Figures in parentheses stand for the reference number.

---

[9] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell Univ. Press, New York (1960) p. 516.

It has been suggested by Duke and Owens[10)] that the transport number of cations in pure molten nitrates can be expressed as $t_+ = r_- / (r_+ + r_-)$, where r_+ and r_- $(= 2.19$ A,[11)] 2.3 A[12)]$)$ are the ionic radius of the cation and nitrate ions respectively. Therefore, the transport number of the cation for nitrates is nearly a linear function of the cationic radius, as is shown in Fig. 3: $t_+ = 1 - r_+/(r_+ + r_-) \fallingdotseq 1 - kr_+$ $(r_+ \ll r_-)$, where k is a constant.

It can be expected that, as the transport number of the cation increases, the value of the internal mass effect will also increase.[13)] In fact, this trend has been observed in these nitrate systems.

[10)] F. R. Duke and B. Owens, *J. Electrochem. Soc.*, **105**, 548 (1958).

[11)] O. J. Kleppa and L. S. Hersh, *J. Chem. Phys.*, **34**, 351 (1961).

[12)] A. F. Wells, "Structural Inorganic Chemistry," 3rd Ed., Oxford Univ. Press, London (1962) p. 171.

[13)] A. Lundén, *Z. Naturforsch.*, *A*, **14**, 801 (1959).

[14)] F. R. Duke and G. Victor, *J. Electrochem. Soc.*, **110**, 91 (1963).