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The Temperature Dependence of the Isotope Effect for Electromigration of Rubidium Ions in Molten Rubidium Nitrate

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The relative difference ($\Delta b/b$) between the internal electromigration mobilities of ^{85}Rb and ^{87}Rb in molten RbNO_3 has been measured over the range 355 to 500 °C. The mass effect $\mu = (\Delta b/b)/(\Delta m/m)$ has a complicated temperature dependence. Thus, the largest mass effect, $-\mu = 0.061$, was obtained at 445 °C, while it is about 0.033 at 350 °C and 0.041 at 500 °C. A similar temperature dependence was found by SAITO et al. for μ_{Na} in pure NaNO_3 , and for both μ_{Rb} and μ_{Na} maxima have been found also in nitrate mixtures (in $\text{KNO}_3\text{--RbNO}_3$ and $\text{NaNO}_3\text{--KNO}_3$).

In molten salts (and in solid phases with a high cation mobility) isotope effects of electromigration should be correlated with the different modes of interaction between the ions of the melt, and a study of temperature dependence of isotope effects might give information on how the relative importance of different modes of interaction changes. A number of studies of temperature effects have been made. Thus, this has been done by KLEMM and different coworkers¹ for both cations and anions in molten halides, and both solid and molten sulfates have been studied by us². Regarding nitrates, we have previously considered temperature effects in pure LiNO_3 , l. c.³, and KNO_3 , l. c.⁴, while other groups have worked on pure NaNO_3 , l. c.⁵ and on the equimolar $\text{NaNO}_3\text{--KNO}_3$ mixture^{6,7}. In the present investigation we have studied pure RbNO_3 over a range above the temperature (350 °C) at which we previously had measured the isotope effect⁸.

Experimental

The experimental procedure was essentially the same as previously^{3,4}, i. e. a Pyrex cell was used where a separation column (length 20 cm, inner diam. about 4 mm) separates a small compartment at the platinum anode from a large compartment on the cathode side. An excess of NO_2 gas was bubbled through the aluminium cathode. In our previous work on LiNO_3 the isotope abundance ratio for the initial salt and for the sample with the highest enrichment differed by 7 to 26%, and in the KNO_3 case this difference was 4 to 15%, while in the present work it is only some 2 to 3%, except for one experiment where it was 5%, cf the separation factors quoted in Table 1. For this reason the accuracy of the calculated mass effect (relative difference in isotope mobility, divided by the relative difference in mass) depends very much on how accurately the initial composition is determined. In order to compensate for the inaccuracy due to the low degree of isotope separation, we made three independent series of mass analyses for each experiment. (We have discussed these evaluation problems previously².) The results are summarized in Table 1, where we also have included our early experiments⁸. Concerning these, it should be remembered that the temperature was at that time only determined by means of a single thermo-

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Table 1. Data of experiments, and results of the present experiments (No. 1–7) as well as of previous ones by us⁸ (A and B) and by OKADA¹⁰ (O 1–3).

Exp. No.	Temp. °C	Duration hours	Transport charge Ah	Separation factor ^a $Q-1$	Mass effect ($-\mu$)				Chosen value
					For each analysis ^b				
A	(354)	120.7	13.00	0.059	0.0350;	0.0351;	0.0351 ^c ;	0.0409 ^c	0.035
B	(346)	38.0	5.16	0.031	0.0412;	0.0363;	0.0363 ^c ;		
O 1	360	46	5.37	0.058	0.0275 ± 0.0052				
O 2	360	48	3.79	0.091	0.0400 ± 0.0047				0.031 ± 0.003
O 3	360	77	4.86	0.107	0.0292 ± 0.0026				
1	355	46.3	8.83	0.020	0.0315;	0.0415;	0.0281		0.034
2	380	24	4.87	0.028	0.0391;	0.0420;	0.0400		0.040
3	428	45.5	11.15	0.053	0.0501;	0.0474;	0.0448		0.047
4	445	23	5.53	0.033	0.0589;	0.0661;	0.0568		0.061
5	450	19	4.07	0.017	0.0409;	0.0444;	0.0381		0.041
6	475	48.0	9.39	0.019	0.0430;	0.0490;	0.0405		0.044
7	500	43.0	8.24	0.028	0.0443;	0.0399;	0.0386		0.041

^a $Q = R_0/R_a$, where R_0 is the abundance ratio ($^{85}\text{Rb}/^{87}\text{Rb}$) of the original salt and R_a that of the sample with the highest enrichment of ^{87}Rb .

^b For experiments in our laboratory (A, B, 1–7) the result quoted for each series of analysis with the mass spectrometer corresponds to the "best value" of the normal composition obtained in that series. For the work in Tokyo (O1–O3) the quoted errors are standard deviations including the errors in chemical analysis as well as in mass spectrometry.

^c Enrichment of ^{85}Rb at the cathode; these mass effects are less accurate than those calculated for enrichment at the anode.

couple, which was not in direct contact with the cell, while we now had three thermocouples at different positions⁴. For this reason our discussion of the temperature dependence will be based only on the present investigation (nos 1–7 in Table 1).

In our previous investigations of pure LiNO_3 and KNO_3 we could detect an anomalous isotope distribution in the separation column, where there was a slight enrichment of the light isotope in the lower parts^{3,4}. As stated above, in the present experiments the maximum enrichment was much less than in the work with the two other nitrates, and it is thus not at all surprising that we could not detect any significant enrichment of the light isotope ^{85}Rb in any part of the separation column. (KANNO⁹ has recently reported on non-ideal behaviour in a binary chlorid mixture, and we have also made some observations on mixtures. We intend to discuss these questions at some other occasion.)

Discussion

The results of the present investigation as well as of our previous one⁸ and of OKADA's¹⁰ are summarized in Fig. 1, where we have used two different symbols for the present results. The reason for this is that there is a surprisingly large difference between the results of no 4 and 5, which were performed at nearly the same temperature. A rapid change in the mass effect at some temperature seems extremely unlikely, and since possible disturbances during an experiment (displacements of the bulk of salt due to e. g. evolving gas bubbles, leakage

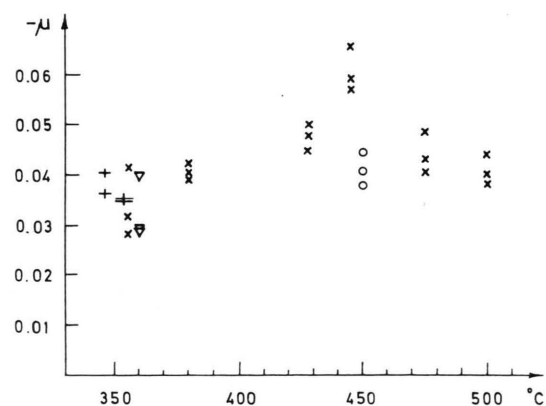


Fig. 1. Temperature dependence of the cation mass effect in pure RbNO_3 . For the present investigation the results marked (○) are considered less accurate than those marked (x). For the previous investigations in our laboratory (+) and by Okada (∇) the temperature was not determined as accurately as in the present investigation.

through cracks, etc.) always result in low apparent mass effects, it seems obvious that no 5 is in error. Such a conclusion is supported by the fact that no 5 was interrupted by a weak explosion at the cathode, but also the two other experiments with a rather short duration (no 2 and 4) were terminated due to some disturbance.

In our previous investigations on LiNO_3 and KNO_3 , l. c.^{3,4}, we have used regression analysis to find a linear correlation between the mass effect and the temperature. If we do so also for the present experiments on RbNO_3 , using data for all

seven experiments, a linear relation is obtained for which the correlation coefficient¹¹ is only 0.33, while if we look for linear correlations on both sides of an assumed maximum at 445 °C, correlation coefficients of the order of 0.9 are obtained both for the combination of no 1–4 and for no 4, 6 and 7 together, cf. equations below. At the low temperature end our present data are in good agreement with our old measurements⁸ as well as with OKADA's¹⁰, especially if one considers that the temperatures quoted in Table 1 for these two sets of experiments are not directly comparable with those for the present experiments. (U-shaped separation tubes were used in previous investigations, and the temperature was measured at only one point in the furnace¹².) The existence of a maximum for the mass effect of Rb is supported by our investigation of cation isotope effects in a KNO_3 – RbNO_3 mixture containing 10 mole per cent RbNO_3 , where an experiment at 420 °C gives a larger isotope effect than the other ones at 378 °C, 473 °C and 526 °C, l. c.¹⁴. Finally, it should be mentioned that an early experiment with a LiNO_3 – RbNO_3 mixture¹³ gave $-\mu_{\text{Rb}} = 0.05$ at a temperature of the order of 400 to 450 °C, l. c.¹². This rather high value for the mass effect was previously considered as due to a concentration effect, but there is now much evidence that isotope effects in nitrate melts are much less sensitive to the composition of the melt than what is the case for chloride melts¹⁵.

Thus, we can conclude that our present results for pure RbNO_3 are in agreement with previous work on pure RbNO_3 as well as on mixtures, and the existence of a maximum for the isotope effect at about 445 °C is thus confirmed. If we, as mentioned above, seek a linear correlation with temperature¹⁶, we obtain

$$-\mu_{\text{Rb}} = 0.0319 \pm 0.0027 + (0.000262 \pm 0.000042)(t - 350) \quad (1)$$

for the range 355–445 °C, while for 445–500 °C the experiments (no 5 excluded) give

$$-\mu_{\text{Rb}} = 0.0571 \pm 0.0024 - (0.000364 \pm 0.000073)(t - 450) \quad (2)$$

where t is the temperature in °C. In spite of the fact that the correlation coefficients are about 0.9

for both these equations, we consider no (2) to be less reliable than no (1). The temperature coefficient is larger than for any of the salts investigated before, thus $\delta \ln \mu_{\text{Rb}} / \delta \ln T = 3.92 \pm 0.63$ at 400 °C.

A maximum in the isotope effect has been found previously for Na in pure NaNO_3 as well as in equimolar NaNO_3 – KNO_3 , l. c.^{5, 6}. From our study of μ_{K} in pure KNO_3 over the range 354 °C to 586 °C we concluded that the isotope effect increased over the whole range. Our data for KNO_3 would, however, permit the alternative interpretation that the mass effect for K increases up to, say, 540 °C and remains constant (or decreases slightly) above that temperature. In that case the equation for μ_{K} would become

$$-\mu_{\text{K}} = 0.0398 \pm 0.0023 + (0.000129 \pm 0.000022)(t - 350) \quad (3)$$

for $354 \leq t \leq 540$ °C instead of

$$-\mu_{\text{K}} = 0.0401 \pm 0.0020 + (0.000124 \pm 0.000015)(t - 350) \quad (4)$$

for $354 \leq t \leq 586$ °C.

The correlation coefficient for Eq. (3) is 0.83 while it is 0.88 for Equation (4). The regression analysis does not give any clear indication whether the isotope effect of KNO_3 increases only up to about 540 °C or over the whole investigated range. We prefer to continue to express the temperature effect in KNO_3 by means of Equation (4).

The result of the present work and previous investigations of the temperature dependence of the electromigration isotope effect of cations in molten nitrates is thus that the situation is quite complicated regarding the sign and magnitude of the temperature coefficients. Alternative interpretations have been discussed by other groups^{5–7}, and we would prefer to postpone our discussion until some experiments on the temperature dependence in nitrate mixtures are completed^{14, 17}.

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- ¹⁶ For run 1 and 4 there is a considerable spread in the obtained values of the mass effect. If we exclude the highest value for these two runs, we obtain an equation for μ_{Rb} with practically the same temperature coefficient as in Eq. (1) but with a 5% lower absolute value at 350 °C.
- ¹⁷ I. OKADA and A. LUNDÉN, work in progress.

Transport Properties of Thoria and Thoria-based Solid Solutions

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The methods for obtaining transport numbers in oxides are described and associated experimental difficulties are discussed. Their reliability is assessed and used in conjunction with related data to offer a consistent picture for thoria and thoria-based solutions between 500° and 1600 °C. Both are ionic conductors within certain ranges of oxygen pressure. It is concluded that, for ThO_2 ,

$$\log P_{\oplus} = -4.5, \quad \log P_{\ominus} \sim -\frac{60.5 \times 10^3}{T} + 23.3$$

and, for $\text{ThO}_2\text{--Y}_2\text{O}_3$ solutions (10–20 mole % $\text{YO}_{1.5}$),

$$\log P_{\oplus} = 1.8, \quad \log P_{\ominus} = -\frac{57.9 \times 10^3}{T} + 12.4$$

where P_{\oplus} and P_{\ominus} , respectively, are the oxygen pressures (atm) where the ionic and p-type and the ionic and n-type conductivities are equal. Ionic conductivity and charge carrier mobilities in thoria are briefly considered.

Transport properties of refractory oxides are important in the oxidation of metals, sintering, solid state reactions, and in their ceramic, electronic, nuclear, and aerospace applications. In the case of ThO_2 -based solid solutions (containing CaO , Y_2O_3 , or a rare earth oxide), they are of further importance since these systems by virtue of a high concentration of oxygen vacancies behave as oxygen-ion conducting solid electrolytes over certain ranges of temperature and oxygen pressure. Although their low ionic conductivities and p-type conductivity at high oxygen pressures preclude their use in batteries or fuel cells, they have found wide application in emf measurements to determine thermodynamic properties, particularly of systems exerting low oxygen potentials¹.

Nevertheless, as difficult high-temperature measurements are involved, the available data on their

transport properties, particularly at low oxygen pressures, are widely scattered. Recently, an analysis was presented for stabilized zirconia electrolytes² in an effort to account for some of the discrepancies existing in their case. Herein, a similar analysis is made for thoria-based solutions. Results for thoria are included for comparison. The emphasis will be on transport numbers since they are of major importance in solid electrolyte applications.

The different experimental techniques available to determine transport numbers in oxides will be briefly reviewed and later discussed and assessed for reliability. From this assessment and related emf data, the best estimate of the transport numbers for thoria and thoria-based solutions will be offered.

Methods of Determining Transport Numbers in Oxides

The most direct method involves measuring the $a\text{--}c$ conductivity as a function of oxygen pressure

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