Cation Mobilities, Including Isotope Effects, for Electromigration in Molten Mixtures of Potassium and Rubidium Nitrate

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Electromigration of cations has been studied in molten KNO_3-$RbNO_3$ mixtures as a function of concentration (11 – 94 mole % $RbNO_3$, about 380 °C) and temperature (about 10 mole % $RbNO_3$, 378 – 560 °C). The mobility of K^+ is slightly larger than that of Rb^+ at all concentrations, the difference being about 3% in KNO_3-rich and 2% in $RbNO_3$-rich mictures. Neither for potassium nor for rubidium is the isotope effected affected much by the composition of the melt, although there is a tendency that the isotope effect for rubidium is somewhat larger in mixtures than in pure salts. Both isotope effects have the same temperature dependence in the investigated mixture as in the pure salts.

The isotope effects for potassium and rubidium have also been determined for ternary $NaNO_3$-KNO_3-$RbNO_3$ mixtures containing about 5 mole percent of $NaNO_3$ and of $RbNO_3$. For comparison, a study of the mass effect for potassium ions in $NaNO_3$-KNO_3 is also reported.

There have been many studies of electromigration in molten nitrate mixtures using different techniques [1], and the results are expressed either as external or internal mobilities, depending on whether some part of the apparatus or one of the abundant ions is chosen as the reference frame [2]. It should be an advantage if the relative mobilities of different ions as well as of the isotopes of these ions were measured in the same experiment. Isotope effects of *one* component have been reported previously for $NaNO_3$-KNO_3 mixtures, either for one of the constituents [3] (Na) or for an impurity [4] (Li). For the system KNO_3-$RbNO_3$ we have studied in the present work the relative internal mobilities of K-Rb, ^{39}K-^{41}K and ^{85}Rb-^{87}Rb.

Experimental

The experimental arrangement was the same as in previously reported investigations of electromigration in pure potassium nitrate [5] and rubidium nitrate [6]. The concentrations of K and Rb as well as of Na (as a possible corrosion product) were determined by means of atomic absorption spectrophotometry, and the isotope abundances for K and Rb were measured with a mass spectrometer. The relative difference in cation mobilities ($\Delta b/b$, where $\Delta b = b_{\text{light ion}} - b_{\text{heavy ion}}$), the transport number (t_K) and the mass effects (μ_K, μ_{Rb}) were calculated in the usual way [7]. All these entities are determined relative to the nitrate ion, i.e. they are internal entities. Two sources of error should be considered, that do not occur in experiments with pure salts. First, concentration changes due to electromigration cause density changes in the anode compartment and separation tube. If, as in the present case, the component with the highest density is enriched in the upper part of the separation tube, this tends to create an unstable situation. In the present case the enrichment of $RbNO_3$ is moderate, and the density change is thus small, and the packing suppresses convection in the column. The part of the column in which the composition has changed (l/L in Table 1) is, however, larger than for the isotope fractionation in experiments with pure nitrates [5, 6, 8]. Concentration changes in a large part of the column were observed also in a previous study of sulphate mixtures [7]. The second source of error is a partial fractionation of the compounds when the melt solidifies. This should be negligible in the present experiments, since the melting point does not vary much with composition [9].

Relative Mobility of Potassium and Rubidium Ions

The results of 13 experiments on the binary system are summarized in Table 1. For runs 7 – 11 the composition of the melt is approximately the same, some 90% KNO_3, while temperature is increased from 378 to 560 °C, while for runs 7, 12 – 19 the temperature is of the order of 380 °C, while the composition of the melt is varied.

Concerning the relative internal mobility of K and Rb, the results are strongly influenced by the

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Table 1. Electromigration in the systems KNO_3-$RbNO_3$ and $NaNO_3$-KNO_3-$RbNO_3$; data of experiments and results. x_K = initial conc. of KNO_3 . l/L = fraction of the separation column in which the composition had changed. The column length (L) is about 20 cm in all experiments. $\Delta b/b$ = relative difference in cation mobility; $\Delta b = b_K - b_{Rb}$. The preferred value corresponds to the quoted initial composition (x_K), while the alternatives are based on other possible values of x_K .

Run No. [a]	100 x_K mole %	Temp. °C	Duration hours	Transp. charge mF	Current density A/cm²	l/L %	$\Delta b/b$ Preferred data	$\Delta b/b$ Alternatives	Transp. number t_K	Mass effects		Deviations [b]	
										$-\mu_K$	$-\mu_{Rb}$	$\delta\mu_K$ %	$\delta\mu_{Rb}$ %
7	89.4	378	18.3	129.7	3.0	27	0.025		0.896	0.038	0.041	1.1	43
8	89.2	420	24.0	171.7	2.8	75	0.039	0.027; 0.049	0.896	0.048	0.064	0.7	53
9	91.2	473	22.6	180.6	3.2	72	0.059	0.025; 0.094	0.917	0.044	0.062	1.6	32
10	91.3	526	24.0	200.1	3.2	76	0.018	0.016	0.914	0.056	0.053	2.5	5.2
11	90.5	560	23.0	179.9	3.3	62	0.036 [c]		0.909	[c]	[c]		
12	86.7	378	48.0	442.2	3.7	69	0.025		0.870	0.049	0.050	6.4	5.7
13	74.5	383	48.0	419.9	3.5	87	0.027	0.025	0.750	0.040	0.041	1.3	4.1
14	67.9	350	48.0	414.8	4.0	100	0.034		0.686	0.047	0.053	2.3	5.6
15	34.6	353	48.0	396.0	3.3	100	0.012	0.005	0.348	0.055	0.059	3.7	5.8
16	20.8	383	33.0	295.8	3.6	83	0.025	0.011; 0.027	0.212	0.032	0.054	5.9	19
17	16.8	369	21.7	148.7	2.8	100	0.022	0.008	0.171	0.038	0.046	13	11
18	14.7	370	48.0	314.3	2.8	94	0.015	0.008; 0.026	0.149		0.034		10
19	6.0	381	48.0	414.2	3.7	72	0.018	0.013	0.061		0.049		16
3 [d]	90.3 [d]	381	37.2	249.4	2.5	100	0.069	0.062; 0.073	0.905 [d]	0.050	0.048	45	19
4 [d]	88.1 [d]	380	30.6	229.7	2.8	100	0.056	0.040; 0.089	0.882 [d]	0.042	0.055	9.6	17
6 [d]	89.5 [d]	344	97.2	797.5	3.1	93	0.039 [e]	0.041	0.896 [d]	0.042	0.046	2.3	2.4

[a] The experiments are numbered in sequence with previously reported experiments on nitrate mixtures [1].

[b] The mass effects are reported as averages from two to four independent abundance ratio measurements. $\delta\mu_K$ and δ_{Rb} indicate how much the extreme value obtained for the mass effect deviated from the reported average.

[c] Fluctuations of the salt level were observed during the run, and it is reason to expect $\Delta b/b$ to be somewhat low. Concerning the mass effects, it is clear that $-\mu_{Rb} < -\mu_K$, but the accuracy is bad.

[d] Experiments 3, 4 and 6 are with ternary mixtures. For these experiments we have $100 \times_{Rb}$ = 4.4, 5.4 and 4.9 mole % respectively, and t_{Rb} = 0.041, 0.051 and 0.047, respectively.

[e] For the mobility difference between Na and K ions this experiment gives b_{12}/b = 0.007; for runs 3 and 4 see [1].

accuracy of the chemical analysis and on what the initial composition is taken to be. To illustrate this we have for some of the runs reported alternative results for $\Delta b/b$ in addition to the data we have accepted as being the best. The uncertainty is too large to allow any definite conclusions on the temperature dependence of $\Delta b/b$ in the range of nearly 200 degrees covered by the runs 7 – 11. There are to our knowledge no other investigations of cation mobilities in KNO_3-$RbNO_3$ mixtures, but in the $NaNO_3$-KNO_3 and $LiNO_3$-KNO_3 ones studied by Lantelme and Chemla [10, 11], and the $LiNO_3$-$RbNO_3$ ones investigated by Okada, Takagi and Kawamura [12], there is a tendency that $\Delta b/b$ decreases when the temperature is increased, and becomes negative at a sufficiently high temperature. (Also in the mixtures $LiNO_3$-$TlNO_3$ and $RbNO_3$-$TlNO_3$ studied by Kawamura, Okada and Odawara [13] it is found that the mobility difference decreases when the temperature is increased.) In our system the radii of the two alkali ions differ by only 10%, while the difference in Pauling radii is larger for the other alkali mixtures. The system KNO_3-$RbNO_3$ is close to an ideal mixture when the equivalent conductivity Λ or the average cation mobility $b = \Lambda/F$ is considered (F = the Faraday constant), although a more detailed analysis is not possible since the density of the mixture has been measured for only four compositions, while the specific conductivity is known for 19 mixtures [14].

Although the mobility of the light ion always is larger than that of the heavy ion, there is a tendency that the mobility difference is reduced when the concentration of Rb^+ increases. Thus, if the experiments at about 380 °C are considered, for the melts rich in KNO_3 (runs 7, 12, 13) $\Delta b/b$ is of the order of 3%, while it is close to 2% for the runs [16 − 19] with melts rich in $RbNO_3$. A least squares fit for runs 7, 12 − 19 gives

$$\Delta b/b = (0.022 \pm 0.002) + (0.012 \pm 0.006)\,(x_K - 0.457)\,.$$

The results are in accordance with the general observation for molten salts that Δb is reduced, when the mole fraction of the light component is lowered. (In mixtures containing Li or Na as the light component, Δb becomes negative below some concentration [10, 11].) The small effect of composition on $\Delta b/b$ is in agreement with the fact that the equivalent conductivity is nearly additive for KNO_3-$RbNO_3$, while there is a negative deviation from additivity for most univalent nitrate mixtures [15]. There are no data available on diffusion in our system, but it might be mentioned that the interdiffusion coefficient varies linearly with composition for the system $NaNO_3$-$RbNO_3$, loc. cit. [16].

Table 1 also includes data on three experiments with ternary mixtures [1] with K^+ as the abundant ion and about 5% each of Na^+ and Rb^+. In these three experiments the concentration of Rb^+ ions was thus about half that of the lowest one for the binary mixtures (runs 7 − 11), and the fact that the $\Delta b/b$ values are high for these runs could have been considered as evidence that the mobility of the Rb^+ ions is reduced considerably when its concentration becomes sufficiently low, had it not been that Honig's [17] study of the mobility of trace amounts of Rb^+ in KNO_3 at 450 °C corresponds to $\Delta b/b = 0.031$ (l.c. [1]). Another explanation of b_K-b_{Rb} being larger in runs 3, 4 and 6 than in the other ones, would be that this mobility difference is influenced by the presence of a third ion, Na^+, but one would need more data before either of these explanations can be accepted. (A third possibility is that the observed separation is caused by fractionation upon solidification is considered less likely, since this would also cause the observed isotope fractionations to be low which does not seem to be the case, cf. below.)

Isotope Effects of Cation Mobilities

The following discussion is, for simplicity, concentrated on the runs with binary mixtures. The results for the ternary ones which are included in the table and the figures, support the conclusions from the work with the binaries.

For each run the mass effect for potassium, μ_K, is obtained as the average from two series of abundance measurements, while two, three or four series were used to calculate μ_{Rb}. The obtained averages are listed in Table 1. The accuracy of the mass effect depends both on that of the mass spectrometer measurements and on that of the transport number determination. Thus for a given ion we expect the accuracy of the mass effect to be better when the ion is abundant than when it is diluted. As an indication of the accuracy we are quoting ($\delta\mu$) how much the extreme value used in the calculation deviates from the reported average. The mass effects are plotted versus the composition in Fig. 1 and the temperature in Figure 2. For comparison we have added the estimated mass effects for the pure salts at 380 °C, $-\mu_K = 0.044$ and $-\mu_{Rb} = 0.040$ and the temperature dependences determined previously for the pure salts [5, 6]. Since the temperature dependence in pure $RbNO_3$ was complicated, the curve given in Fig. 2 is of course very approximate. Our run at the highest temperature 560 °C (run 11) was not quite successful, since the salt level fluctuated during the run, which probably caused a certain remixing. It was, however, possible to conclude from this ex-

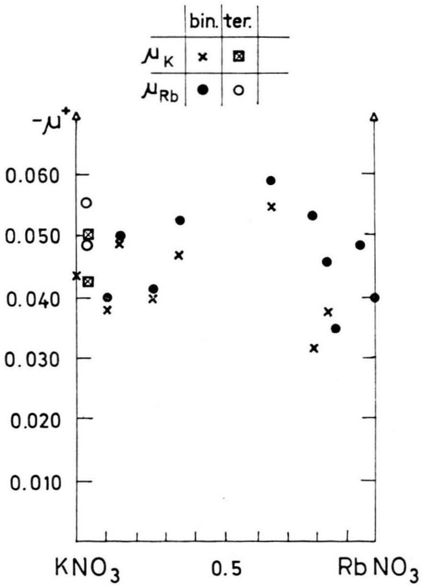

Fig. 1. Mass effects at about 380 °C. Potassium (×, ⊠) and rubidium (●, ○) in KNO_3-$RbNO_3$ (×, ●), runs 7 and 12−19, and in $NaNO_3$-KNO_3-$RbNO_3$ (⊠, ○), runs 3 and 4. For the ternary mixtures the points are placed according to the concentration of $RbNO_3$. The mass effects in pure KNO_3 and $RbNO_3$ are according to previous studies [5, 6].

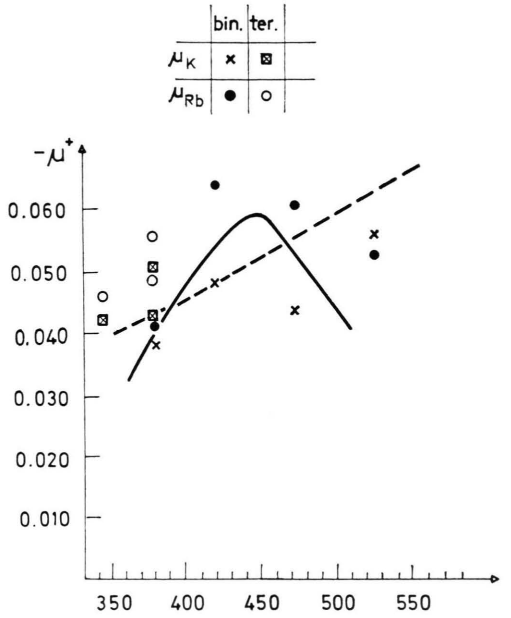

Fig. 2. The temperature dependence of the mass effects for potassium (×) and rubidium (●) in a mixture of 90% KNO_3 with 10% $RbNO_3$ (runs 7 – 10) and for potassium (☒) and rubidium (○) in a mixture of 90% KNO_3 with 5% $RbNO_3$ (runs 3, 4 and 6). The temperature dependence in pure KNO_3 (— — —) and in pure $RbNO_3$ (———) are shown for comparison [5, 6]. The latter curve gives only a rough indication of the complicated correlation in pure $RbNO_3$.

periment that $-\mu_K$ was much larger than $-\mu_{Rb}$ at this temperature (and this is also to be expected from our studies of the pure salts).

With the exception of the two runs above 500 °C (10 and 11), all our experiments give a larger mass effect for rubidium than for K, and the question arises whether this is only apparent and due to some systematic error in the interpretation. In order to get μ_K/μ_{Rb} larger than unity one needs to choose lower values of t_K than we have done, which would require $\Delta b/b$ to be considerably smaller ($b_K < b_{Rb}$ at least in some cases). This does not seem likely, and we arrive at the conclusion that there is a general tendency for μ_{Rb} to be somewhat larger in the mixtures than in pure $RbNO_3$, and for μ_K to be about the same. (For a comparison with μ_K in $NaNO_3$-KNO_3 see the appendix.) Concerning temperature dependences, a mixture containing about 90 mole% KNO_3 shows the same general tendency as the two pure salts, namely that $-\mu_K$ increases when the temperature goes up, and that $-\mu_{Rb}$ has a maximum somewhere around 450 °C. For this mixture $-\mu_{Rb}$ is larger than $-\mu_K$ in a range of at least 370 to 500 °C, while for the pure salts this is the case in a much smaller region. In addition to the general observation stated above concerning μ_K and μ_{Rb} in mixtures, one might add that there might be a tendency for at least $-\mu_{Rb}$ to have a maximum in nearly equimolar mixtures, and also for $-\mu_K$ to decrease when K^+ becomes sufficiently diluted. Both these indications are opposite to previous results on halide and sulphate melts, namely that $-\mu_{Li}$ in $LiCl$-$PbCl_2$ and $-\mu_K$ in $LiCl$-KCl and in Li_2SO_4-K_2SO_4 increase when the ion in question becomes sufficiently diluted, for Ref. see [2], while, on the other hand, $-\mu_{Sn}$ is much lower in mixtures with $PbCl_2$ or $ZnCl_2$ than in pure $SnCl_2$, loc. cit. [21, 22]. Our present results are, however, in agreement with the fact that neither μ_{Li} nor μ_{Na} seem to depend on the composition of a $NaNO_3$-KNO_3 mixture [2 – 4], see also the appendix.

The magnitude of electromigration isotope effects should be correlated with the degree of interaction between ions of opposite as well as of the same charge (corresponding to nearest and next-nearest neighbours). The weak correlation between isotope effect and composition of the melt indicates that cation-anion interaction dominates strongly over cation-cation interaction in nitrate melts. For Rb^+ the interaction is somewhat weaker in our mixtures than in the pure salt, while it seems to be about the same for K^+ ions.

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Appendix

On the Isotope Effect for Potassium in a Mixture of Sodium and Potassium Nitrate

We have previously [1] reported on a study of relative cation mobilities for a $NaNO_3$-KNO_3 mixture containing 8.2 mole% KNO_3. Three series of measurements have now been performed of the potassium isotope abundance ratio, and for each of these the mass effect μ_K has been calculated under different assumptions. Due to various difficulties it is not surprising that there are large deviations between the obtained values for μ_K, but nevertheless it is possible to draw some conclusions.

As reported earlier, the obtained apparent difference between the cation mobilities was much larger than that determined by other methods [1]. If our result for Δb were correct, the transport number t_K would be only 0.037, and the mass effect would be of the order of -0.13 to -0.27, while if we as the other extreme assume that $b_{Na} = b_K$, cf. the study by Lantelme and Chemla [10], the range for the mass effect would instead be -0.057 to -0.12. Also in the latter alternative $-\mu_K$ for dilute K^+ ions is thus larger in $NaNO_3$-KNO_3 than in KNO_3-$RbNO_3$, see Table 1, or in pure KNO_3, for which $-\mu_K = 0.044$ at 380 °C.

Since only one experiment was made for $NaNO_3$-KNO_3 we know neither how μ_K depends on the composition of the melt, nor on the temperature. However, if we also consider the determination of μ_{Na} by Wuhl, Lantelme and Chemla [2, 3], there are similarities between the systems $NaNO_3$-KNO_3 and KNO_3-$RbNO_3$, namely that there is a certain tendency that the isotope effect of the heavy ion is larger in a mixture than in the pure salt, while that of the light ion is approximately independent of the composition.

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