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

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The relative difference $(\Delta b/b)$ between the internal electromigration mobilities of ^{6}Li and ^{7}Li in molten $LiNO_3$ has been measured over the range 313° to 488 °C. The mass effect, $\mu = (\Delta b/b) / (\Delta m/m)$, is found to be

$$-\mu = 0.0845 + (0.00002 \pm 0.00002)\,(t-300)$$

where t is the temperature in °C and the quoted error is the standard deviation. There is thus in this case no significant influence of the temperature upon the mass effect. Some previous investigations of molten $LiNO_3$ gave smaller values for the mass effect. The reasons for these apparent discrepancies are discussed. A slight, but significant, anomalous enrichment of the light isotope is obtained in the middle of the cell, as has been previously observed in experiments with KNO_3.

The mass effects have now been measured for all five alkali ions in the pure molten nitrates. For a corresponding temperature chosen 5% above the melting point none of the experimental values differ more than 14% from the relation

$$\mu_+ = -0.0848\,(1 + m_+/46)^{-1}.$$

The obtained relations are interpreted in terms of cooperative motion of the ions in a molten salt.

The isotope effect for electromigration of lithium ions in molten lithium nitrate was first detected by HOOVER and HOLLOWAY[1], who, however, made no attempt to determine the relative difference between the mobilities of the two cations $(\Delta b/b)$. This was done by LUNDÉN, MONSE and SJÖBERG[2], who had to rely upon a insensitive method for determining isotope abundances, and as soon as a suitable mass spectrometer became available in our laboratory we found that the mass effect, $\mu = (\Delta b/b)\,(\Delta m/m)$, where m is the ionic mass, we had reported was too low[3,4]. The isotope effect of electromigration has also been studied in several other laboratories, both in pure $LiNO_3$[5–8] and in mixtures with other nitrates[9]. A related technique, zone electrophoresis, has been used to study the isotope effect for traces of $LiNO_3$ in other nitrate mixtures[10]. However, this latter method is based on another reference frame than ours for the ion mobilities[3]. Partly due to some discrepancies between different investigations, partly for the need to study the influence of temperature we have performed a number of experiments in addition to those reported previously[2].

Experimental

Electromigration experiments are performed in molten $LiNO_3$ with a platinum anode and a stainless steel cathode through which a mixture of NO_2 and O_2 bubbles into the melt[2]. The two electrode compartments are separated by a packed column of 20 cm length. For temperature measurements thermocouples are fitted onto the cells at three positions[11]. In the chemical analysis we searched for nitrite, oxide, sodium and potassium, since it was possible that the first two impurities could be produced by thermal decomposition, and that alkali ions could be exchanged between the melt and glass. (The cells were made of Supremax glass.) As expected, the nitrite content was found to increase with increasing temperature, and it reached about 12% for exp. No. 8. (The second highest concentration was found for No. 11.) It is reasonable to assume that the nitrate-nitrite equilibrium does not affect the isotope effect for the lithium ions, cf. our investigation of KNO_3-KNO_2 mixtures[11]. For most experiments no oxide was detectable. The amount of potassium was always negligible, while for three of the experiments (Nos. 5 – 7) the concentrations of sodium were so high in some samples that an uncertainty of more than one per cent is introduced regarding the calculated mass effect. Problems concerning impurity cat-

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[1] J. I. HOOVER and G. E. HOLLOWAY, NRL 3897 [1951].

[2] A. LUNDÉN, E. U. MONSE, and N. G. SJÖBERG, Z. Naturforsch. **11 a**, 75 [1956].

[3] A. LUNDÉN, Z. Naturforsch. **14 a**, 801 [1959].

[4] A. LUNDÉN, Z. Naturforsch. **21 a**, 1510 [1966].

[5] L. PERRET, L. ROZAND, and E. SAITO, A/conf. 15/P/1267 [1958].

[6] VALLET, KEPES, BEAUFILS, and BELILOWSKY, A/Conf. 15/P/1270 [1958].

[7] French Patent no 1 207 421 [1960].

[8] I. OKADA, Thesis, Tokyo 1966.

[9] F. LANTELME and M. CHEMLA, J. Chim. Phys. Paris **60**, 250 [1963].

[10] M. CHEMLA, J. Chromatogr. **1**, 2 [1958].

[11] A. LUNDÉN and A. EKHED, Z. Naturforsch. **23 a**, 1779 [1968].

Exp. no.	Temp. °C	Duration hours	Transp. charge Ah	Separation factor $-(Q_a - 1)$	$Q_c - 1$	x_{max} cm	Mass effect $(-\mu)$ for each analysis
1	320[a]	28.8	5.63	0.194	[b]	10.5	0.0921; 0.0891
2	315[a]	12.1	2.45	0.019	0.0044	1.5	0.0778[c]; 0.0770[c]
3	320[a]	21.2	5.68	0.048	0.0129	9.3	0.0856[d]; 0.0839[d]
4	313	23.4	5.48	0.222	0.0071	12.8	0.0878; 0.0891
2	326	23.2	4.78	0.255	0.0113	9.3	0.0804; 0.0775
6	412	24.1	5.23	0.191	0.0098	6.1	0.0833; 0.0819
7	429	24.0	4.85	0.158	0.0015	17.8	0.0898; 0.0863
8	487	24.0	4.84	0.065	0.0031	13.3	0.0471; 0.0440
9	339	9.5	2.10	0.084	0.0023	6.3	0.0594; 0.0683; 0.0651
10	411	9.7	1.96	0.112	0.0045	7.9	0.0878; 0.0915
11	488	6.5	1.28	0.086	0.0010	2.4	0.0754[e]; 0.0853[e]; 0.0845; 0.0970

Table 1. Data of experiments and results. [a] Temperature was measured at only one position in the furnace. [b] U-shaped cell [14]. [c] Some salt was lost during the chemical analysis. [d] Calculations strongly influenced by the choice of the reference. [e] Accuracy of mass spectrometer lower than usual. $Q_a = R_0/R_a$; $Q_c = R_0/\overline{R}_c$. The abundance ratios ($^7Li/^6Li$) correspond to the initial salt (R_0), the sample with the highest enrichment of ^7Li (R_a), and the average of several samples from the bottom part of the column ($\overline{R}_c$).

ions affecting the evaluation of mass effects have been discussed elsewhere [11].

For each experiment at least two independent series of mass analyses were made. By reversing from one series to another the order in which the samples were analysed, it was possible to prove that our mass spectrometer measurements were not influenced by memory effects. Mass effect calculations were made separately for each series [11]. The results are given in Table 1.

Due to the use of an insensitive method for measuring isotope abundances it was necessary to let our first experiments [2] last for several days. Most of the experiments reported now lasted about a day, but some were deliberately much shorter.

Evidence for Anomalies in the Isotope Distribution

The experiment is designed for giving an enrichment of the heavy isotope in the small anode compartment and the upper part of the separation tube. For reasons discussed previously [12], the highest enrichment of ^7Li is not found in the sample from the anode compartment but in a sample from the top of the separation tube. For this sample (denoted by subscript a) the separation factor $Q = R_0/R_a$ is calculated, where R is the isotope abundance ratio ($^7Li/^6Li$), and the reference is a sample of the initial salt (subscript 0). We have recently reported from a study of electromigration in molten potassium nitrate using the same type of cell that there was a slight but significant enrichment of the light isotope in the low part of the separation tube which opens into the large cathode compartment. In order to see if a similar enrichment occurs in the present experiments the mean value of abundance ratios measured for all the samples below the zone with an enrichment of ^7Li, R_c, is compared with the initial salt's R_0. As seen in Table 1, $Q_c > 1$ for all experiments, i. e. there is a slight enrichment of ^6Li in the low part of the separation tube. The zone with this enrichment covered two to seven samples, depending on the duration and on how the separation tube was divided into samples. If we go into detail and consider the separation factors for individual samples, Q_i, we find the following:

A. For the experiments with a duration of about 24 hours (no 3 – 6 and 8 considered [13]) we find that every single Q_i (a total of 36 measurements considered) is larger than unity. Numerically, the Q_i of experiment 8 are smaller than the others. Since this experiment also gives a significantly lower enrichment of ^7Li than the other experiments, it seems obvious, that some disturbance occurred during this experiment. No 8 was therefore omitted from the calculations. For runs 3 – 6 the average values for the lowest part of the tube (sample c1), the next lowest sample (c2) and the one above that (c3) become:

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[12] See e. g. V. Ljubimov and A. Lundén, Z. Naturforsch. **21 a**, 1592 [1966].

[13] Contrary to the cells used for runs 2 – 11 the cell used for run 1 had an U-shaped separation tube [14]. For run 7 it was found that the enrichment of ^7Li extended through nearly the whole column, i. e. much farther than in the other experiments. For these reasons runs 1 and 7 will be excluded from this part of the discussion.

[14] A. Lundén, Ann. N. Y. Acad. Sci. **79**, 988 [1960].

$$Q_{c1} = 1.0105 \pm 0.0016\,,$$
$$Q_{c2} = 1.0123 \pm 0.0013\,,$$

and

$$Q_{c3} = 1.0104 \pm 0.0014\,,$$

where the quoted error is the standard deviation of the mean.

B. For the experiments with a duration of 6 – 12 hours (No. 2 and 9 – 11) $Q_i > 1$ was obtained in 41 cases of 51, and the individual Q_i were smaller for these short runs than for those of about 24-hour duration.

The general conclusion is that a slight enrichment of the light isotope is built up in the low part of the separation tube simultaneously to the "ordinary" enrichment of the heavy isotope in the upper part. The cause of the enrichment of the light isotope will be considered elsewhere [15]. This phenomenon is of importance for the calculation of the mass effect [11]. The selected "best value" for each series of mass analysis, see Table 1, is in most cases based only on the initial salt and the cathode compartment (these two samples were in good agreement regarding R), although it was in some cases preferable to include also other samples in the reference. E. g. for runs 4 – 6 extreme choices of reference would give 5 to 11% higher values for the mass effect. Experiment 3 turned out to be much more sensitive than the others to the choice of reference [16] and, depending on how this is done, μ-values are obtained, which range from 80 – 110% of the selected best value quoted in Table 1.

Temperature Dependence of the Mass Effect

The 11 experiments summarized in Table 1 cover the temperature range 313 – 488 °C. During the analysis of experiment 2 a small sample was spoiled and could not be considered in the evaluation; the obtained μ-value is thus expected to be slightly low. Two experiments (8 and 9) give μ-values that fall far below those obtained for the other experiments; this is a strong indication that some disturbance has occurred. There are thus three experiments which should not be considered in an attempt to establish how the mass effect depends on temperature. Of the remaining 8 experiments four ones (4 – 7) are of nearly the same duration and they are given twice the weight as those for which either the temperature measurement was less accurate (1 and 3) or the duration was short (10 and 11). By considering two values for μ for each of the eight experiments we computed the linear relationship

$$-\mu = (0.0860 \pm 0.0012) + (0.000020 \pm 0.000020)\,(t - 375) \qquad (1)$$

for $313 \leqq t \leqq 488$ °C. The errors are standard deviations.

According to OKADA's measurements the temperature relation is instead

$$-\mu = (0.0718 \pm 0.0007) - (0.000048 \pm 0.000012)\,(t - 360^\circ) \qquad (2)$$

for $265 \leqq t \leqq 460$ °C. The cause of the deviation between Okada's results and ours will be discussed below. Also ARNIKAR's study of the separation of ^{6}Li and ^{7}Li in a mixture of $NaNO_3 - KNO_3$ gave a pronounced decrease of μ_{Li} with increasing temperature [17].

Comparison with Other Investigations on $LiNO_3$

In Table 2 data for our present investigations are compared with previous work [2, 6, 8]. Our old experiments can be omitted from the discussion, since the accuracy of the isotope abundance measurements was low. There is a significant difference between our present results and those of VALLET et al. and OKADA. There is however also a difference regarding the parameter $L\,\tau^{-1/2}$, which is about 4 for our experiments but does not exceed 2 for the others. This parameter is considered since the range of enrichment in a separation column is expected to depend on the duration (τ) and the effective coefficient of diffusion (D_{eff}) according to the relation [18]

$$x_{\max} = \sqrt{\pi\, D_{\text{eff}}\, \tau}\,. \qquad (3)$$

The estimation of $x_{\max}$ depends with necessity on the accuracy of the isotope abundance measurements. As seen from Table 1, $x_{\max}$ is less than half the column length for most of our experiments. If

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[15] A. LUNDÉN, Z. Naturforsch., to be published.

[16] Note that the ratio $(Q_a - 1)/(Q_c - 1)$ is unusually low for this experiment. The accuracy of electromigration experiments has been considered recently [12].

[17] H. J. ARNIKAR, Ann. Phys. Paris (13) **4**, 1291 [1959].

[18] A. KLEMM, Z. Phys. **123**, 10 [1944].

Investigation	Exp. no.	Cell type	Separation column material	length	diam	Current density	Temp.	Duration	Transp. charge	$L\tau^{-1/2}$	Mass effect ($-\mu$)
				cm	mm	A/cm^3	°C	hours	Ah		
LUNDÉN et al.[2]	C	conc.	su, qu	26	4,5	2.5	300	48	8.3	5.3	0.057[a]
	D	,,	,,	22	4	4.5	270	74	18	2.6	0.055[a, b]
VALLET et al.[6]	I	hor.	ste.	30	7	0.25	290	240	12	1.9	0.030
	II	,,	,,	30	7	1	290	408	82	1.5	0.057
	III	,,	,,	3.5	5	2.45	290	144	36	0.3	0.023
	IV	,,	,,	27	12	0.42	290	175	46	2.0	0.057
OKADA[8], 7 exp.[c]		conc.	vy, qu	12	4	2.5	265–460	48	4.8	1.7	0.078–0.069
Present, 11 exp.[c]		,,	su	20	4	3.4	313–488	24	5.1	4.1	0.085–0.88

Table 2. Comparison of different investigations on electromigration in molten $LiNO_3$. [a] Mass analysis by neutron irradiation. [b] Recalculated with a different value for the initial isotope abundance. [c] Several experiments; either the range or typical values are quoted for the different parameters. Abbreviations: conc. = vertical cell with the separation column surrounded concentrically by the large cathode compartment. hor. = horizontal separation column. su, qu = separation column of Supremax glass packed with quartz. ste. = steatite. vy, qu. = separation column of Vycor packed with quartz. su. = Supremax. For convenience the length is in cm and the duration in hours when the parameter $L\tau^{-1/2}$ is calculated.

Eq. (3) is applied, the calculated D_{eff} cover a wide range, with a median value of $36 \cdot 10^{-5}$ cm^2 s^{-1}. This is in fair agreement with our previous experiments with lithium halides, while D_{eff} was considerably higher for sulfate mixtures [19]. It is obvious that L must exceed $x_{\max}$, if correct results are to be obtained. If D_{eff} is about $36 \cdot 10^{-5}$ cm^2 s^{-1} the parameter $L\tau^{-1/2}$ should exceed 2 cm/h$^{1/2}$. Although the D_{eff} of our 11 experiments do not show any correlation with temperature, one should expect that D_{eff} increases, and thus that the critical value of $L\tau^{-1/2}$ decreases, when the temperature is raised. Thus if $L\tau^{-1/2}$ is too low for a set of experiments one might expect an apparent decrease of the measured mass effects with increasing temperature. This might explain why OKADA has found another temperature dependence than we have. Howevere, it must be remembered that arguments of this kind are of uncertain value, since D_{eff} is not a property of matter in the same way as e. g. a self-diffusion coefficient, but depends on many experimental parameters, such as grain size and type of packing in the column and the current density. OKADA's columns were packed with quartz grains of a finer sieve fraction than we used (sieve opening about 0.10 – 0.15 mm in his case, 0.20 – 0.25 mm in ours), and he reports effective diffusion coefficients of the order of $7 \cdot 10^{-5}$ cm^2 s^{-1}, which means that it might be necessary to search for another explanation of the observed deviation [20]. A further difficulty when discussing possible causes of deviations between measurements in different laboratories, is that the non-ideal behaviour observed for our columns, see above, need not be of the same importance for all types of cells. A general argument when evaluating experiments for studying mobility differences is that high values are more likely to be correct than low ones, since all disturbances during the experiment tend to reduce the obtained changes in distribution and thus to give low values for the mass effect. The result can become too high only due to errors in the (chemical or mass spectrometrical) analysis or to an incorrect interpretation (e. g. the choice of "normal composition").

Comparison with Other Salts

The mass effect of the lithium ion has so far been determined in two solid and four molten salts, see Table 3. It is well known from experiments with halides that μ^+ decreases when the cation-anion mass ratio (m_+/m_-) increases. A semiempirical relation has been developed, which now exists in a couple of modifications regarding the values of the two numerical coefficients [21]. For our purpose it is suffi-

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[19] A. LUNDÉN and V. LJUBIMOV, Z. Naturforsch. **23 a**, 1558 [1968].

[20] OKADA (personal communication) has considered the possibility that a non-negligible fraction of the lithium ions diffuses into or migrates through the quartz packing and the Vycor glass walls of his separation columns. The loss of lithium ions should increase with increasing temperature, i. e. the obtained temperature coefficient of the mass effect would become too low. It is however doubtful whether the whole discrepancy between the two sets of measurements can be explained in this way.

[21] A. JORDAN and A. KLEMM, Z. Naturforsch. **21 a**, 1584 [1966].

Salt	Temp. °C	$-\mu_{\mathrm{exp}}$	$-\mu_{\mathrm{calc}}$
LiH, solid	600	0.04	0.035
LiCl	610	0.111	0.137
	900	0.187	0.137
LiBr	600	0.148	0.144
LiI	500	0.15	0.146
Li_2SO_4, solid	700	0.135	0.145
$LiNO_3$	270	0.0838	0.142
KNO_3	355	0.0407	0.115
$RbNO_3$	350	0.033	0.091

Table 3. Cation mass effects for lithium salts and for those alkali nitrates that were used to compute Eq. (5). The experimental data are compared with mass effects calculated from Klemm's original equation for halides, Eq. (4).

cient to consider the original relation

$$-\mu_+ = 0.15(1 + m_+/2.1\ m_-)^{-1}. \qquad (4)$$

As seen from Table 3, this relation applies well also to LiH[22] and Li_2SO_4, but it gives too high values for $LiNO_3$, as also for other nitrates. This observation might have to do with the sulfate ion being spherically symmetrical while the nitrate ion is disk-shaped. The mass effect has now been measured for all five alkali nitrates, see Fig. 1. The two mono-isotopic ones (Na and Cs) have been measured only by OKADA[8] while the three other ones have been studied both by him and in this laboratory[4, 11]. In order to compute a relation between μ^+ and m^+ it is necessary to chose a reference temperature, and to decide which weights should be assigned to the different experiments. A great number of combinations were tried, and the equation that fits best with the experiments is

$$-\mu_+ = 0.0848(1 + m_+/46)^{-1}. \qquad (5)$$

This equation corresponds to a reference temperature 5% above the melting point, and it is based on the mass effects of $LiNO_3$, KNO_3 and $RbNO_3$, see Table 3, to which the weights 3, 3 and 1 were assigned; the average of our and Okada's value for μ_{Rb} was chosen. For none of the five alkali nitrates does the derivation from Eq. (5) exceed 14%, provided that of the two experiments with $NaNO_3$ the one with the longest separation tube as well as the shortest duration is considered more reliable than the other one, i. e. that $\mu_+ = 0.051$ is chosen for this salt[23]. Whichever combination of data is chosen when computing a relation between μ_+ and m_+ for nitrates, μ_{exp} always becomes larger than μ_{calc} for $LiNO_3$ and this is the case also for $TlNO_3$, for which $\mu_+ = -0.035$, according to SAITO and OKADA[24]. (Our computations are based on the alkali nitrates, but the relations are tested also on $TlNO_3$.)

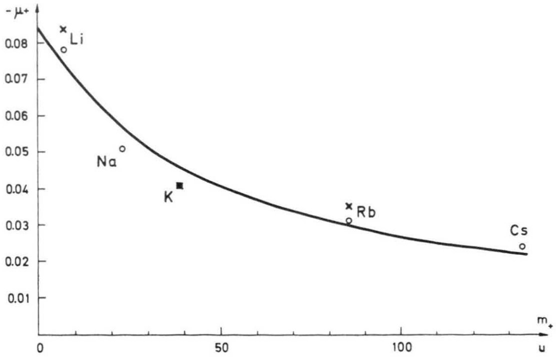

Fig. 1. Correlation for alkali nitrates between the mass effect and the mass of the cation. Measurements by OKADA et al. are indicated by a ring (o) and those done in our laboratory by a cross (×). For series that covered a wide temperature range the results are given for a reference temperature 5% above the melting point. The solid line corresponds to Eq. (5). According to Saito and Okada the mass effect for $TlNO_3$ ($m_+ = 204$) is -0.035, which is more than twice the value predicted by Eq. (5).

As an alternative it is tempting to try to correlate the mass effect with the radius (r_+) or the volume (V_+) of the cation, see Fig. 2 and 3, where the following cation radii are chosen[25]: Li^+ 0.68, Na^+ 0.97, K^+ 1,33, Rb^+ 1.47, Tl^+ 1.47 and Cs^+ 1.67 Å.

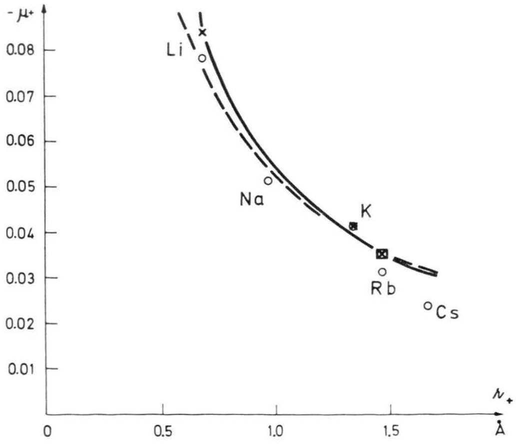

Fig. 2. The cation mass effect for alkali nitrates (×, o) and $TlNO_3$ (☐) correlated with the ionic radius. The dashed line corresponds to Eq. (6) and the solid one to Eq. (7).

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[22] B. COLLÉN, Acta Chem. Scand. **18**, 839 [1964].

[23] N. SAITO, I. TOMITA, and I. OKADA, J. Nucl. Sci. Technol. **3**, 140 [1966].

[24] N. SAITO and I. OKADA, unpublished.

[25] Handbook of Chemistry and Physics, Chemical Rubber Co., Cleveland, Ohio, 46th Ed., p. F-117 [1965–66].

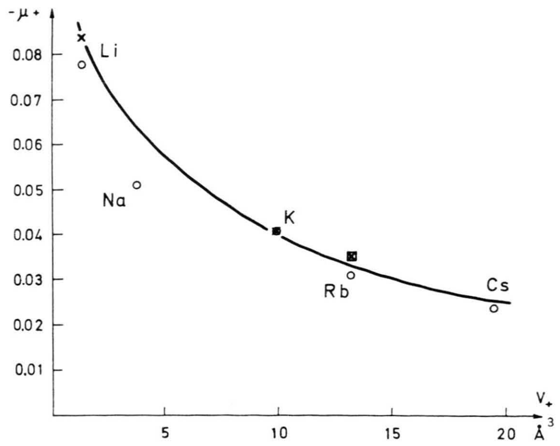

Fig. 3. The mass effect correlated with the volume of the cation. The solid line corresponds to Eq. (8).

Five of the six nitrates show a remarkably good corelation with the simple relation

$$\mu_+ \, r_+ = 0.0523\,. \tag{6}$$

Linear regression analyses with the same weights as used for Eq. (5) give

$$-\mu^+ = 1/(20.9\,r_+ - 2.4) \tag{7}$$

and

$$-\mu^+ = 1/(9.91 + 1.51\,V_+)\,. \tag{8}$$

For the halides KLEMM has found that the correlation with (r_+/r_-) appears to be stronger than with (m_+/m_-), loc. cit. [26]. This seems to be the case also for the nitrates. It might be of interest to notice that μ_{Li} fits better with the Eq. (6) – (8) – the deviation being 9%, 1% and 0.4%, respectively – than with Eq. (5) and the other correlations with m_+ that we have tried. The value of this observation is however limited by the fact that there is considerable disagreement in the literature regarding ionic radii.

Discussion

Ion motion in a condensed phase involves interaction between a number of particles. KLEMM has proposed several models, which differ in details (l. c. [19, 21, 26, 27]) but which all make it plausible to expect relations of the type

$$\mu_+ = A/(1 + M_+/M_-) \tag{9}$$

and a corresponding relation for anion migration. The factor A is $-1/2$ (and $M_+ = m_+$, $M_- = m_-$) for an ionic gas [21], while its numerical value is less in a condensed phase where both spontaneous and induced jumps can occur. The number of the first type of jumps depends on the vibrating frequencies i. e. on the mass of the jumping entity (M_+) and the counter-vibrating mass (M_-). Simplifying the picture, M_+ is proportional to the cation mass m_+, and M_- to the anion mass m_-. These proportionality constants can hardly be determined by electromigration experiments, but one should be able to obtain the ratio between them. Hence, Eq. (9) might be replaced by

$$\mu_+ = A/(1 + m_+/B\,m_-)\,. \tag{10}$$

If it is assumed that the factors A and B are the same within a series of salts, such as the alkali nitrates, equations like (4) and (5) can be obtained. However, we know that this involves rough approximations. The mass effects often depend on temperature as well as on the composition of a mixture [19, 28]. Thus, if e. g. the mass effect increases with increasing temperature, this corresponds to an increase in A or in B. If A grows this means that a larger fraction of the total number of jumps are spontaneous, while a rise of B is caused either by a decoupling of cations (M_+/m_+ decreases) or an increased coupling of anions (M_-/m_- increases).

Table 4 summarizes the information available up to now on the temperature dependence of mass effects (μ), including eigen-mass effects (μ_+^0). The latter is determined by comparing the electrical conductivities of isotopically pure species; $\mu^0 = (\Delta\varkappa/\varkappa)/(\Delta m/m)$. So far such measurements have been done only for three lithium compounds (l. c. [27, 29]). Table 4 also gives the temperature dependence of $(D/T\,\Lambda)$, where D is the self-diffusion coefficient, T the absolute temperature and Λ the equivalent conductivity. The standard deviation is quoted whenever possible [30].

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[26] A. KLEMM, J. Chim. Phys. Paris **60**, 237 [1963].

[27] S. JORDAN, R. LENKE, and A. KLEMM, Z. Naturforsch. **23 a**, 1563 [1968].

[28] While marked concentration effects have been found in those mixtures where one of the cations has been very light (Li and Pb or K), the mass effects of the two cations do not seem to vary much in the system KNO_3-RbNO_3; A. EKHED and A. LUNDÉN, unpublished.

[29] A. KVIST, Z. Naturforsch. **21 a**, 487 [1966].

[30] The cation mass effect of $PbCl_2$ was measured at only two temperatures; A. LUNDÉN, G. HORLITZ, and P. SIGNER, Z. Naturforsch. **11 a**, 280 [1956].

As a principle the numerical values presented by the original authors are always used for μ, μ^0 and D (and their standard deviations when given) also in those cases where our own least squares analysis based on the published data give deviating values. In those cases where there exists more than one investigation, only the most recent one is considered here. Most of the equivalent conductivites of interest have been measured several times, and for the molten salts the values for $\delta \ln \Lambda / \delta \ln T$ selected in a recent compilation have been used here [36].

The accuracy of conductivity measurements is generally considered as better than for diffusion experiments. When estimating the standard deviation (s) of $D/T\,\Lambda$ we have for simplicity assumed that $s_\Lambda = 0.2\, s_D$ in all cases but one. (For RbCl we have instead assumed that s_Λ is equal to the average of the published standard deviations of D_+ and D_-.) It is however to be remembered that the standard deviations obtained by means of a least squares analysis only account for random errors, and that in all measurements considered here significant contributions from systematic errors might exist. Nor is account taken of the subjective factor that is introduced, when the experimental data are weighed before the least squares analysis [37]. Furthermore all the three entities considered in Table 4 (μ, μ^0 and $D/T\,\Lambda$) are in principle to be considered as differences between measurable quantities, which means that the relative errors become magnified. Thus, e. g. the calculated $D/T\,\Lambda$ depend strongly on which compilation Λ is selected from. Thus using another source [38] for the activation energy Q_Λ ($Q_\Lambda / R\,T = \delta \ln \Lambda / \delta \ln T$), according to which Q_Λ for $LiNO_3$ is 4.7% higher, $\delta \ln (D_+ / T\Lambda) / \delta \ln T$ becomes 0.55, i. e. 31% higher. It is evident from considerations like these that the accuracy of the entities we discuss here is far less than indicated by the calculated standard deviations.

Although it is necessary to make reservations regarding the significance of parts of the interpretation, some conclusions can be drawn from the data of Table 4:

1. The ratio $n = \mu^0 / \mu$ is to be interpreted as the average number of cations that form a group in a single transition [27]. There are indications that n varies with the temperature, but this is surely not significant for lithium nitrate [27] and barely so for lithium chloride. (See the interpretation below.)

2. Regarding the mass effect μ, a temperature dependence seems to be firmly established in seven cases, being positive in five and negative in two

	$\frac{\delta \ln \mu_+}{\delta \ln T}$	$\frac{\delta \ln (D_+/T\Lambda)}{\delta \ln T}$	$\frac{\delta \ln \mu_-}{\delta \ln T}$	$\frac{\delta \ln (D_-/T\Lambda)}{\delta \ln T}$	$\frac{\delta \ln \mu_+^0}{\delta \ln T}$	$\frac{\delta \ln n}{\delta \ln T}$	n	Ref. for self-diffusion
$LiNO_3$ 400 °C	0.16 ± 0.15	0.42 ± 0.12	—	1.05 ± 0.21	0.57 ± 0.13	0.41 ± 0.20	2.21	31
KNO_3 400 °C	1.81 ± 0.22	0.46 ± 0.23	—	0.63 ± 0.29	—	—	—	31
LiCl 750 °C	1.80 ± 0.60	—	—	—	0.40 ± 0.04	− 1.40 ± 0.60	2.39	—
KCl 850 °C	1.40 ± 0.48	0.55 ± 0.23	− 0.11 ± 0.06	0.66 ± 0.22	—	—	—	32
RbCl 825 °C	1.22 ± 0.52	0.65 ± 0.03	1.37 ± 0.87	0.38 ± 0.04	—	—	—	33
RbBr 800 °C	0.32 ± 0.31	—	0.11 ± 0.68	—	—	—	—	—
TlCl 500 °C	− 0.79 ± 0.06	− 0.40 ± 0.16	− 1.31 ± 0.23	− 0.38 ± 0.31	—	—	—	34
$SnCl_2$ 400 °C	− 0.21	—	—	—	—	—	—	—
$PbCl_2$ 585 °C	− 0.02	1.15 ± 0.19	—	1.14 ± 0.25	—	—	—	34
Li_2SO_4 700 °C (solid)	− 0.27 ± 0.62	− 1.91 ± 0.51	—	—	a	a	2.0	35
$(Li, K)_2SO_4$ (80% Li) 700 °C	0.68 ± 0.77	—	—	—	—	—	—	—

Table 4. Temperature dependence of μ, $D/T\,\Lambda$, μ_0 and n. For the experiments performed in Mainz, the mass effects are according to the latest compilation [27], and the equivalent conductivity data are according to JANZ [36]. [a] The temperature dependence is less than the experimental accuracy.

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cases, while the temperature has no significant influence on the μ_+ of $LiNO_3$, Li_2SO_4 (pure solid salt as well as molten eutectic mixture with K_2SO_4), RbBr and $PbCl_2$ and the μ_- of KCl and RbBr [39].

3. Klemm has several times stressed that one should expect a correlation between the temperature dependences of the mass effect and $D/T\,\Lambda$ [21, 40]. This is established in six cases, in five of which it is certain, and in one very likely, that the mass effect has a more pronounced temperature dependence than $D/T\,\Lambda$ has, while in the other four cases it is either clear or probable that instead $D/T\,\Lambda$ changes more rapidly, and in these four cases it is even not sure that the two temperature coefficients have the same sign.

4. If the discussion is restricted to the cation mass effects of the five lithium and potassium salts, it might be possible to estimate the importance of geometrical parameters. Of the polyatomic anions the nitrate ion is disk-shaped [41], while the sulfate ion has spherical symmetry. For both of these ions, there is probably not sufficient space for free rotation [41, 42]. (However, some authors prefer to use a nitrate ion radius that allows this [43, 44].) This requires cooperative motion for all transport processes where the anions are involved. This might be expected to favour a stronger coupling also of the cations, which should explain why the factor A of Eq. (9) and (10) tends to be lower for nitrates than for most halides. (For halides with divalent cations the ionic radius if found to be important for the mass effect [35, 46], and for a number of these salts it seems preferable to replace the numerator of Eq. (4) with 0.079.) It should then also be expected that the ratio $n=\mu^0/\mu$ is higher for a nitrate than for a halide, cf. however Table 4.

5. For three of the five lithium and potassium salts now considered the mass effect increases with increasing temperature. A plausible explanation is that the coupling between the cations tends to reduce for LiCl, KCl and KNO_3 (corresponding to an increase in A or a decrease in M_+/m_+) while it remains about the same for $LiNO_3$ and Li_2SO_4. (This interpretation is in agreement with the indication that $\delta \ln n/\delta \ln T$ is negative for LiCl and close to zero for $LiNO_3$, see above.) This might mean that the coupling of cations is at least partly of a different nature in the two later lithium salts than in the other salts considered. The cause for this should be sought by considering geometrical parameters. The ones discussed above (spherical symmetry, free rotation) do not help us to explain why the temperature dependences are so different. It remains to consider the distance between two like ions and the size of the cation relative to that of the anion. The ratio of the radii, r_+/r_-, is much lower for LiCl than for the potassium salts but it is higher than for $LiNO_3$ and Li_2SO_4, and there is a possibility that there might be a critical limit for the radius ratio beyond which transport behaviour becomes abnormal, as several authors claim for lithium nitrate [43, 44]. Anion-anion contact is possible for all three lithium salts, but while for both $LiNO_3$ and Li_2SO_4 the voids are "too large" for the lithium ion [43], they are likely to fit well for LiCl. The importance of geometrical properties might become clearer if the temperature dependence of the mass effect is studied also for LiBr, $NaNO_3$ and Na_2SO_4.

6. If, as suggested in the preceding paragraph, the ionic dimensions are of importance for the coupling, it might be reason to expect that there is an exception for $LiNO_3$ from the empirical rule that the factor A of Eq. (9) is approximately the same within a series of salts. This would explain why all attempts to correlate μ_+ with m_+ for alkali nitrates showed the same tendency for $LiNO_3$, namely that the calculated mass effect becomes lower than the experimental one. In order to prove a possible anomaly for $LiNO_3$ more measurements of mass effects for heavy alkali nitrates are required.

Summarizing, one finds that the studies done so far of the temperature dependence of mass effects allow some conclusions on cooperative ion transport in molten and solid electrolytes, and that it is de-

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[39] For $SnCl_2$ only the temperature equation $-\mu_+=0.069\,[1-0.0003\,(t-340)]$ for $340 \leqq t \leqq 590\ {}^\circ\mathrm{C}$ has so far been reported to us; V. Ljubimov, personal communication. Until further information on the experiments become available, we have assumed that the indicated temperature effect is not quite significant.

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sirable to coordinate studies of this kind with investigations of other properties such as selfdiffusion and eigen mobilities.

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Zur Kinetik der Ionenaustauscher

III. Die Filmdiffusion bei vollständigen Umbeladungen

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The selectivity coefficient $K_2{}^1$ of an ion-exchange process is in general a function of the ionic composition of the material. As a result, the value of $K_2{}^1$ will change continuously during a complete conversion of the ion-exchanger. Equations for the kinetics of such a conversion with variable $K_2{}^1$ are given for a film diffusion controlled ion-exchange reaction.

Befindet sich ein Kationenaustauscher im Gleichgewicht mit einer Lösung, die einwertige Kationen 1 und 2 mit den Molenbrüchen γ_1 und γ_2 enthält, so werden diese Ionen in der Austauscherphase mit den Molenbrüchen $\bar{\gamma}_1$ und $\bar{\gamma}_2$ vorliegen. Definiert man den Selektivitätskoeffizienten $K_2{}^1$ als

$$K_2{}^1 = \bar{\gamma}_1 \cdot \gamma_2 / \bar{\gamma}_2 \cdot \gamma_1 \,, \qquad (1)$$

so sieht man, daß diese Größe ein Maß für die selektive Adsorption des Ions 1 gegenüber dem Ion 2 in der Austauscherphase darstellt. Im Fall reiner Film-Kinetik zeigen nun sowohl theoretische Überlegungen als auch experimentelle Befunde, daß dieser Selektivitätskoeffizient $K_2{}^1$ – neben den Diffusionskoeffizienten der Ionen – die Geschwindigkeit des Austausches weitgehend bestimmt [1–3]. Bei den bisherigen theoretischen Untersuchungen zur Kinetik des Ionenaustausches wurde $K_2{}^1$ immer als unabhängig vom Molenbruch der Ionen im Austauscher angesehen. Wie experimentelle Untersuchungen zeigen, trifft diese Annahme jedoch nur in Ausnahmefällen zu. Bei der überwiegenden Anzahl von Ionenaustauschern hängt $K_2{}^1$ erheblich vom Mischungsverhältnis der Ionen in der Austauscherphase ab [4]. Da sich dieses Mischungsverhältnis während des Austauschprozesses kontinuierlich verändert, wird auch eine laufende Veränderung von $K_2{}^1$ während dieses Vorganges erfolgen. Die Annahme eines konstanten $K_2{}^1$ ist daher nur als Näherung für differentielle Umbeladungen gerechtfertigt [3].

Will man den Ionenaustausch für den häufig auftretenden Fall einer vollständigen Umbeladung des Austauschers von der reinen Form 1 in die reine Form 2 beschreiben, so darf man die während des Austausches erfolgende Veränderung von $K_2{}^1$ nicht unberücksichtigt lassen. Dazu muß die Differentialgleichung für die Geschwindigkeit des Ionenaustausches bei Film-Kinetik mit einem variablen Selektivitätskoeffizienten gelöst werden. Diese Gleichung lautet bei konstant gehaltener Konzentration c der Außenlösung [3]

$$\frac{\mathrm{d}x}{\mathrm{d}t} = \frac{C\, c\, R\, D_1\, D_2\, K_2{}^1 (x-1)}{[K_2{}^1 (C - C_1{}^\infty) + C_1{}^\infty]\,[C_1{}^\infty\, x\, D_1 - x\, D_2\, K_2{}^1\, C_1{}^\infty + C\, D_2\, K_2{}^1]} \,. \qquad (2)$$

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