Isotope Effect of Cation Electromigration
in Molten Lithium Chloride-Nitrate-Mixtures

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Molten mixtures of lithium chloride and nitrate, including the decomposition products nitrite and oxide, were electrolysed at about 600 °C with gaseous electrodes. The relative mobilities of the lithium isotopes were studied. The mass effect (relative difference in mobility divided by relative difference in mass) is 0.063 for a mixture with 20% Cl^- and 0.069 for 80% Cl^-, which both are more than 30% smaller than those interpolated from the isotope effects of pure $LiNO_3$ and LiCl. It is concluded that the lithium ions interact more strongly (with the anions and/or with each other) in a melt containing several anions than in a pure melt. The experiments also yield some information about the mobilities of the anions present in the melt.

A large number of investigations has been performed on isotope effects of electromigration in pure salts, where the isotope effect for a given cation is found to depend on the type of anion in the melt. Some studies have also been made on mixtures with a common anion. Several nitrate systems have been studied over wide ranges, and the cation isotope effects are nearly independent of the composition of the mixture [1]. For halide systems it has been found that in $SnCl_2$-$PbCl_2$, $SnCl_2$-$ZnCl_2$ and $SnCl_2$-$CdCl_2$ the isotope effect for Sn is much smaller than in pure $SnCl_2$ (l. c. [2, 3]), while in the following cases the isotope effect has been found to increase when the ion becomes sufficiently diluted: K in LiCl-KCl, Li in LiCl-$PbCl_2$ and K in Li_2SO_4-K_2SO_4 (l. c. [4-6]).

For a further understanding of the migration mechanism in melts, it is reason to study the isotope effect of the common cation in mixtures containing several anions. One might expect more marked effects in a halide-nitrate mixture than in one containing two halides or in a halide-sulphate mixture, since in the first case the anions have the most different geometry. This difference is, however, associated with a large difference in melting points between nitrates and halides, and it is necessary to operate at temperatures, where a considerable thermal decomposition of the nitrates is known to occur [7]. We decided to mix LiCl and $LiNO_3$, since the temperature dependence of the cation isotope effect is known for both these salts [8, 9]. The fact that $LiNO_3$ is less stable than the other alkali nitrates is to some extent compensated by the melting point being lower for LiCl than for the other alkali chlorides, which makes it possible to work at temperatures around 600 °C. For the phase diagram see e. g. [10].

Experimental

In order to study how the cation isotope effect depends on the anion composition of the melt, one should design an experiment where a change of cation isotope composition takes place in a region in which the concentration of the anions remains unchanged. Thus one should need to work with a boundary which is impermeable to Li ions but allows the passage of all anions without any change in their transport (relative to the cation). In principle this condition could be fulfilled at the boundary between regions with different cations A and B but with the same initial anion mixture and the same relative differences of the internal mobilities of the anions. However, it seemed difficult to find such a system and we decided to work with only one cation and to study the change of (lithium) isotope composition near the anode. The condition that the X-Y ratio remains constant would require that the anode reaction gave no preference of discharge for either X or Y. However, we on the contrary expected the nitrate to discharge easier than the chloride, see below, and we had to accept that the X-Y ratio would not remain constant in the cell, see Appendix. Also with this deviation from the ideal arrangement, however, it should be possible to get some of the desired information.

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We used a cell of Supremax glass. A separation column (200 mm long, 4 mm diameter) packed with glass powder was concentrically surrounded by a large salt volume, which was part of the cathode compartment, while the anode compartment of the cell was small. Both electrodes were made of silicon carbide. (We used Silit rods commercially available as heaters for electrical furnaces.) The cathode was formed as a tube through which nitrogen dioxide gas was bubbled into the melt. In some runs the gas evolving from the anode was collected for analysis in a trap containing a 2 N KOH-solution. After the cell had been quenched it was divided into samples, which were analysed for Cl^-, NO_3^-, NO_2^-, O_2^- and the lithium isotopes. The isotopic abundances of lithium were determined with a mass spectrometer.

In our previous study of the temperature dependence in pure $LiNO_3$ we went up to about 490 °C and there was a considerable amount of nitrite present in the melt at those temperatures. We do not know of any studies of thermal decomposition of nitrates at the operating temperature of the present experiment, but we expected a high degree of thermal composition to occur. This should be the cause of the disturbances, which occurred much more frequently in the present study than in most of our previous investigations of other melts. The data of the runs are summarized in Table 1.

Results and Discussion

Regarding the discharge reaction at the anode, there is little information in the literature, but from a study under conditions quite different from ours, Rempel and Malkova found the discharge potential of nitrate ions to be some 0.8 V less than of chloride ions [11], while we know of no studies of the discharge of nitrite or oxide ions in multi-anion mixtures. We tried to check on the anode reaction in two ways. The analysis of the gas leaving the anode gave a current efficiency for chlorine (y_{Cl}) of 0.8%, 1.9% and 27% for melts with an initial chloride content (x_{Cl}) of 20, 40 and 80% respectively. These results might, however, be systematically too low, since the absorption in the trap might have been incomplete. The other check was done by comparing the sum of the amount of chloride found in all samples with that corresponding to the initial concentration of chloride. Although the accuracy of such a comparison is moderate, it seems also from this check that very little chlorine was liberated from the melts containing 20 or 40% Cl^-, but that for the melts with 80% Cl^- the ratio y_{Cl}/x_{Cl} is of the order of 0.3 to 0.7.

The chemical analysis was made not only for the runs listed in Table 1 but also for some other ones not considered suitable for isotope effect estimates. Large variations of the anion concentrations were found along the separation columns. We concluded that the observed concentration changes had been caused not only by preferential discharge of some ion and by electromigration, but also by reactions (nitrate-nitrite etc.) and by a non-negligible stratification when the melt solidified. Thus it was not possible to calculate anion mobilities in the way discussed in the Appendix, but some information was obtained on the mobility of Cl-ions relative to the average anion mobility. In the big volume on the cathode side of the separation column the chloride concentration was found to remain constant during the run, except for a slight decrease for the 80 mole % runs, see above. In this volume the oxide concentration was usually of the order of 1 equivalent-%,

Table 1. Electromigration experiments in melts containing LiCl, $LiNO_3$, $LiNO_2$ and Li_2O. Less weight is to be given to the experiments ranked in class B, since this means either that there was some disturbance or that the duration of the experiment was shorter than desired.

Exp. no	LiCl mole %	Temp. °C	Duration hours	Transp. charge mFaraday	Class	Number of mass analysis	Range for mass effect $(-\mu)$	Chosen mass effect $(-\mu)$
1	20	573	4.5	20.9	B	2	0.028−0.035	
2	20	604	11.0	70.8	A	3	0.056−0.067	0.063
3	20	522	5.1	51.8	B	2	0.028−0.033	
4	40	621	3.0	20.7	B	4	0.057−0.068	
5	40	633	1.4	6.9	B	3	0.024−0.107	0.058
6	40	611	7.2	43.9	A	4	0.052−0.058	
7	60	595	6.0	18.2	B	3	0.057−0.114	0.086
8	80	615	10.2	78.7	A	2	0.051−0.074	0.069
9	80	605	10.3	75.0	A	2	0.072−0.080	

while there were some 5 to 9 percent nitrite present. Concerning the isotope effect for lithium, two to four independent series of analysis with the mass spectrometer were made for each experiment, and the mass effect (μ) was calculated for each series (by dividing the relative difference in isotope mobility with the relative difference in mass). The extreme results are quoted (as the "range for mass effect") in Table 1, and the spread gives an indication of the accuracy that can be obtained. The individual experiments are divided into two classes, where B means either that some disturbance was observed during or at the end of the run, or that the duration of the experiment was shorter than normally desired. The experiments of class A were given a higher weight than those of class B when a best choice of mass effect was made for each concentration studied, see Table 1. The results for 20 and 80% LiCl are considered to be more accurate than for 40 and 60% LiCl. The mass effect has previously been measured for pure LiNO$_3$ in the range $313 - 488\,^{\circ}$C and for LiCl between 674 and 895 $^{\circ}$C, loc. cit. [9, 8]. Extrapolations give $-\mu_{\mathrm{LiNO_3}} = 0.0905$ and $-\mu_{\mathrm{LiCl}} = 0.108$ at 600 $^{\circ}$C, and if a linear relation is assumed, we arrive at calculated mass effects of 0.0940 for 20% LiCl and 0.1045 for 80% LiCl. The experimental value is in the first case 67% and in the second case 66% of the calculated value. Since the distribution profile of the lithium ions in the separation column is similar for the present experiments to what we get for experiments with pure salts, it does not seem likely that the observed stratification upon solidification (see above) or other bulk flow of anions has influenced the isotope distribution to such an extent that there is any systematic error in the determination of the isotope effects. Thus, it seems verified by the present experiments that the presence of several types of anions reduces the isotope effect for the lithium ions. The usual interpretation of such a decrease in isotope effect is that the ionic interaction becomes stronger in the mixture than it is in either of the pure salts. We might expect that the cation-anion interaction increases when we have different geometrical shapes and sizes of the anions (and thus also of the voids occupied by cations), and in addition there are also divalent anions in the melt. There is also the possibility that the cation-cation interaction increases, although the first explanation seems more likely.

Appendix: Relative Anion Mobilities

The usual practice in electromigration experiments is to determine concentration changes in a zone limited by a boundary that is impermeable to the ionic species the mobility difference of which is to be determined. Since the present experiments were designed primarily for studying isotope effects of cation mobilities, gaseous electrodes were used at both sides of the cell, and the electrode reactions have to be taken into account when anion mobilities are estimated. For simplicity, let us consider a binary anion mixture, where the initial equivalent fractions of the components are x_1 and x_2 and the anion mobilities (relative to the cations) are b_1 and b_2. If the fractions discharged at the anode are y_1 and y_2, and the transport of Q Faradays causes an increase of ΔN equivalents of component 1 in a zone limited by the anode on one side, and by a region with the initial composition on the other side, it follows (c. f. e. g. Ref. [12]) that

$$\frac{\Delta b}{b} = \frac{\Delta N/Q - x_1 + y_1}{x_1(1 - x_1)} \qquad (1)$$

where $\Delta b = b_1 - b_2$ and $b = \lambda/F$, with λ = the equivalent conductivity and F = the Faraday constant. Since the relative concentrations of NO$_3^-$, NO$_2^-$ and O^{2-} should depend on thermal equilibria as well as on the electrode reactions, it is not possible to estimate $b_{\mathrm{NO_3}}$, $b_{\mathrm{NO_2}}$ and b_{O} individually, but since Cl$^-$ is a stable ion we might be able to say something about $\Delta b = b_{\mathrm{Cl}} - b_{\mathrm{rest}}$, where b_{rest} is the average mobility for the three oxygen-containing ions. Since we, however, cannot separate the contributions of different processes (electromigration, decomposition, stratification, etc. see above) to the concentration changes in the cell, the results of calculations according to Eq. (1) showed such a wide spread that it seems of little interest to report

any figures for $\Delta b/b$. For most of the runs this entity became negative for the assumption that $y_{Cl} = 0$, while it always becomes positive for the case that $y_{Cl} = x_{Cl}$. Since we expect y_{Cl} to be close to zero, or at least considerably smaller than x_{Cl},

we have arrived at the conclusion that it is likely that the mobility of the chloride ion is smaller than the average anion mobility for the mixtures studied by us.

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