MD-Simulation of Molten (Li, K)Cl at the Eutectic Composition. Self-Exchange Velocities of Li- and K-Isotopes near the Cl^--Ions

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Molecular dynamics simulation (MD) has been done for a molten (Li, K)Cl mixture of the eutectic composition at about 700 K, 950 K and 1100 K and, for comparison, also for pure LiCl and KCl at about 950 K and 1100 K. The atomic masses of half the Li^+ and K^+ ions have been set at 6.941 and 39.098, respectively. Self-exchange velocities (SEV's) of these cations have been calculated. The Chemla effect is reflected by the SEV's. The isotope effects of the SEV's in the mixture increase slightly with temperature. The motions of the cations with respect to the adjacent Cl^- are classified into four modes: (1) an oscillating motion, (2) a leaving motion, (3) a wandering motion and (4) a coming-back motion. It is found that the velocity of the leaving motion is dependent only on the masses and the temperature, and independent of the kind of cations and the composition.

Introduction

In [1] we determined the internal mobilities of Li^+, K^+, and their isotopes in molten (Li, K)Cl at about the eutectic composition in the temperature range (729–976) K. The main results were as follows: (1) The Chemla effect occurs at this composition in the whole investigated temperature range, i.e., the mobility of K^+ is greater than that of Li^+ . (2) With increasing temperature the mobility ratio b_{Li}/b_K decreases. (3) The isotope effect on the mobilities of Li and K seems to increase slightly with temperature. (4) The absolute value of the reduced isotope effect $d \ln b / d \ln m$ [2], where m is the ionic mass, is greater for Li than for K.

In [3] we did a molecular dynamics (MD) simulation of molten LiCl and calculated the self-exchange velocities [4] in order to interpret the known [5] isotope effects on the internal mobilities of Li in isotopically pure and mixed LiCl.

In the present study this method is extended to the eutectic (Li, K)Cl mixture in order to understand the trends of the internal mobilities in this system. Simulations of pure LiCl and KCl have also been done. The total number of the ions per unit cell was twice that in [3] and larger fictive mass differences have been chosen.

The Simulation

In all the runs, totally 432 particles were disposed in a periodic cube whose edge length was set from the density data [6, 7]. For the simulation of the eutectic mixture (58.5 mol% LiCl [7]) these were 126 Li^+, 90 K^+ and 216 Cl^- ions, which corresponds to 58.3 mol% LiCl. Half of both the Li^+ and K^+ were assumed to have the masses 6.941 and 39.098, respectively. For simplicity, these will often be named 7 and 39. The mass of Cl^- was set at 35.453. Pair potentials of the Born-Mayer-Huggins type with the parameters given by Tosi and Fumi [8] were used, although these parameters yield too short peak positions for the unlike pair correlation functions [9]. The parameters of the pair potentials for the mixture were determined by the combination rule recommended by Larsen et al. [10]. The time step was 4 fs. The Ewald method [11] was used for the calculation of the Coulombic forces. Constant-energy simulation was performed. The aimed temperatures were 700, 950 and 1100 K; the melting point of the eutectic mixture is reported to be 628 K [7]. Some conditions of the simulation are given in Table 1.

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Table 1. Some conditions and the resulting pressure of the MD runs. The time steps are the ones after equilibration. Temperatures in parentheses are the aimed values.

Salt	Time steps	Edge length (nm)	Temperature (K)	Pressure (MPa)
LiCl	3 600	2.1774	950.6 (950)	230
	3 000	2.2103	1082.1 (1100)	209
(Li, K)Cl	10 800	2.2909	702.0 (700)	370
(58.3 mol%	5 400	2.3434	946.1 (950)	350
LiCl)	4 200	2.3960	1095.6 (1100)	228
KCl	3 000	2.5664	973.3 (950)	298
	3 600	2.6155	1100.3 (1100)	224

Table 2. Data on the cation-anion correlation functions $g_{+-}(r)$ and the equivalent coordination numbers n_{eq} of the cations. R_M, R_2, and R_m are the positions of the first maximum, the second unity point and the first minimum of $g_{+-}(r)$, respectively. n_{eq} is the equivalent number of cations within R_2 around an anion divided by the mole fraction of these cations [15].

Salt	Cation	Temp. (K)	R_M position (pm)	R_M $g(R_M)$	R_2 (pm)	R_m (pm)	n_{eq}
LiCl	Li	950	221	3.81	281	350	3.14
		1100	220	3.71	281	350	3.03
(Li, K)Cl	Li	700	223	5.36	279	350	3.39
(58.3 mol%	K		301	3.22	369	450	4.91
LiCl)	Li	950	219	5.16	279	350	3.14
	K		298	2.98	369	450	4.51
	Li	1100	218	5.01	283	350	3.50
	K		295	2.83	372	450	4.45
KCl	K	950	294	3.87	368	450	4.16
		1100	294	3.79	371	450	3.98

Results and Discussion

Pair Correlation Functions

MD simulations of the eutectic mixture have already been done in [12−14] with the same potential parameters as used here, but these publications give no self-exchange velocities.

In Table 2, some data of pair correlation functions between unlike ions are given.

In the mixture, R_M decreases appreciably with rising temperature, as was pointed out for a pure salt [16]. $g(R_M)$ for LiCl is higher in the mixture than in pure LiCl. This provides evidence that the association increases when some of the smaller cations are replaced by larger cations in a binary mixture with a common anion [17]. R_m is generally difficult to specify accurately. In Table 2 the R_m values are given tentatively to three significant digits, although these can be determined virtually to an accuracy of only 10 pm.

Self-Exchange Velocities

The self-exchange velocity (SEV) has been defined as [4, 16]

$$v = (R_2 - \bar{R}_2)/\tau, \tag{1}$$

where $\bar{R}_2$ is the average of the distances $< R_2$ between cation and anion, and $t = \tau$ is the average time in which the average distance of such particles becomes R_2.

We have found that experimentally obtained internal mobilities are strongly related to the SEV's [4]. The SEV's of the isotopic ions are given in Table 3. For a further insight, the motion of the cations with respect to the adjacent Cl^- ions is examined. In Fig. 1 the time evolution of the distances of distinct Li^+ and K^+ ions located within the respective R_2's at $t = 0$ from a distinct Cl^- ion in the mixture is shown for the cases of 700 K and 1100 K.

We shall consider four classes of this motion:

(i) The cation starts within R_2 at the time $t = 0$ and passes R_m for the first time at the time t (oscillating motion = O-process).

Table 3. Self-exchange velocities of marked cations from their reference Cl^- ions. The ratios for the two isotopes are given in parentheses. The ratios for Li-7 and K-39 in the mixture are given in brackets.

Salt	Isotope	SEV/m s^{-1} 700 K	950 K	1100 K
LiCl	Li-7		109.3	149.8
			(1.21)	(1.36)
	Li-39		90.3	110.2
(Li, K)Cl	Li-7	31.0	73.2	104.6
(58.3 mol%		(1.16)	(1.16)	(1.29)
LiCl)	Li-39	26.7	63.2	81.3
	K-7	36.4	103.5	163.5
		(1.25)	(1.22)	(1.23)
	K-39	29.2	85.0	133.0
		[1.06]	[0.861]	[0.786]
KCl	K-7		92.6	122.5
			(1.22)	(1.25)
	K-39		75.8	98.0

(ii) The cation passes R_2 for the last time at the time $t = 0$ and passes R_m for the first time at time t (leaving motion = L-process).

(iii) The cation passes R_m at the time $t = 0$ in the outward direction and does not pass R_2 (wandering motion = W-process).

(iv) The cation passes R_m in the outward direction at the time $t = 0$ and passes R_2 for the first time at the time t. The section of this motion leading from R_m to R_2 is named the coming-back motion (= C-process).

The percentage of cations having performed the O-process is shown as a function of time in Fig. 2; the time at which 20% are reached is given in Table 4. The average velocity of the L-process is given in Table 5. This velocity seems to depend only on the masses of the cation and anion and the temperature, but not on the chemical species, i.e. the length of the range from R_2 to R_m; this distance is considerably larger for K than for Li, as seen from Table 2. It is interesting to note that the difference between the pair potentials for the Li−Cl and K−Cl pairs does not explicitly play a role in the L-process. The velocity during the L-process is found to be proportional to the sum of the mean velocities of "ideal-gas like" cations and anions; these are $v_c = \sqrt{8RT/\pi M_c}$ and $v_a = \sqrt{8RT/\pi M_a}$, respectively, where M_c and M_a are the respective atomic masses. In Fig. 3 the velocity during the L-process is plotted versus $(v_c + v_a)$, from which the slope of the straight line is estimated to be 0.577 ± 0.005. The corresponding values calculated for LiCl with other combinations of masses, such as $M_c = 23$ and $M_a = 127$ in the previous paper (Table 5 in [3]) also lie on the same straight line within statistical errors. Thus, the L-process should be regarded as a purely physical process in which the isotope effect is large.

Table 4. Time after which 20% of the cations located within R_2 from the reference Cl^- ions have left the range R_m for the first time. The ratios for two isotopes are given in parentheses.

Salt	Isotope	Time/ps		
		700 K	950 K	1100 K
LiCl	Li-7		0.324	0.262
			(1.44)	(1.59)
	Li-39		0.469	0.416
(Li, K)Cl (58.3 mol% LiCl)	Li-7	0.832	0.470	0.376
		(1.40)	(1.38)	(1.44)
	Li-39	1.16	0.648	0.539
	K-7	0.505	0.294	0.239
		(1.63)	(1.45)	(1.63)
	K-39	0.826	0.427	0.350
KCl	K-7		0.399	0.313
			(1.46)	(1.55)
	K-39		0.583	0.484

Table 5. Velocity of the L-process. The ratios for two isotopes are given in parentheses.

Salt	Isotope	Velocity/m s^{-1}		
		700 K	950 K	1100 K
LiCl	Li-7		1394±25	1442±16
			(1.60±0.03)	(1.61±0.03)
	Li-39		873±7	893±13
(Li, K)Cl (58.3 mol% LiCl)	Li-7	1165±21	1357±24	1444±19
		(1.54±0.04)	(1.57±0.04)	(1.56±0.03)
	Li-39	758±11	862±12	923±11
	K-7	1156±18	1347±20	1485±21
		(1.51±0.03)	(1.53±0.04)	(1.57±0.03)
	K-39	765±9	878±20	948±8
KCl	K-7		1389±28	1494±20
			(1.59±0.04)	(1.61±0.03)
	K-39		873±8	931±15

The percentage of the C-process with respect to all particles exceeding R_m is shown in Figure 4. The C-processes result in an effective prolongation of the O-process. As a measure of the effective duration of the O-process, the time is calculated, see Table 6, for one third of the marked cations to leave the region within the distance R_2 from the reference Cl^- ion.

The Chemla Effect of the SEV

As seen in Fig. 2 there is a considerable difference between Li^+ and K^+ ions concerning the duration of the O-process, while no such chemical effect is found for the L-process. For Li^+ ions the duration of the O-process is considerably longer in the mixture than in pure LiCl, while for K^+ ions the duration is instead shorter in the mixture than in the pure KCl, see Table 4.

This can be understood from the potential profiles given in Fig. 5 for cations (Li^+ top, K^+ bottom) located on a straight line between two Cl^- ions. They are obtained by superposing the pair potentials for Li−Cl and K−Cl used in the present

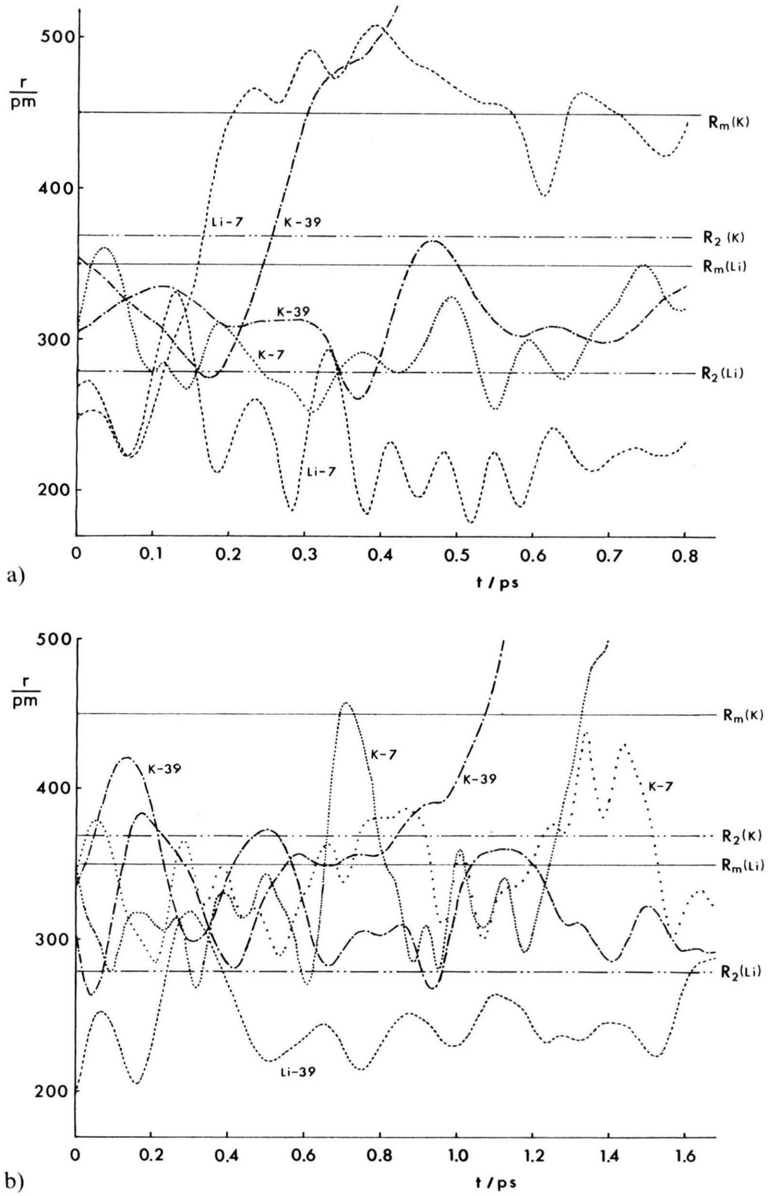

Fig. 1. Time evolution of distances of Li^+ and K^+ ions located within the respective R_2's at $t = 0$ from an arbitrary Cl^- ion. The distances corresponding to R_2 and R_m for Li–Cl and K–Cl pairs are marked with dash-dotted and solid horizontals, respectively. (a) 1100 K (two Li-7, one K-7 and two K-39 ions); (b) 700 K (one Li-39, two K-7 and two K-39 atoms). The scale of the abscissa for (a) is twice as large as that for (b).

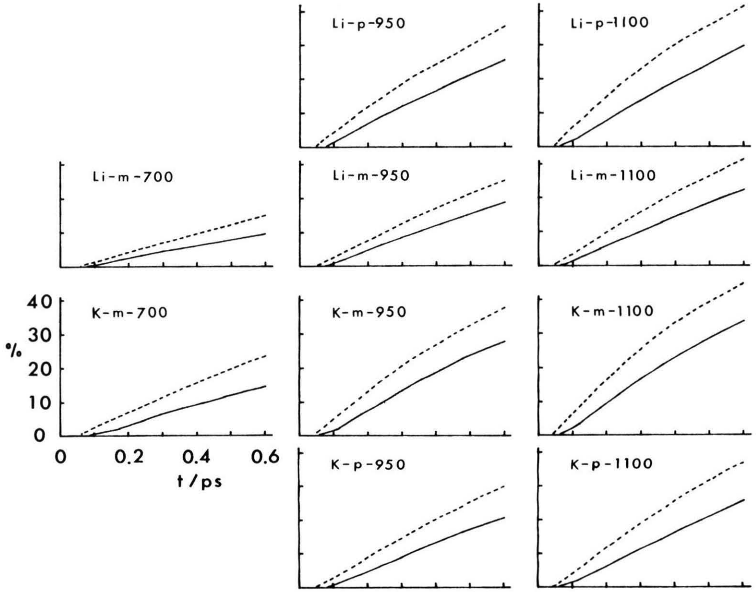

Fig. 2. Percentage of cations located within R_2 from a reference Cl^- ion at $t = 0$ and exceeding the distance R_m for the first time at the time t. For example, Li-m-700 refers to Li^+ ions in the mixture at about 700 K, and K-p-1100 refers to K^+ ions in pure KCl at about 1100 K. Legend for the abscissa and the coordinate is dropped except for the case of K-m-700. The dashed and solid lines refer to the lighter and heavier isotopes, respectively.

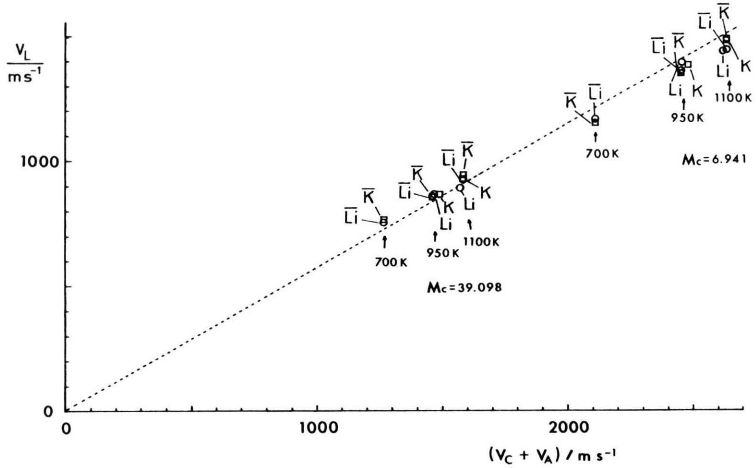

Fig. 3. The velocity in the L-process vs. $(v_c + v_a)$. Chemical symbols with and without a bar refer to mixtures and the pure salts, respectively. M_c = atomic mass of both cations, if present.

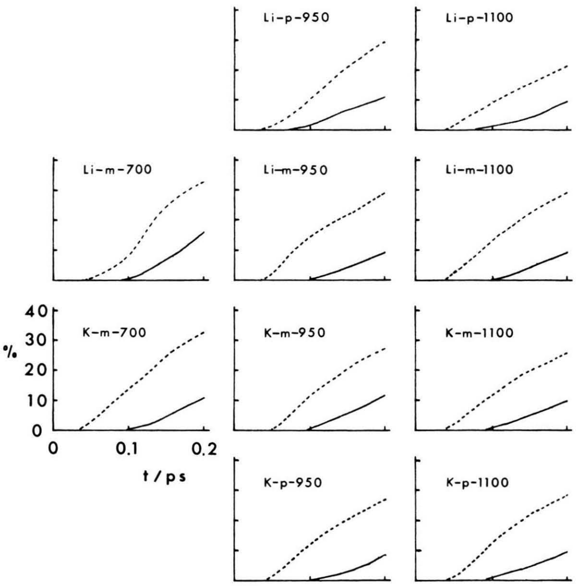

Fig. 4. Percentage of ions which have returned to within R_2 during the time t after having exceeded R_m. For further explanations cf. legend of Figure 2.

MD simulation [8], which also are shown in the figure. The distances between two Cl^- ions are taken here as $d_1 = 580$ pm, $d_2 (= d_3) = 640$ pm and $d_4 = 680$ pm, which correspond approximately to the Cl–Cl distances at 950 K for melts of the fictive NaCl-type crystalline structure of pure LiCl, an equimolar LiCl–KCl mixture and pure KCl, respectively. The magnitude of the kinetic energy, $3kT/2$, at this temperature is shown for comparison.

The distance d varies in the course of the motions of the two Cl^- ions. The larger the average value of this distance is, the longer it will take before the conditions for a barrier jump are reached.

In a pure LiCl melt, the Cl^- ions are coordinating tetrahedrally rather than octahedrally to a Li^+ ion [9], and the distance between two Cl^- ions that are on either side of a Li^+ ion should on the average be shorter than the d_1 given in Figure 5. Thus a Li^+ ion can move after a relatively short O-process.

Since the distance d becomes larger with increasing concentration of KCl, the barrier h becomes higher, and the duration of the O-process becomes considerably longer.

Similarly, also for the K^+ ions, an increase of the concentration of KCl is accompanied by an increase of d. Thus, h increases and the duration of the O-

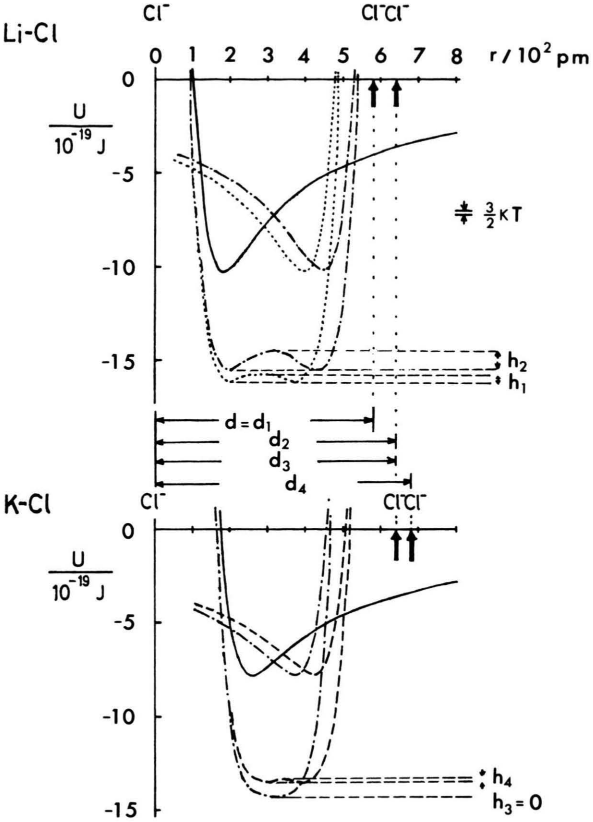

Fig. 5. Potentials for a cation located between two Cl^- ions separated by the distance d (top: Li^+, bottom: K^+). (----: $d_1 = 580$ pm, -—-—-: $d_2 = d_3 = 640$ pm and ———: $d_4 = 680$ pm). The relevant pair potentials [8] are also shown.

Table 6. Time after which one third of the marked cations within R_2 from the reference Cl^- ions have left this region. The ratios for two isotopes are given in parentheses.

Salt	Isotope	Time/ps		
		700 K	950 K	1100 K
LiCl	Li-7		0.466 (1.19)	0.325 (1.38)
	Li-39		0.553	0.509
(Li, K)Cl (58.3 mol% LiCl)	Li-7	2.38 (1.11)	0.888 (1.09)	0.620 (1.30)
	Li-39	2.64	0.968	0.807
	K-7	1.31 (1.38)	0.398 (1.33)	0.264 (1.31)
	K-39	1.81	0.533	0.347
KCl	K-7		0.633 (1.27)	0.468 (1.23)
	K-39		0.798	0.580

process becomes longer. In the present case $h_3 = 0$ for the equimolar mixture.

The magnitude of $\mathrm{d}h/\mathrm{d}d$ is larger for Li^+ than for K^+, since, near the minimum, the attraction part of the pair potential curve is steeper for the Li–Cl pair than for the K–Cl pair. If, for example, d_2 and d_3 are equal, a K^+ ion would move away from a Cl^- ion with a shorter average duration of the O-process than a Li^+ ion would. Thus, the Chemla effect occurs.

The influence of temperature on the ratio v_{Li}/v_K can be accounted for in a similar way. Since $\mathrm{d}h/\mathrm{d}d$ is greater for Li^+ than for K^+, as seen in Fig. 5b, an increase of d caused by a temperature increase will be less favourable for v_{Li} than for v_K, and v_{Li}/v_K thus decreases. This reflects the observed trend for the internal mobility ratio b_{Li}/b_K.

At 700 K the SEV is somewhat greater for ^7Li than for ^{39}K in the mixture, whereas the mobility of Li^+ is smaller than that of K^+ at this temperature [1]. At 700 K the duration of the O-process is about the same for the light ^7Li ions as for the heavy ^{39}K ions (see fig. 2), while it is evident that the C-process occurs more frequently for the former than for the latter (see Fig. 4); however, the velocity of the L-process must be greater for the former. The velocity of the W-process within the time range τ is inevitably included in the calculation of the SEV's, although the motion of the W-process corresponds to the situation where neighbouring ion pairs are rather far away from each other. This may be the reason for the discrepancy at 700 K that the measured mobility b_K is larger than b_{Li}, but the calculated SEV is larger for Li^+ than for K^+.

An attempt has been made previously [12] to estimate the specific conductance of this mixture from the self-diffusion coefficients obtained by MD by means of the Nernst-Einstein equation. This attempt might, however, be inappropriate, since it was overlooked that, although the Chemla effect occurs in the mobilities, it need not necessarily occur also in the calculated self-diffusion coefficients. If a cation moves along the "surface" of a neighbouring anion, this motion is not included in the SEV, but it is in self-diffusion.

The Isotope Effect of the SEV

For the L-process the isotope effect is large. If, as stated above, the velocity in the L-process is proportional to $(v_c + v_a)$, the ratio of the velocities of the two isotope ions should be $(1/\sqrt{6.941} + 1/\sqrt{35.453})/(1/\sqrt{39.098} + 1/\sqrt{35.453}) = 1.67$. As seen from Table 5, the ratios obtained from the MD simulation are rather close to this value.

Concerning the duration of the O-process, the ratio of the times quoted in Table 4 is also quite large for isotopic ions, and there is an indication that the magnitude of the isotope effect decreases when the duration of the O-process increases. If we restrict the discussion to the 8 cases for 950 K and 1100 K (the 700 K cases are considered below), there is a tendency that the isotope effect is greater, the shorter the duration of the O-process is. (The data for pure KCl are, however, somewhat greater than expected from this tendency, and the reason for this will also be considered below.) Such a tendency is expected from simple considerations, and it can also be seen from Figure 1. The average cycle of the oscillations is shorter for a light isotope than for a heavy one. The cycle is irregular, and the influence of the ion mass on the positions of the oscillation maxima decreases as time elapses. Thus, the shorter the duration of the O-process, the larger the isotope effect will be.

The details of the oscillation cycle are of importance for the magnitude of the isotope effect on the duration of the O-process. The more regular the cycle is, the larger an isotope effect should be expect. This explains both the apparent deviations mentioned above. Pure KCl is much more regular than the other melts due to the similar size of the K^+ and Cl^- ions, and the oscillation cycles are thus more regular. The free space is smaller at 700 K than at the other temperatures, and a small free space should mean a more regular cycle. Thus we can expect large isotope effects at 700 K in spite of the rather long duration, and this effect should be more pronounced for the large K^+ ions than for the small Li^+ ones, which seems to be the case.

The C-process has also to be taken into account when the "effective" duration of the O-process was introduced. The probability that the C-process occurs seems to decrease with increasing temperature, with a few exceptional cases probably due to statistical errors, see Figure 4. This probability is always largest for the light isotope, and this reduces the isotope effect of the effective duration of the O-process. This reduction can also be seen from a comparison of Tables 4 and 6. In summary, the isotope effect of the effective duration of the

O-process does not show any simple correlation with their temperature or concentration.

In pure LiCl the isotope effect of the effective duration of the O-process is larger at 1100 K than at 950 K. This is mainly due to the rather small probability that the C-process occurs for the light isotopes at 1100 K. This probability might be so small because the environment changes quickly due to an agitation effect caused by the presence of many Li^+ ions of a small size.

In the mixture the probability of the C-process is high for the light K^+ isotopes at 700 K, owing to the small free space. This will to some extent compensate the high isotope effect on the duration of the O-process, and this isotope effect becomes nearly independent of the temperature (see Fig. 4, Table 4, and Table 6). Thus, for the mixture, the isotope effect of the SEV remains nearly constant when the temperature is increased.

In pure KCl the isotope effect of the duration of the O-process increases slightly with increasing temperature (Table 4). However, for the light K^+ ions the probability of the C-process is nearly independent of the temperature (Figure 4). The explanation is that, also at high temperatures, the environment changes only slowly since the K^+ and Cl^- ions are spherical and of nearly the same size. Therefore, when a K^+ ion occasionally leaves its reference ion, it is more likely that it returns readily than continues further away.

According to experiment, for the pure salts KCl [18] and LiCl [5] the isotope effect of the internal cation mobility increases with increasing temperature; the temperature dependence being larger in the LiCl case. In the eutectic mixture the isotope effects of both cations are nearly independent of the temperature [1]. Thus for the two pure salts as well as for the mixture, the temperature dependence of the experimental isotope effects for the cations seems to agree reasonably well with those of the SEV's.

The general trend that the isotope effects of the SEVs increase with increasing temperature (Table 3) should be attributed to an increasing relative importance of the L-process for which the isotope effect is larger than for the (effective duration of the) O-process.

The isotope effect of the SEV's (Table 3) is nearly the same for Li^+ and K^+ ions. It could therefore be assumed that the mobility isotope effects of these two cations would have been much the same, if their masses had been the same. The reason why the mass effect (i.e. the relative difference in velocities divided by the relative difference in masses) is larger for lithium than for potassium should thus be that the dependence of the internal mobility on the mass of the cation is non-linear.

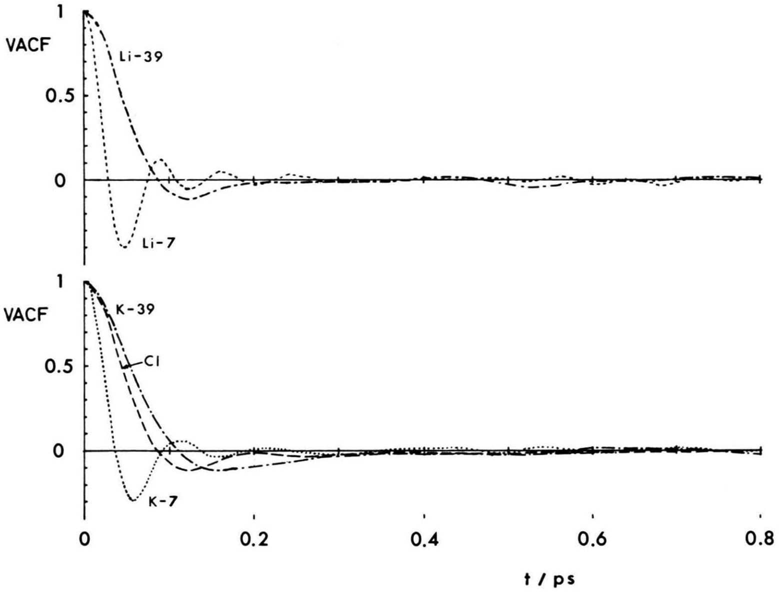

Fig. 6. Velocity autocorrelation functions for the mixture at 1100 K.

Velocity Autocorrelation Function

The velocity autocorrelation function is defined as

$$\mathrm{VACF}_i(t) = \frac{\langle v_\mathrm{i}(0) \cdot v_\mathrm{i}(t) \rangle}{\langle v_\mathrm{i}^2(0) \rangle},$$

where v_i is the thermal velocity of species i and $\langle\ \rangle$ means the average for i. The velocity autocorrelation functions have also been calculated. As an example, those of the mixture at 1100 K are shown in Figure 6. The general shape of the profiles appears to depend on the mass rather than on the kind of chemical species. It may be fortuitous that the velocity autocorrelation functions of the Cl^- ion is quite similar to that of the $^{39}Li^+$ ion.

For all three kinds of ions the first minimum becomes more shallow when the temperature is increased, while it becomes deeper if the concentration of KCl is increased. These obtained trends agree with those calculated for similar conditions by Lantelme and Turq [14]. However, our first minimum is much deeper than theirs (about − 0.2), and the reason for this discrepancy is not clear at present.

In conclusion, the following trends are observed for the SEVs of molten (Li, K)Cl near the eutectic composition (58.3 mol% LiCl) in the range between 700 K and 1100 K. (1) The ratio $(v_{\mathrm{Li}}/v_{\mathrm{K}})$ decreases with increasing temperature, and it is less than unity at higher temperatures, that is the Chemla effect occurs. (2) The isotope effect of v_{Li} seems to increase very slightly with increasing temperature, while that for v_{K} is nearly constant. The general tendency seems to be similar for the MD calculations and the experimental results obtained for internal mobilities.

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