A Molecular Dynamics Simulation of Molten (Li-Rb)Cl Implying the Chemla Effect of Mobilities

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A new transport property, the self-exchange velocity (SEV) of neighbouring unlike ions, has been evaluated from molecular dynamics simulations of molten LiCl, RbCl and $LiRbCl_2$ at 1100 K and the mixture at 750 K. From the increase of the SEV's in the order Rb^+(pure salt) < Li^+(mixture) < Rb^+(mixture) < Li^+(pure salt), it is conjectured that there is a strong correlation between the SEV's and the internal mobilities. An interpretation of the Chemla effect in its dependence on temperature is given. The pair correlation functions and the self-diffusion coefficients are also calculated and discussed.

Introduction

Chemla discovered that in the molten binary system (Li-K)Br the mobilities of the cations become the same at a certain composition and temperature [1]. Further investigations have shown that the difference in mobilities of the cations in such charge-symmetric binary systems may change sign on a change in temperature and/or concentration [2, 3]. This phenomenon has been named the Chemla effect [4].

The Chemla effect has been qualitatively interpreted in terms of quasi-complexes [2, 3, 5–9] or polarized anions [10]. The former model assumes the presence of associated species such as LiBr and $LiBr_2^-$, an assumption of which is not confirmed by computer simulations of molten salts. The latter model cannot explain the temperature dependence of the Chemla effect.

In order to interpret the Chemla effect from another point of view, we have performed molecular dynamics simulations of LiCl, RbCl and the mixture $LiRbCl_2$. This system was chosen because the masses and ionic radii of the two cations differ considerably and because the pair potentials of the two pure salts have been tested in several simulations (LiCl [11–13], RbCl [13–15]).

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The Molecular Dynamics Simulation

For the simulation, the usual pair potentials of the Born-Mayer-Huggins type with parameters obtained for the corresponding crystals by Tosi and Fumi [16] were adopted:

$$\varphi_{ij} = \frac{z_i z_j e^2}{r} + A_{ij} b \exp\{(r_i^0 + r_j^0 - r)/\varrho\} - \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8}. \quad (1)$$

The values of A, b, ϱ, r^0, c and d are given in Table 1.

In a basic cell, 108 cations and 108 anions were contained in all cases. The side length L of the basic cell for the pure salts was derived from the densities [17], and that for the mixture from the assumption of additivity of the molar volumes, although experimental values for the mixture were available [18]. The adopted values for L are given in Table 1.

The parameters for the pair potentials of the mixture were obtained in a way analogous to that used for the (Na-K)Cl mixture in the Monte Carlo study [19].

An isothermal molecular dynamics procedure [11] was performed at 1100 K. In order to learn about the effect of the temperature on the mixture, a simulation of the mixture at 750 K was also carried out. For the calculation of the Coulomb force,

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Table 1. The parameters used in the calculation.

Salt	Ion pair	A_{ij}	$1/\varrho$ (nm^{-1})	c_{ij} (10^{-79} J m^6)	d_{ij} (10^{-99} Jm^8)
LiCl	Li^+-Li^+	2.000		0.073	0.03
	Li^+-Cl^-	1.375	29.24	2.0	2.4
	Cl^--Cl^-	0.750		111.0	223.0
RbCl	Rb^+-Rb^+	1.250		59.4	82.0
	Rb^+-Cl^-	1.000	31.45	79.0	134.0
	Cl^--Cl^-	0.750		130.0	260.0
$LiRbCl_2$	Li^+-Li^+	2.000		0.073	0.03
	Li^+-Rb^+	1.625		1.84	1.65
	Rb^+-Rb^+	1.250	30.30	59.4	82.0
	Li^+-Cl^-	1.375		2.0	2.4
	Rb^+-Cl^-	1.000		79.0	134.0
	Cl^--Cl^-	0.750		120.4	241.4

$b = 0.338 \times 10^{-19}$ J, $r^0_{Li} = 0.0816$ nm, $r^0_{Rb} = 0.1587$ nm, $r^0_{Cl} = 0.1585$ nm; L(nm): 1.75429 (LiCl, 1100 K), 2.16081 (RbCl, 1100 K), 1.97845 ($LiRbCl_2$, 1100 K), 1.89896 ($LiRbCl_2$, 750 K).

the Ewald method [20] was adopted. The time step was 5×10^{-15} s.

The pressure fluctuated considerably from step to step (cf. [21]). The average pressures were 0.25 GPa(LiCl), 0.19 GPa(RbCl), 0.13 GPa ($LiRbCl_2$ at 1100 K), and 0.36 GPa ($LiRbCl_2$ at 750 K).

The Pair Correlation Functions

The pair correlation functions of the pure salts and of the mixture are shown in Figures 1 to 4.

The positions of the first peaks of the pair correlation functions $g_{Li\text{-}Cl}$ and $g_{Rb\text{-}Cl}$ are much the same in the mixture and the pure salts.

As for the peak heights, $g_{Li\text{-}Cl}$ and $g_{Rb\text{-}Cl}$ are more and less sharply peaked in the mixture than in the pure salts, respectively. It has been found in simulations of pure KI that lowering the density results in a higher first peak g_{+-} [22]. To explain this, Dixon and Sangster have presumed that with decreasing density the second-neighbour ions move out, having more space available to them, and consequently unlike ions can cluster round a reference ion with less interference from the second neighbours [22]. We believe that this holds for the present case as well.

The position of the second peak of g_{+-} is more distant for Li-Cl and less distant for Rb-Cl in the mixture than in the respective pure salt, as seen from Figures 1 and 2. The position of the second peaks is strongly affected by the number density, as pointed out for pure salts in [22, 23].

Another characteristic of g_{+-} of the mixture as compared to that of the pure salts is the more rapid disappearance of the pair correlation in the long distance. This is due to the presence of cations with quite different sizes in the mixture.

It is interesting to note (cf. Table 2 and Fig. 3) that the distance of the first peak of $g_{Li\text{-}Li}$ is somewhat smaller in the mixture than in the pure salt in spite of the lower number density of the mixture.

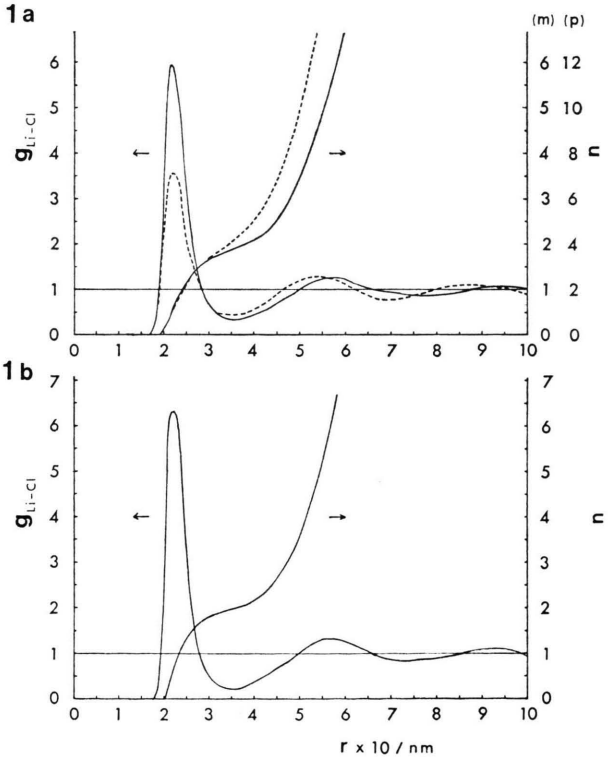

Fig. 1. Pair correlation functions $g_{Li\text{-}Cl}$ and running coordination numbers n. (1a) 1100 K; (1b) 750 K. Broken line: pure LiCl, solid line: $LiRbCl_2$. Characters p and m in parentheses indicate pure salt and the mixture, respectively.

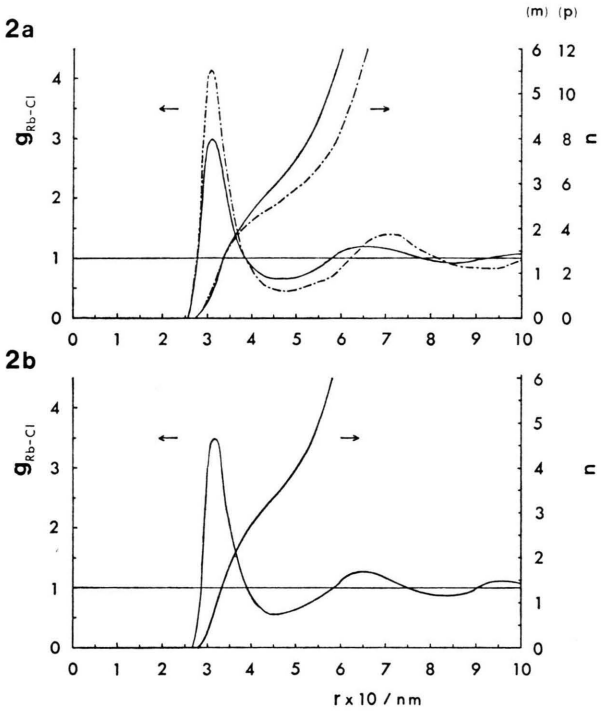

Fig. 2. Pair correlation functions g_{Rb-Cl} and running coordination numbers n. (2a) 1100 K; (2b) 750 K. Chain line: pure RbCl, solid line: $LiRbCl_2$.

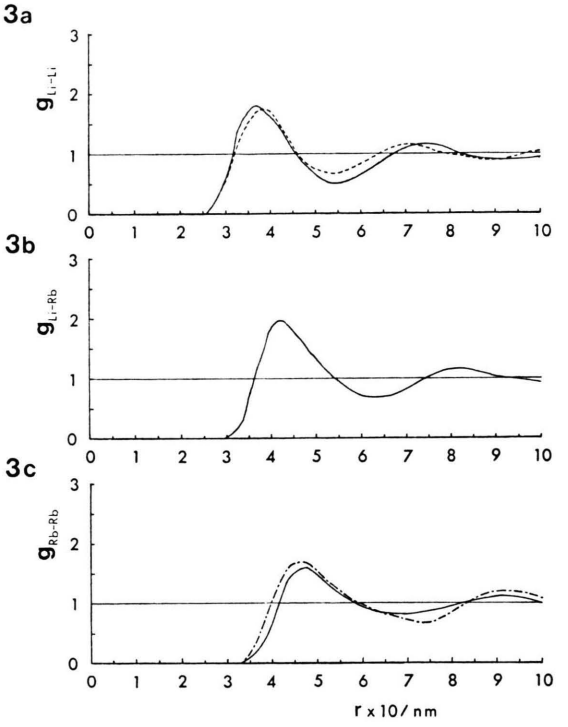

Fig. 3. Pair correlation functions of g_{++} at 1100 K. (3a) g_{Li-Li}; (3b) g_{Li-Rb}; (3c) g_{Rb-Rb}. Broken line: pure LiCl chain line: pure RbCl, solid line: $LiRbCl_2$.

Table 2. Data of pair correlation functions.

Salt	Temp.	Ion pair	First maximum		First minimum		Second maximum	
	(K)		distance (10^{-1} nm)	value	distance (10^{-1} nm)	value	distance (10^{-1} nm)	value
LiCl	1100	Li^+-Li^+	3.77	1.77	5.4	0.71	7.0	1.17
		Li^+-Cl^-	2.21	3.69	3.6	0.49	5.4	1.33
		Cl^--Cl^-	3.69	2.09	5.4	0.65	7.0	1.23
RbCl	1100	Rb^+-Rb^+	4.69	1.90	7.3	0.68	9.1	1.22
		Rb^+-Cl^-	3.09	4.06	4.7	0.46	7.1	1.41
		Cl^--Cl^-	4.69	1.76	7.3	0.68	9.2	1.23
$LiRbCl_2$	1100	Li^+-Li^+	3.67	1.83	5.5	0.50	7.5	1.15
		Li^+-Rb^+	4.17	1.97	6.5	0.72	8.3	1.16
		Rb^+-Rb^+	4.69	1.64	7.4	0.79	9.1	1.12
		Li^+-Cl^-	2.20	5.77	3.6	0.34	5.7	1.25
		Rb^+-Cl^-	3.17	3.00	4.7	0.63	6.4	1.21
		Cl^--Cl^-	3.88	1.85	5.6	0.85	7.6	1.05
$LiRbCl_2$	750	Li^+-Li^+	3.60	1.85	5.3	0.50	7.5	1.24
		Li^+-Rb^+	4.01	2.23	6.2	0.60	8.1	1.27
		Rb^+-Rb^+	4.63	1.74	7.1	0.87	8.7	1.18
		Li^+-Cl^-	2.21	6.38	3.6	0.27	5.6	1.36
		Rb^+-Cl^-	3.17	3.49	4.5	0.57	6.4	1.29
		Cl^--Cl^-	3.81	2.05	5.4	0.75	7.2	1.16

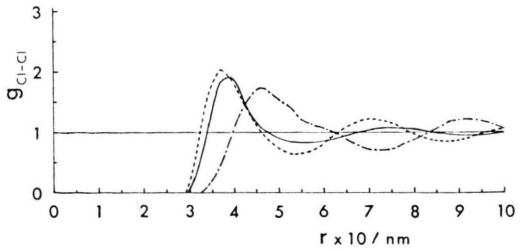

Fig. 4. Pair correlation functions g_{Cl-Cl} at 1100 K. Specification of curves as in Figure 3.

Evidently, the pair correlation between the Li^+ ions around a Cl^- ion becomes stronger in the mixture.

The values of $g_{+\,+}$, $g_{+\,-}$ and $g_{-\,-}$ in the two pure salts are in good agreement with those already obtained with simulations using the same potentials (LiCl [13], RbCl [15]), if the difference in the temperatures is taken into consideration.

The Self-exchange velocity of Neighbouring unlike Ions

The strict formula to obtain mobilities of binary systems with a common anion from an equilibrium simulation has been given by Klemm [24]. Its use, however, requires extensive calculations and is correspondingly expensive at present. We therefore propose a simple method for estimating ionic mobilities. We assume that there is a strong correlation between internal mobilities (b) and self-exchange velocities of neighbouring unlike ions (SEV), the SEV's being defined as the difference between the distance where the pair correlation function crosses unity for the second time (R_2) and the average distance of unlike ions within $R_2(\bar{R})$, divided by the average time in which the unlike ions within R_2 move to an average distance R_2. During the same time, of course, as many ions move from an distance R_2 to an average distance $\bar{R}$. The distance R_2 may be regarded as the end of the nearest neighbour interaction (cf. [25]).

The number of the ions within the distance R_2 is given in Table 3, together with that within the first minimum, R_{min}.

The cations within the distance R_2 around each Cl^- ion were marked. Then the number of the marked cations remaining within R_2 was followed during the course of time (Figure 5). The average distance of the marked cations from the referenced anions is followed in Figure 6. For totally 3240 Cl^- ions and the cations surrounding them, the average value was

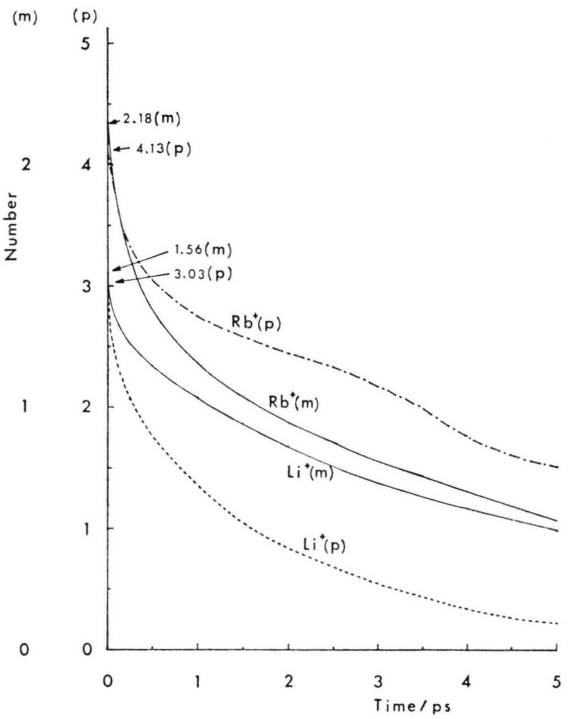

Fig. 5. Average numbers of marked cations remaining with the elapse of time within R_2 centreed on a Cl^- ion at 1100 K. For the characters p and m, see the legend of Figure 1.

Salt	Temp. (K)	Li^+	Rb^+
LiCl	1100	3.03 ($R_2 = 0.282$ nm) 4.16 ($R_{min} = 0.360$ nm)	—
RbCl	1100	—	4.13 ($R_2 = 0.390$ nm) 5.37 ($R_{min} = 0.470$ nm)
$LiRbCl_2$	1100	1.56 ($R_2 = 0.285$ nm) 1.89 ($R_{min} = 0.360$ nm)	2.18 ($R_2 = 0.387$ nm) 3.22 ($R_{min} = 0.470$ nm)
	750	1.68 ($R_2 = 0.281$ nm) 2.02 ($R_{min} = 0.360$ nm)	2.48 ($R_2 = 0.383$ nm) 3.33 ($R_{min} = 0.450$ nm)

Table 3. The number of cations around a Cl^- ion.

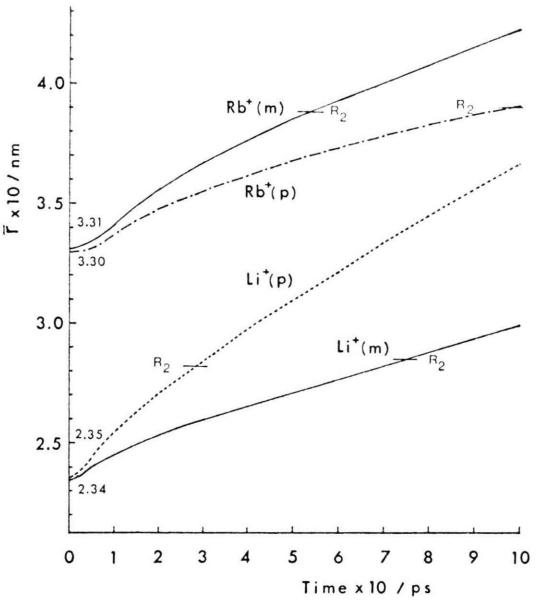

Fig. 6. Evolution of the average distances of marked cations from a Cl^- ion. See also the legend of Figure 5.

Table 4. Self-exchange velocities of neighbouring unlike ions.

Salt	Temp. (K)	Li^+-Cl^- (10 m/s)	Rb^+-Cl^- (10 m/s)
LiCl	1100	16.5	—
RbCl	1100	—	6.32
$LiRbCl_2$	1100	6.61	10.0
	750	2.27	2.87

taken in each case. Figure 5 shows that the number does not decrease exponentially. The decay rate at a relatively early time, say 0.3 ps, is in the order: Rb^+(pure RbCl) < Li^+(mixture) < Rb^+(mixture) < Li^+(pure LiCl). This order is not necessarily maintained at longer times, as seen from Figure 5.

The SEV's obtained are tabulated in Table 4. Average SEV's ($\bar{v}$) are plotted in Fig. 7 against the average internal mobilities $\bar{b}$ as experimentally determined at 1100 K (the pure salts [17]; the mixture [18]). It seems that there is an approximately linear relation between the two entities. Thus, the assumption that there is a strong correlation between internal mobilities and SEV's seems to be verified.

Measurements of the internal mobilities of the system (Li – Rb)Cl are now in progress [26]. Preliminary results reveal that the internal mobility

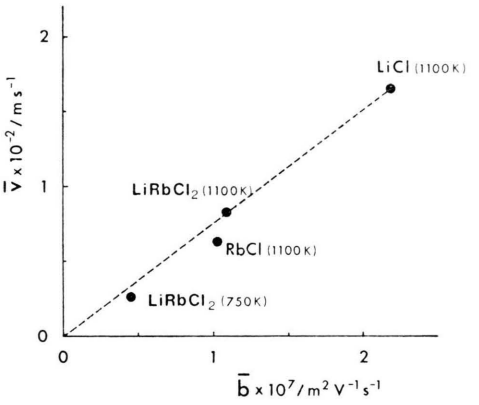

Fig. 7. Relationship between average internal mobilities ($\bar{b}$) and average SEV's ($\bar{v}$). The broken line is tentatively drawn so that it connects the point for LiCl at 1100 K with the origin.

of Rb^+ is larger than that of Li^+ in $LiRbCl_2$ at 1100 K. The internal mobilities at 1100 K seem to be in the order Rb^+(pure salt) < Li^+(mixture) < Rb^+(mixture) < Li^+(pure salt). This order has been reproduced by the SEV's, as shown in Table 4. Thus, the Chemla effect of this system is reproduced by the SEV's obtained from the simulation.

Self-diffusion

The self-diffusion coefficients D were calculated from the mean square displacements according to the Einstein equation

$$D = \frac{1}{6}\frac{\mathrm{d}}{\mathrm{d}\tau}\left\langle \{r_i(t+\tau) - r_i(t)\}^2 \right\rangle , \qquad (2)$$

where τ is the period during which the mean square displacement lies on a straight line and the angled brackets denote an ensemble average of time origins.

The mean square displacements $\langle \Delta r^2 \rangle$ for the mixture and the pure salts are shown in Figure 8. Totally more than 3000 cations and 3000 anions were taken for the calculation of the average values in each case.

In Table 5, the calculated values of D are given along with the duration τ taken into account in the calculation. It cannot be judged at present whether the slope in the mean square displacements up to 5 ps at the longest yields values for self-diffusion coefficients satisfactorily comparable with experimental ones measured in a much longer time scale. At least, Fig. 8 suggests that the slope for shorter than 2 ps from the time origin is apt to lead

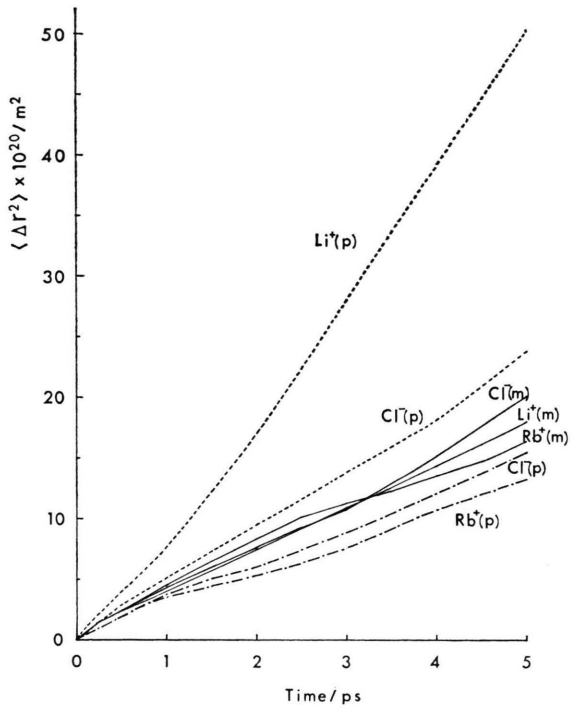

Fig. 8. Mean square displacements at 1100 K. See the legend of Figure 5.

to incorrect values for self-diffusion coefficients of the order of 10^{-9} m²/s.

The self-diffusion coefficients of our mixture have not yet been measured. The results obtained with the simulation predict that in this mixture the self-diffusion coefficient of Li^+ would be larger than that of Rb^+ at 750 K and 1100 K. This is consistent with observations on other systems where the Chemla effect is observed but the self-diffusion coefficients of the cations remain in the order found for the pure salts [5, 7, 27].

Discussion

The order of the SEV's given in Table 4 may be explained as follows.

The well of the pair potential between the Li^+ and Cl^- ions is relatively deep. Therefore, although the small size and mass of a Li^+ ion facilitate its motion along the "surface" of the nearest neighbouring Cl^- ion, the Li^+ ion cannot move away from the Cl^- ion unless another Cl^- ion is near by.

In pure LiCl, the number density is rather high and the average distance between the Cl^- ions is small (cf. Fig. 4), which is favourable for a Li^+ ion to move from one Cl^- ion to another. In the mixture with RbCl, the average distance between two Cl^- ions becomes larger because of the presence of the large Rb^+ ions. This makes it difficult for a Li^+ ion to leave one Cl^- ion for another. Besides this, the presence of the large Rb^+ ions itself is an obstacle for the exchange of Li^+ ions.

As for the Rb^+ ion, two factors should be taken into consideration when the SEV in the mixture is to be compared with that in the pure salts. One is the free space and the other is the electrostatic screening of the Cl^- ions by the Li^+ ions.

If there is too little free space, the motion of Rb^+ will be hampered. This has been evidenced by experiments in the range of high $LiNO_3$ concentrations in the system $(Li-Rb)NO_3$ [4]. The high pressure experiments show that the molar conductivity of

Table 5. Self-diffusion coefficients.

Salt	Temp. (K)	Li^+ (10^{-9} m²/s)	Rb^+ (10^{-9} m²/s)	Cl^- (10^{-9} m²/s)
LiCl	1100	18.7 ± 0.0	—	9.45 ± 0.03
		[2.2 — 5.0 ps]		[4.0 — 5.0 ps]
		(17.3 ± 0.8[a])		(8.34 ± 0.3[a])
RbCl	1100	—	4.21 ± 0.02	5.59 ± 0.03
			[3.8 — 5.0 ps]	[3.0 — 5.0 ps]
			(6.43 ± 0.09[b])	(5.60 ± 0.18[b])
$LiRbCl_2$	1100	6.00 ± 0.02	4.62 ± 0.08	8.46 ± 0.04
		[3.5 — 5.0 ps]	[4.0 — 5.0 ps]	[3.8 — 5.0 ps]
	750	1.31 ± 0.02	0.42 ± 0.01	1.67 ± 0.01
		[3.5 — 5.0 ps]	[2.0 — 5.0 ps]	[3.0 — 5.0 ps]

The given errors of the calculated values are standard deviations in the least squares fit. The duration taken into account in the calculation is given in the brackets. The values in parentheses are experimental data; a: extrapolated values with respect to temperature (maximum temp.: 1033 K) of data from [29], b: data from [30].

molten RbCl decreases sharply with increasing pressure [28]. This would indicate that less free space than in pure RbCl at ambient pressure is unfavourable for the SEV of Rb^+. Thus, as far as the amount of free space is concerned, an increase of the concentration of the Li^+ ions would diminish the SEV of the Rb^+ ions. On the other hand, due to the high thermal velocity and small momentum of the Li^+ ions the shape of the free space will change the faster and its walls will become the softer for the Rb^+ ions, the more Li^+ ions are present, and this will tend to increase the SEV of the Rb^+ ions with increasing concentration of the Li^+ ions.

The second factor to be considered is the electrostatic screening effect. The small average next neighbour distance of the Li^+ ions from the Cl^- ions will reduce the electric force fields outside such pairs and will allow the Rb^+ ion to move more freely in the mixture than in pure RbCl.

As the temperature increases, the free space increases. The volume expansion itself is unfavourable for the mobility of Li^+ ions, while it would be presumably favourable for the mobility of Rb^+ ions. Consequently, as temperature increases, the SEV of the Li^+ ions somewhat increases, while that of the Rb^+ ions increases sharply. Therefore, with increasing temperature the cross-over point of the isotherms of the SEV's of two cations will shift to higher concentrations of the smaller and lighter cation.

We think that these deliberations also hold for the internal mobilities and that they are therefore apt to explain the Chemla effect and its temperature dependence.

In the present simulation the pair potentials are based on a rigid ion model, that is, polarization has not been taken into consideration explicitly. Nevertheless, the Chemla effect is realized. This would imply that the anion polarization effect, if any, will not play a main role for the Chemla effect.

In the simulation the shape and the size of ionic agglomerates are changing continually and very quickly. It would be therefore untenable to postulate the existence of definite isolated species such as LiCl, Li_2Cl^+ and $LiCl_2^-$ for an extended time.

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