Self-Exchange Velocities in Molten (Li, Na, K)Cl of the Eutectic Composition Reflecting the Chemla Effect for the Internal Mobilities

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Molecular dynamics (MD) simulation has been performed on molten (Li, Na, K)Cl of nearly the eutectic composition at 773 K, 873 K and 973 K. The employed pair potential parameters are based on the Tosi-Fumi ones except the softness parameter, which is somewhat modified. The self-exchange velocities (SEV's) of Li^+, Na^+ and K^+ with reference to Cl^- have been calculated. The sequence of the internal mobilities of these cations is well reproduced by the corresponding SEV's, v; that is $v_{Li} < v_K < v_{Na}$ at 773 K, $v_{Li} < v_{Na} \cong v_K$ at 873 K and $v_{Li} < v_{Na} < v_K$ at 973 K.

Introduction

After having shown by molecular dynamics (MD) simulation that in molten (Li, Rb)Cl [1] and (Li, K)Cl [2, 3] the cation with the greater internal mobility has the greater cation-anion self-exchange velocity (SEV), in the present paper it was to be shown if this correlation also holds in case of molten (Li, Na, K)Cl of the eutectic composition (53.5–8.6–37.9 mol%[4]), where the order of the mobilities, b, is temperature-dependent [5]:

$$b_{Li} < b_K < b_{Na} \quad \text{below ca. 873 K,} \qquad (1a)$$

$$b_{Li} < b_{Na} \cong b_K \quad \text{at ca. 873 K,} \qquad (1b)$$

$$b_{Li} < b_{Na} < b_K \quad \text{above ca. 873 K.} \qquad (1c)$$

We have previously performed structural analyses of the present system at 625 K by a combination of X-ray diffraction and MD simulation [6], and by neutron diffraction [7].

Molecular Dynamics Simulation

432 particles were disposed in a periodic cube whose edge length L was determined from the molar volume calculated from those of the pure melts on the assumption of additivity. This assumption is justified since the excess molar volumes on mixing two alkali chlorides are very small [8]. There were 115 Li^+, 19 Na^+, 82 K^+ and 216 Cl^- particles in the basic cell, which corresponds to a mixture of 53.2 mol% LiCl, 8.8 mol% NaCl, and 38.0 mol% KCl.

Pair potentials of the Born-Mayer-Huggins type were used:

$$u_{ij}(r) = z_i z_j e^2/4\pi\varepsilon_0 r + A_{ij}\, b \exp[(\sigma_i + \sigma_j - r)/\varrho] - c_{ij}/r^6 - d_{ij}/r^8, \qquad (2)$$

where z is the positive or negative charge number, e the elementary charge, ε_0 the permittivity of vacuum, and A the Pauling factor. For pure alkali halide crystals of the NaCl-type, values of b, σ and ϱ have been given by Tosi and Fumi [9], and values of c and d by Mayer [10]. The corresponding parameters for the mixture were determined by the combination rule presented by Larsen et al. [11]. Since the parameters given by Tosi and Fumi yield shorter distances by 10–30 pm for the first peak position of the cation-anion pair correlation functions in melts [12, 13], a modification factor 0.92 has been multiplied to the softness parameter ϱ, as was done previously in studies [2, 6]. The employed parameters are given in Table 1.

The Ewald method [14] was used for the calculation of the Coulomb forces; the cutoff distance in real space was $L/2$, and the reciprocal lattice vectors $|\boldsymbol{n}|^2$ were counted up to 27. The convergence parameter α was $5.6/L$ and time step 4 fs.

At the beginning, MD runs were performed with the constant temperature method proposed by Woodcock [15] and somewhat modified by us [16]. After constant temperature runs of several thousand steps, these were switched to constant energy runs. From the runs dur-

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Table 1. Parameters for the pair potentials.

Ion pair	A_{ij}	$\frac{c_{ij}}{10^{-79}\ \mathrm{J\ m^6}}$	$\frac{d_{ij}}{10^{-99}\ \mathrm{J\ m^8}}$
Li–Li	2.000	0.073	0.030
Li–Na	1.625	0.341	0.151
Li–K	1.625	1.220	0.853
Na–Na	1.250	1.680	0.800
Na–K	1.250	6.270	4.590
K–K	1.250	24.3	24.0
Li–Cl	1.375	2.0	2.4
Na–Cl	1.000	11.2	13.9
K–Cl	1.000	48.0	73.0
Cl–Cl	0.750	116.5	234.0

$b = 0.338 \times 10^{-19}$ J, $\sigma_{\mathrm{Li}} = 81.6$ pm, $\sigma_{\mathrm{Na}} = 117.0$ ppm,
$\sigma_{\mathrm{K}} = 146.3$ pm, $\sigma_{\mathrm{Cl}} = 158.5$ pm, $\varrho = 31.1$ pm.

Table 2. Some conditions and the results of the MD simulations. Temperatures in parentheses are the aimed values.

Edge length pm	Temperature K	Pressure MPa	Potential energy kJ mol^{-1}
2310	764 (773)	240	−750.4
2334	869 (873)	230	−745.5
2359	980 (973)	230	−740.9

ing more than 5000 time steps after attainment of equilibrium, the structure and other properties were obtained.

Some conditions of the MD simulations and calculated thermodynamic properties are given in Table 2.

Results and Discussion

Pair Correlation Functions

Some data of the obtained pair correlation functions $g_{\mathrm{Li-Cl}}(r)$, $g_{\mathrm{Na-Cl}}(r)$, $g_{\mathrm{K-Cl}}(r)$ and $g_{\mathrm{Cl-Cl}}(r)$ are given in Table 3. The R_{M}'s for unlike ion pairs are nearly independent of temperature, while R_{M} for the Cl–Cl pair increases with temperature, as is expected.

The previous neutron diffraction study of the present system at 625 K has revealed that the first peak of the Li–Cl radial distribution function is located at 240 pm [7], which is longer than the 231 pm also obtained by MD simulation without the modification factor but the same pair potentials as used in the present study [6]. This suggests that the use of a common softness parameter for all the pairs is not appropriate; however, this will not lead to any essential change in the following discussion.

Table 3. Characteristic values of the $g_{ij}(r)$'s for cation-anion and anion-anion pairs. R_1 and R_2 are the distances where $g_{ij}(r)$ crosses unity for the first and second time, respectively. R_{M} and R_{m} are the distances at the first maximum and minimum, respectively. $n_{\mathrm{eq}}(R_2)$ is the partial equivalent coordination number within R_2 of a cation, which is equal to the coordination number of $\mathrm{Cl^-}$ around the cation.

Pair		T/K			
		625	773	873	973
Li–Cl	R_1/pm	204	202	201	199
	R_{M}/pm	231	229	299	229
	$g(\mathrm{R_M})$	5.82	5.76	5.53	5.34
	R_2/pm	283	284	286	288
	$n_{\mathrm{eq}}(R_2)$	3.77	3.54	3.44	3.39
	R_{m}/pm	350	350	360	360
Na–Cl	R_1/pm	240	237	236	234
	R_{M}/pm	268	267	266	266
	$g(R_{\mathrm{M}})$	4.50	4.27	4.05	3.84
	R_2/pm	326	328	330	331
	$n_{\mathrm{eq}}(R_2)$	4.59	4.23	4.09	3.95
	R_{m}/pm	390	400	410	420
K–Cl	R_1/pm	277	276	274	272
	R_{M}/pm	307	305	305	305
	$g(R_{\mathrm{M}})$	3.72	3.38	3.24	3.09
	R_2/pm	369	373	375	375
	$n_{\mathrm{eq}}(R_2)$	5.63	5.08	4.95	4.71
	R_{m}/pm	440	440	450	450
Cl–Cl	R_1/pm	333	337	337	337
	R_{M}/pm	375	381	385	389
	$g(R_{\mathrm{M}})$	2.34	2.17	2.07	1.97
	R_2/pm	451	467	473	475
	R_{m}/pm	530	540	550	550

Coordination Numbers

Percentages of the partial equivalent coordination numbers $(n_{\mathrm{eq}})_i$ of the cations around a $\mathrm{Cl^-}$ ion at different temperatures are given in Table 4. R_2 is taken as the radius of the coordination sphere and may be regarded as the end of the nearest neighbour interaction [17]. For $\mathrm{Na^+}$, the statistical errors may be greater owing to the small number of $\mathrm{Na^+}$ ions. For $\mathrm{Li^+}$, the most probable partial equivalent coordination number changes from 4 to 3 with an increase in temperature from 773 K to 973 K. On the other hand, for $\mathrm{Na^+}$ and $\mathrm{K^+}$, the second probable partial equivalent coordination numbers change from 5 to 3 and from 6 to 4, respectively. The distribution of the partial coordination numbers becomes less sensitive to temperature in going from $\mathrm{Li^+}$ to $\mathrm{K^+}$.

Table 4. Percentages, $(\%)_i$, of the partial equivalent coordination numbers $(n_{\mathrm{eq}})_i = i$, at different temperatures. $10^{-2} \sum_i (\%)_i (n_{\mathrm{eq}})_i = n_{\mathrm{eq}} = n/x_{\mathrm{salt}}$, where n is the coordination number of the cation around a Cl^- and x_{salt} the mole fraction of the salt.

	$(n_{\mathrm{eq}})_i$	T/K			
		625	773	873	973
Li^+	1	0.01	0.07	0.10	0.17
	2	1.85	4.09	5.70	7.17
	3	27.20	41.13	47.05	49.66
	4	65.25	53.02	45.63	41.60
	5	5.63	1.67	1.51	1.39
	6	0.06	0.02	0.01	0.01
Na^+	1	0	0.03	0.01	0.09
	2	0.27	1.07	1.56	3.00
	3	6.06	14.77	19.55	24.66
	4	40.63	50.10	51.46	50.17
	5	43.92	30.72	25.01	20.56
	6	9.09	3.27	2.39	1.49
	7	0.13	0.04	0.02	0.03
K^+	1	0	0.01	0.01	0.01
	2	0.02	0.22	0.45	0.82
	3	0.95	3.99	5.63	8.76
	4	9.12	22.77	26.10	32.45
	5	34.34	41.79	41.45	39.16
	6	41.05	26.37	22.39	16.70
	7	13.58	4.58	3.78	2.01
	8	0.93	0.27	0.19	0.09
	9	0.01	0	0	0

Table 5. Self-exchange velocities and internal mobilities.

T/K	v (m s^{-1})			b [5] (10^{-8} m^2 V^{-1} s^{-1})		
	Li–Cl	Na–Cl	K–Cl	Li–Cl	Na–Cl	K–Cl
625	8.1	8.1	6.9	–	–	–
773	30.5	37.4	35.8	6.20	7.05	6.93
873	46.8	56.3	56.8	8.41	9.64	9.64
973	67.1	77.4	82.4	10.92	12.43	12.82

Angular Correlation Functions

The angular correlation functions

$$P_{-+-}(\cos\theta) = -C\, \mathrm{d}n(\cos\theta)/\mathrm{d}(\cos\theta) \tag{3}$$

have been calculated, where C is the normalization factor chosen so that

$$\int_{-1}^{1} P_{-+-}(\cos\theta)\, \mathrm{d}(\cos\theta) = 1,$$

and $\mathrm{d}n(\cos\theta)$ is taken here as the number of Cl^- around a cation within R_2 between $\cos(\theta - \Delta\theta/2)$ and $\cos(\theta + \Delta\theta/2)$ ($\Delta\theta = 1°$).

$P_{-+-}(\cos\theta)$'s are shown for + = Li, Na, and K in Figs. 1 a, 1 b, and 1 c, respectively. For all $P_{-+-}(\cos\theta)$'s, the peak positions are nearly independent of temperature, and much the same as that derived in a previous investigation at 625 K [6]. The peak heights decrease with increasing temperature. The trend is most distinct for ∢ Cl–Li–Cl. It is interesting to note that for ∢ Cl–Li–Cl the peak height at 625 K is between those at 773 K and 873 K, whereas for ∢ Cl–Na–Cl and ∢ Cl–K–Cl the peak heights monotonically decrease with increasing temperature.

As seen from Table 4, percentages of $(n_{\mathrm{eq}})_5$ for Li^+ are not negligible at 625 K owing to the high density. At higher temperature such as 773 K, nearly regular-tetrahedral coordination around a Li^+ prevails, and thereby the peak around 102° becomes higher. With further increasing temperature Li^+'s with $(n_{\mathrm{eq}})_3$ become more abundant, and therefore the peak height around 102° decreases.

For Na^+ the peaks are located around 90° and 180°. This suggests that the Cl^-'s around a Na^+ are arranged nearly in the NaCl-type even if $(n_{\mathrm{eq}})_i < 6$.

As for K^+, the interaction with Cl^- is weakest among the three cations. Almost all Cl^-'s are coordinated by at last one Li^+, since the mole fraction of Li^+ is 0.53, and therefore the adjacent structure of Cl^- is fixed mainly by Li^+'s; the probable structure around K^+ is shown in Fig. 8 of [6]. Since K^+ is relatively large, the angular distribution around K^+ is rather insensitive to a change in density and hence in temperature.

Self-Exchange Velocities

The separating motion of cation-anion pair can be expressed in terms of the self-exchange velocity, v, whose definition is given in previous papers [1, 3].

The SEV's calculated in the present study are given in Table 5. Those at 625 K are not so accurate as the others. The orders of the v's are

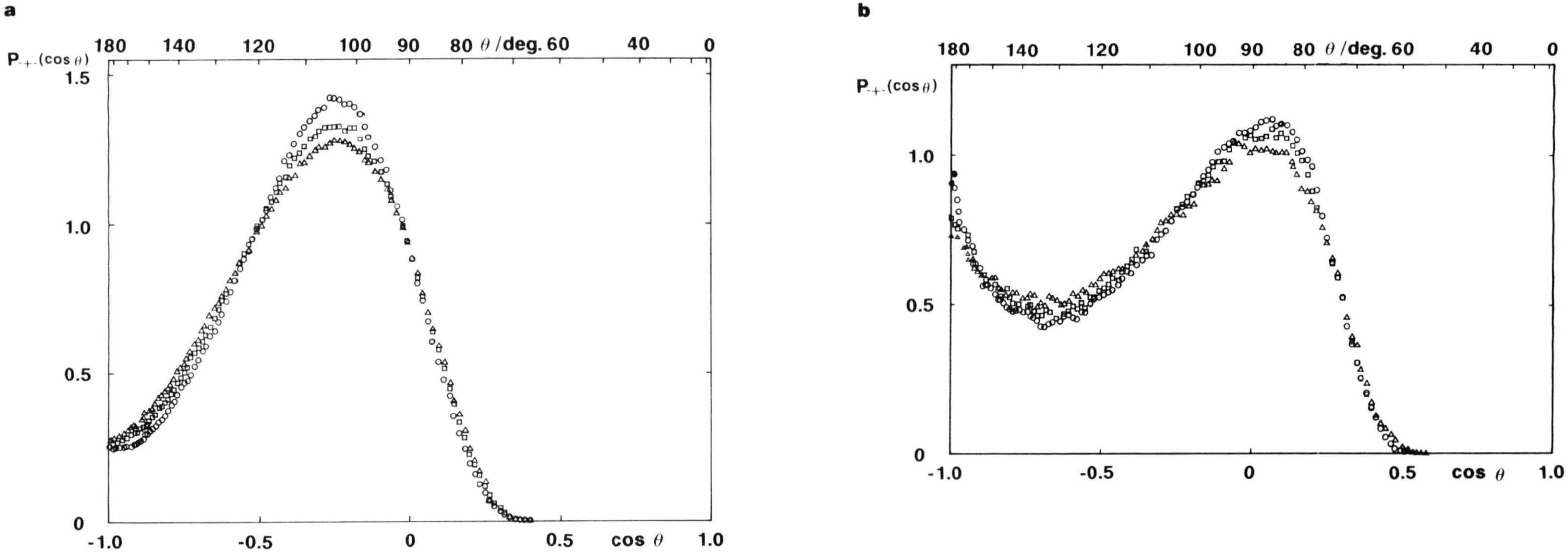
$$v_{\mathrm{Li}} < v_{\mathrm{K}} < v_{\mathrm{Na}} \quad \text{at 773 K,} \tag{4a}$$

$$v_{\mathrm{Li}} < v_{\mathrm{Na}} \cong v_{\mathrm{K}} \quad \text{at 873 K,} \tag{4b}$$

$$v_{\mathrm{Li}} < v_{\mathrm{Na}} < v_{\mathrm{K}} \quad \text{at 973 K.} \tag{4c}$$

These orders are in good agreement with those for the internal mobilities obtained experimentally [cf. (1)]; the excellent agreement at 873 K of (1 b) with (4 b) may be fortuitous.

The strong correlation between internal mobilities and SEV's for some alkali chlorides is shown in Fig-



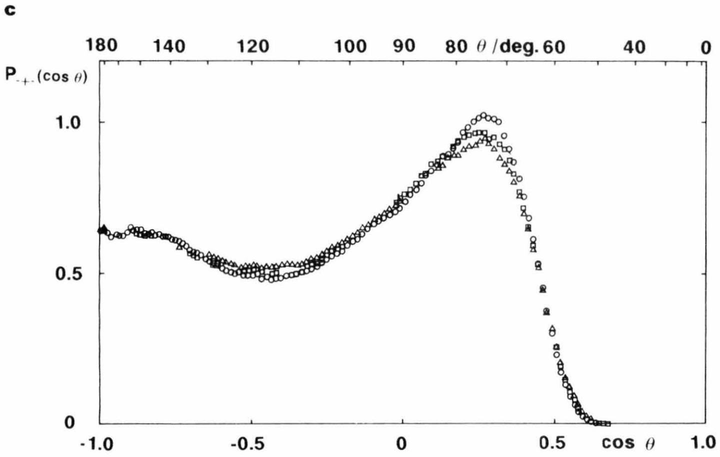


Fig. 1. Angular correlation functions $P_{-+-}(\cos\theta)$ for (a) ∡Cl–Li–Cl, (b) ∡Cl–Na–Cl, and (c) ∡Cl–K–Cl. ○: 773 K, □: 873 K, △: 973 K.

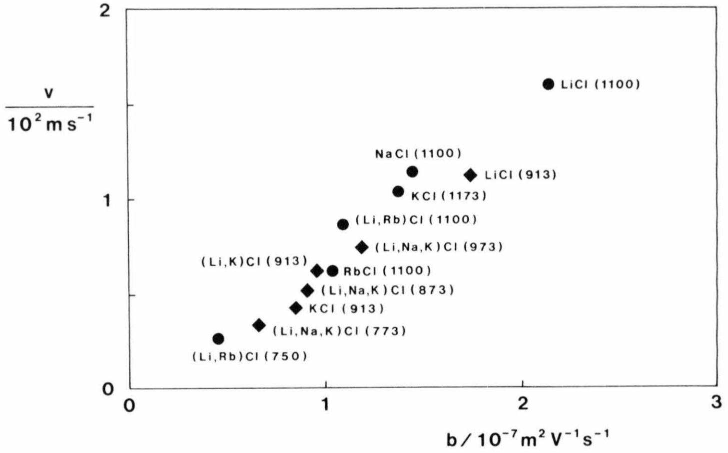


Fig. 2. Relationship between SEV (v) and internal mobility (b). For the mixtures, points corresponding to the average value of v and b of the constituent cations are plotted. The values in parentheses refer to temperature in K. The SEV's are taken from the following references: LiCl (1100) [1], LiCl (913) [2], NaCl [18], KCl (913) [2], KCl (1173) [19], RbCl [1], (Li, K)Cl [2] and (Li, Rb)Cl [1]. ●: The Tosi-Fumi potentials, ◆: the modified ones.

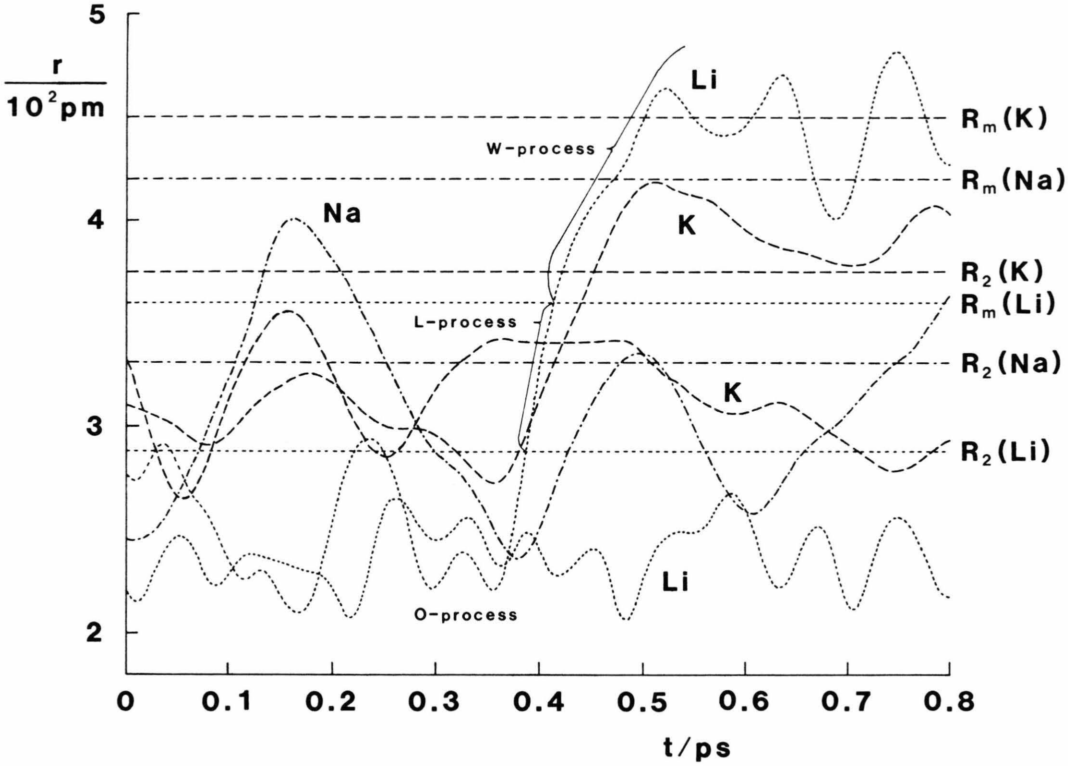


Fig. 3. Examples of the time evolution of distances of cations located within the respective R_2's from an arbitrarily chosen Cl^- ion at $t = 0$. The O-, L-, and W-processes are defined as shown, as an example, for the motion of a Li^+–Cl^- pair. The distances corresponding to the R_2's and R_m's are marked.

ure 2. We have previously found this correlation between internal mobilities and SEV's calculated by using the Tosi-Fumi potentials [1, 3]. The present SEV's calculated with the modified potentials are somewhat smaller without impairing the correlation. A similar trend is observed for molten LiCl, KCl and (Li, K)Cl of the eutectic composition [2], as seen from Figure 2.

The relative differences in the SEV's,

$$\varepsilon_{\alpha\beta} = (v_\alpha - v_\beta)/(x_{Li}\, v_{Li} + x_{Na}\, v_{Na} + x_K\, v_K)$$

are compared with those in the corresponding mobilities in Table 6; the suffixes α and β refer to two ions among Li^+, Na^+ and K^+, and x is the mole fraction.

The absolute values of ε for the SEV's are larger than those for the internal mobilities. The agreement is satisfactory in view of the fact that the ε values are very sensitive to the internal mobilities or the SEV's.

In [5] we have already explained relations (4) in terms of the potential profiles felt by these cations located collinearly between two Cl^- ions. In brief, temperature variation leads to a change in the number density of the common anion, which in turn causes a change in the potential felt by these cations located between two Cl^- ions; even this apparently small change in the potentials is considerable compared with the magnitude of the kinetic energy. This is the reason why the SEV's of Na^+ and K^+ are reversed at a certain temperature (around 873 K).

Table 6. Relative differences in the self-exchange velocities. Values in parentheses are the correspondig values of the internal mobilities.

T/K	ε_{LiNa}	ε_{NaK}	ε_{LiK}
773	−0.21 (−0.13)	0.05 (0.02)	−0.16 (−0.11)
873	−0.18 (−0.14)	−0.01 (0.00)	−0.19 (−0.14)
973	−0.14 (−0.13)	−0.07 (−0.03)	−0.21 (−0.16)

Motion of Cations Around Cl^- Ion

The time evolution of distances of cations located within the respective R_2's at $t=0$ from an arbitrarily chosen Cl^- ion at 973 K is shown in Figure 3. Fig-

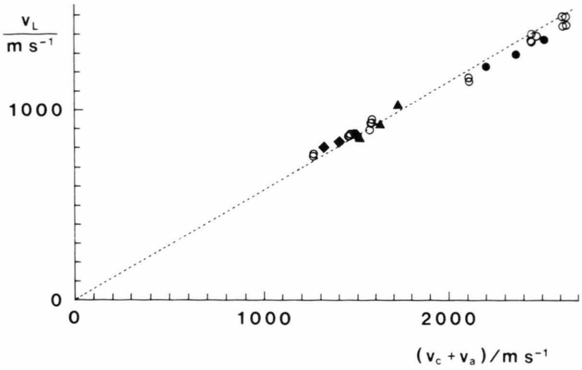


Fig. 4. Relationship between v_L and (v_c+v_a). The dotted line is drawn according to $v_L=0.577\ (v_c+v_a)$. ●: Li, ▲: Na, ◆: K, ○: Li or K under various conditions of masses, concentrations and temperatures [3]. v_c and v_a are the thermal velocity of gaslike cations and anions, respectively.

Table 7. The velocities of the separating motion of unlike ion pairs in the L-process.

T/K	Li–Cl m s⁻¹	Na–Cl m s⁻¹	K–Cl m s⁻¹
773	1221 ± 28	856 ± 26	800 ± 18
873	1294 ± 27	915 ± 25	831 ± 16
973	1369 ± 26	1020 ± 26	874 ± 16

ure 3 reveals that Li^+ ions are oscillating with more frequent cycles than Na^+ and K^+ ions; this is attributable to the light mass.

The motion of cations with respect to the neighbouring anions may be classified into four modes: oscillating (O-process), leaving (L-process), wandering (W-process) and coming back (C-process) [3]. We have previously found the following empirical relation for the velocity v_L of the separating motion during the L-process [3]:

$$v_L = (0.577 \pm 0.005)\,(v_c + v_a), \tag{5}$$

where v_c and v_a are the average velocities of the ideal gas-like cations and anions, respectively, i.e.,

$$v_c = \sqrt{8RT/\pi M_c} \quad \text{and} \quad v_a = \sqrt{8RT/\pi M_a}$$

(M_c and M_a are the molar masses of the cations and anions, respectively). The velocities v_L are given in Table 7, and the relationship between v_L and (v_c+v_a) is shown in Figure 4. The calculated v_L's and (v_c+v_a) obey much the same relationship as the previous study [3], although the softness parameter of the present pair potential is different from that in the previous study. This certifies that v_L is expressed by (5) independently of the used potentials.

Thus, the v_L's of these cations may be, independently of temperature, concentration and density, in the order

$$v_L(\mathrm{K{-}Cl}) < v_L(\mathrm{Na{-}Cl}) < v_L(\mathrm{Li{-}Cl}). \tag{6}$$

This sequence is quite different from those in (4). Thus, the duration of the O-process, i.e. the frequency of the L-process plays a dominant role for the SEV.

In conclusions, the SEV's of Li^+, Na^+ and K^+ in (Li, Na, K)Cl of the eutectic composition well reflect the Chemla effect in the internal mobilities experimentally obtained for these cations. That is, the sequences $b_{Li} < b_K < b_{Na}$ below 873 K and $b_{Li} < b_{Na} < b_K$ above 873 K are well reproduced by the corresponding SEV's.

The MD simulations were performed with the HITAC M-680 H computers at the Institute for Molecular Science (Okazaki) and the National Laboratory for High Energ Physics (Tsukuba). The computer time made available for this work is gratefully acknowledged.

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