# A Molecular Dynamics Simulation of the Molten Ternary System (Li, K, Cs)Cl

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The self-exchange velocity (SEV) of neighboring unlike ions, has been evaluated by molecular dynamics simulations of molten CsCl, (Li, K)Cl and (Li, K, Cs)Cl at 673 K. From the increase of the SEV's in the same order as the internal mobilities it is conjectured that there is a strong correlation between these two properties. The pair correlation functions, and the self-diffusion coefficients and the SEV's of $Li^+$, $K^+$, and $Cs^+$ with reference to $Cl^-$ have also been calculated. The results allow to conclude that the self-exchange velocity of the cations become $v_{Cs} < v_K < v_{Li}$ at $x_{Cs}$ =0.1 and $v_{Li} < v_K < v_{Cs}$ at $x_{Cs} > 0.4$. The sequence of the self-diffusion coefficients agrees with that of the SEV's. The results enable to conclude that it is possible to enrich Cs at up to $x_{Cs} \approx 0.3$ - 0.4 in the molten LiCl-KCl eutectic system.

*Key words:* Chemla Effect; Internal Cation Mobility; Molten Ternary System; Molecular Dynamics Simulation; Self-exchange Velocity; Self-Diffusion Coefficient.

## 1. Introduction

Chemla discovered that in the molten binary system (Li, K)Br the mobilities of the cations become equal at a certain composition and temperature [1]. Further investigations have shown that the difference in the mobilities of cations in such charge-symmetric binary systems may change sign on a change in temperature and/or concentration [2, 3]. This Chemla effect in binary molten alkali binary chloride mixtures [4 - 10] has been qualitatively interpreted in terms of quasi-complexes [2, 3, 5 - 9] or polarized anions [8]. However, few papers dealt with ternary molten alkali chloride systems [9, 10]. We have recently measured the electric conductivity and internal cation mobilities of molten (Na, K, Cs)Cl [11]. We have also calculated the self-exchange velocities, self-diffusion coefficients and electric conductivity of this system by MD simulation [12]. In order to interpret the Chemla effect from another point of view, in the present work we have performed molecular dynamics simulations of CsCl, (Li, K)Cl and (Li, K, Cs)Cl.

These systems are of interest in nuclear energy technology because of the possibility to enrich Cs in LiCl-KCl eutectic mixtures [13]. The enrichment of Cs in LiCl-KCl eutectic melts by countercurrent electromigration is limited by the Chemla crossing point. In order to apply the electromigration method in a practical plant for nuclear waste treatment we have arranged the column so as to recover concentrated fission products like Cs continuously [11]. On the other hand, for this purpose we have performed an electrochemical investigation of the alloy formation mechanism of electrochemically negative elements ($Eu^{2+}$ [14, 15], $Sr^{2+}$ [14, 15], $Ba^{2+}$ [16, 17], and $Cs^+$ [18]) in molten chloride and fluoride systems by means of transitory techniques, i. e., voltammetry, chronopotentiometry and electrochemical impedance spectroscopy. We also suggested a recovery system combining the electromigration and electrowinning methods [19].

## 2. The Molecular Dynamics Simulation

For the MD simulation of this ternary alkali chloride system, 1000 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

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Table 1-1. The parameters used in the calculation for pure salt and binary systems.

| System (Li:K:Cs) | Ion Pair | $\rho$/nm | $c_{ij}/10^{-79}$J·m$^6$ | $d_{ij}/10^{-99}$J·m$^8$ |
|---|---|---|---|---|
| (0:0:100) | Cs-Cs | 0.334 | 152.0 | 278.0 |
| | Cs-Cl | | 129.0 | 250.0 |
| | Cl-Cl | | 129.0 | 260.0 |
| (60:40:0) | Li-Li | 0.340 | 0.073 | 0.03 |
| | Li-K | | 1.216 | 0.850 |
| | Li-Cl | | 1.984 | 2.4 |
| | K-K | | 24.3 | 24.0 |
| | K-Cl | | 47.143 | 70.624 |
| | Cl-Cl | | 116.429 | 233.859 |

two alkali chlorides are very small [20]. Pair potentials of the Born-Mayer-Huggins type were used:

$$\Phi_{ij} = \frac{z_i z_j e^2}{4\pi\varepsilon_0 r} + A_{ij} b \exp\left[(\sigma_i + \sigma_j - r)/\rho\right] \quad (1)$$
$$- \frac{c_{ij}}{r^6} - \frac{d_{ij}}{r^8},$$

$$A_{ij} = 1 + \frac{z_i}{n_i} + \frac{z_j}{n_j}, \quad (2)$$

where $z$ is the positive or negative charge number, $e$ the elementary charge, $\varepsilon_0$ the permittivity of vacuum and $A$ the Pauling factor. The first term in (1) represents the Coulomb interaction, the second the Born-Huggins exponential repulsion with parameters obtained by Tosi and Fumi [21], and the third and fourth terms represent the dipole-dipole and dipole-quadrupole dispersion energies with parameters obtained by Mayer [22]. The corresponding parameters for the mixture were determined by the combination rule presented by Larsen et al. [23]. Some data of the adopted values of $A$, $b$, $\rho$, $r$, $c$, and $d$ are listed in Tables 1-1 and 1-2. The Ewald method [24] was used for the calculation of the Coulomb forces; the cutoff distance in real space was $L/2$, and the reciprocal lattice vectors $|n^2|$ were counted up to 27. The convergence parameter $\alpha$ was $5.6/L$ and the time step 5fs. At the beginning, MD runs were performed with the constant temperature method proposed by Woodcock [25]. After constant temperature runs of several thousand steps, these were switched to constant energy runs. From the runs during more than $10^4$ time steps, using Verlet's Algorithm, after attainment of equilibrium the structure and the other properties were obtained.

Table 1-2. The parameters used in the calculation for molten alkali ternary systems.

| System (Li:K:Cs) | Ion Pair | $\rho$/nm | $c_{ij}/10^{-79}$J·m$^6$ | $d_{ij}/10^{-99}$J·m$^8$ |
|---|---|---|---|---|
| (54:36:10) | Li-Li | 0.3394 | 0.073 | 0.03 |
| | Li-K | | 1.216 | 0.850 |
| | Li-Cs | | 2.837 | 3.177 |
| | Li-Cl | | 1.994 | 2.413 |
| | K-K | | 24.3 | 24.0 |
| | K-Cs | | 60.107 | 84.648 |
| | K-Cl | | 47.385 | 71.003 |
| | Cs-Cs | | 152.0 | 278.0 |
| | Cs-Cl | | 125.831 | 241.476 |
| | Cl-Cl | | 117.666 | 236.425 |
| (48:32:20) | Li-Cl | 0.3388 | 2.004 | 2.426 |
| | K-Cl | | 47.626 | 71.382 |
| | Cs-Cl | | 126.478 | 242.760 |
| | Cl-Cl | | 118.903 | 238.991 |
| (42:28:30) | Li-Cl | 0.3382 | 2.014 | 2.439 |
| | K-Cl | | 47.868 | 71.760 |
| | Cs-Cl | | 127.124 | 244.044 |
| | Cl-Cl | | 120.145 | 241.570 |
| (36:24:40) | Li-Cl | 0.3376 | 2.024 | 2.452 |
| | K-Cl | | 48.109 | 72.138 |
| | Cs-Cl | | 127.770 | 245.327 |
| | Cl-Cl | | 121.393 | 244.163 |
| (30:20:50) | Li-Cl | 0.3370 | 2.034 | 2.465 |
| | K-Cl | | 48.350 | 72.516 |
| | Cs-Cl | | 128.415 | 246.609 |
| | Cl-Cl | | 122.647 | 246.768 |
| (24:16:60) | Li-Cl | 0.3364 | 2.044 | 2.477 |
| | K-Cl | | 48.591 | 72.894 |
| | Cs-Cl | | 129.060 | 247.891 |
| | Cl-Cl | | 123.907 | 249.386 |
| (18:12:70) | Li-Cl | 0.3358 | 2.054 | 2.490 |
| | K-Cl | | 48.832 | 73.272 |
| | Cs-Cl | | 129.704 | 249.171 |
| | Cl-Cl | | 125.172 | 252.017 |
| (12:8:80) | Li-Cl | 0.3352 | 2.064 | 2.503 |
| | K-Cl | | 49.072 | 73.649 |
| | Cs-Cl | | 130.347 | 250.452 |
| | Cl-Cl | | 126.443 | 254.661 |
| (6:4:90) | Li-Cl | 0.3346 | 2.074 | 2.516 |
| | K-Cl | | 49.313 | 74.026 |
| | Cs-Cl | | 130.990 | 251.731 |
| | Cl-Cl | | 127.719 | 257.319 |

## 3. Results and Discussion

The pair correlation functions for increasing content of Cs of this ternary system are shown in Figure 1. Some characteristic properties of pair correlation functions and running coordination numbers are summarized in Table 2. A comparison of the pair correlation functions of pure CsCl and (Li, K)Cl with

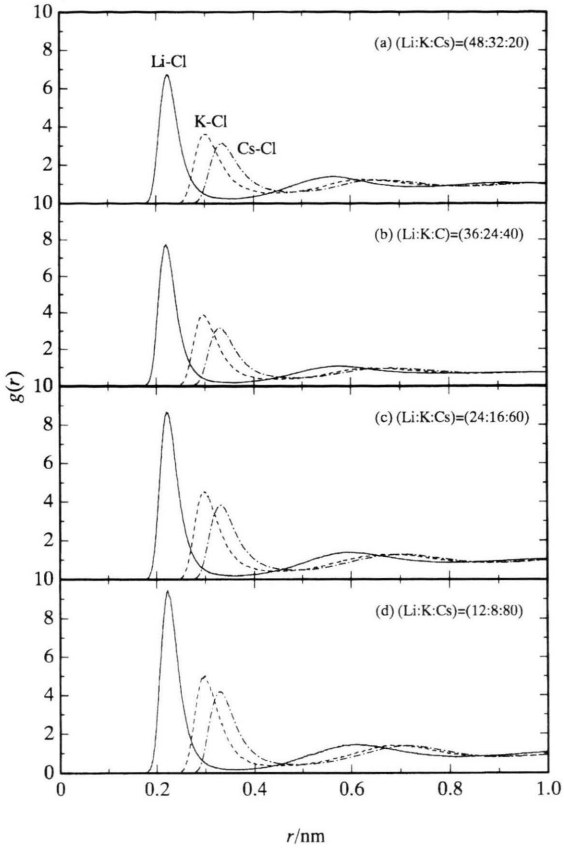


Fig. 1. Pair correlation functions of the molten ternary system (Li, K, Cs)Cl, —: $g_{\mathrm{Li-Cl}}$, - - -: $g_{\mathrm{K-Cl}}$, - · -: $g_{\mathrm{Cs-Cl}}$.

the ternary mixtures for various compositions shows that the positions of the first peaks of the pair correlation functions $g_{\mathrm{Li-Cl}}$, $g_{\mathrm{K-Cl}}$, and $g_{\mathrm{Cs-Cl}}$ are much the same in the binary mixtures and the pure salts. As for the peak heights, $g_{\mathrm{Li-Cl}}$ and $g_{\mathrm{K-Cl}}$ are more sharply peaked in the ternary mixture than in the binary mixtures. $g_{\mathrm{Cs-Cl}}$ is less sharply peaked in the ternary mixtures than in the pure CsCl salt. The increasing rate of the peak heights for Li and K is larger than for Cs. The position of the second peak of $g_{+-}$ is more distant for LiCl and KCl, and less distant for CsCl in the ternary mixture than in the respective binary and pure salts.

The separating motion of a cation-anion pair can be expressed in terms of the self-exchange velocity (SEV), which can be calculated from a molecular dynamics simulation. The evolution of the average distance of marked cations from a $Cl^-$ ion for each composition is shown in Figure 2. The SEV is defined

Table 2. Characteristic values of the pair correlation functions $g_{ij}(r)$ 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. $R_{\mathrm{M}}$ and $R_{\mathrm{m}}$ are the distances at the first maximum and minimum, respectively. $n_{\mathrm{eq}}(R_2 - R_{\mathrm{m}})$ is the partial equivalent coordination number within $R_2 - R_{\mathrm{m}}$ of a cation, which is equal to the coordination number of $Cl^-$ around the cation.

| System (Li:K:Cs) | Ion Pair | $R_1$ /nm | $R_{\mathrm{M}}$ /nm | $g(R)_{\mathrm{M}}$ | $R_2$ /nm | $R_{\mathrm{m}}$ /nm | $n_{\mathrm{eq}}$ $(R_2 - R_{\mathrm{m}})$ |
|---|---|---|---|---|---|---|---|
| (60:40:0) | Li-Cl | 0.196 | 0.224 | 5.45 | 0.277 | 0.348 | 3.36 – 4.09 |
| | K-Cl | 0.270 | 0.303 | 3.18 | 0.367 | 0.446 | 4.86 – 6.91 |
| (48:32:20) | Li-Cl | 0.196 | 0.222 | 6.68 | 0.277 | 0.356 | 3.31 – 3.80 |
| | K-Cl | 0.269 | 0.301 | 3.57 | 0.366 | 0.450 | 4.28 – 6.07 |
| | Cs-Cl | 0.303 | 0.335 | 3.10 | 0.406 | 0.492 | 5.26 – 7.52 |
| (36:24:40) | Li-Cl | 0.193 | 0.219 | 7.71 | 0.274 | 0.360 | 3.08 – 3.47 |
| | K-Cl | 0.267 | 0.298 | 3.77 | 0.358 | 0.453 | 3.72 – 4.97 |
| | Cs-Cl | 0.298 | 0.332 | 3.13 | 0.392 | 0.495 | 4.11 – 5.99 |
| (24:16:60) | Li-Cl | 0.193 | 0.222 | 8.67 | 0.277 | 0.364 | 3.26 – 3.74 |
| | K-Cl | 0.267 | 0.301 | 4.42 | 0.369 | 0.450 | 4.29 – 5.42 |
| | Cs-Cl | 0.301 | 0.332 | 3.74 | 0.403 | 0.495 | 4.83 – 6.50 |
| (12:8:80) | Li-Cl | 0.193 | 0.222 | 9.36 | 0.279 | 0.358 | 3.33 – 3.76 |
| | K-Cl | 0.264 | 0.298 | 4.97 | 0.364 | 0.450 | 4.25 – 5.17 |
| | Cs-Cl | 0.295 | 0.332 | 4.16 | 0.400 | 0.492 | 4.73 – 6.19 |
| (0:0:100) | Cs-Cl | 0.298 | 0.332 | 4.33 | 0.404 | 0.513 | 4.30 – 5.81 |

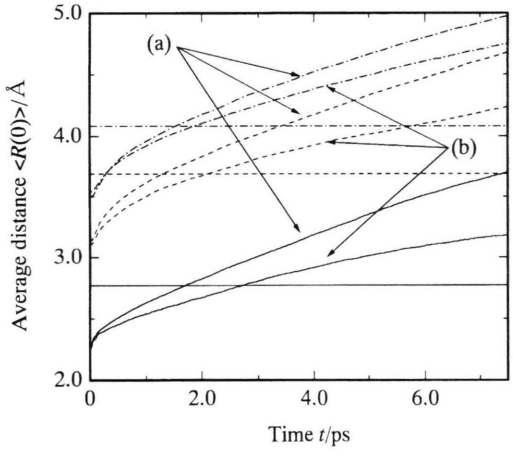


Fig. 2. Evolution of the average distance of marked cations from —: $Li^+$, - - -: $K^+$, - · -: $Cs^+$ to $Cl^-$, (a) $x_{\mathrm{Cs}} = 0.2$, (b) $x_{\mathrm{Cs}} = 0.6$.

by the equation

$$\nu = \frac{R_2 - \langle R(0) \rangle}{\tau}, \tag{3}$$

where the parentheses indicate ensemble averages. $R_2$ is the distance where the cation-anion correlation function crosses unity for the second time. $\langle R(0) \rangle$ is

Table 3. Relative differences of the self-exchange velocities at 673 K.

| $x_{Cs}$ | $\varepsilon_{LiK}$ | $\varepsilon_{LiCs}$ | $\varepsilon_{KCs}$ | $\varepsilon_{Cs,solv.}$* |
|---|---|---|---|---|
| 0 | 0.208 | — | — | — |
| 0.1 | 0.126 | 0.234 | 0.107 | –0.187 |
| 0.2 | –0.072 | 0.070 | 0.142 | –0.101 |
| 0.3 | –0.070 | 0.064 | 0.134 | –0.094 |
| 0.4 | –0.042 | –0.047 | –0.006 | 0.031 |
| 0.5 | –0.028 | –0.079 | –0.050 | 0.067 |
| 0.6 | –0.151 | –0.195 | –0.044 | 0.133 |
| 0.7 | –0.105 | –0.155 | –0.050 | 0.112 |
| 0.8 | –0.164 | –0.200 | –0.036 | 0.133 |
| 0.9 | –0.355 | –0.390 | –0.035 | 0.244 |

* the calculated values based on the quasi-binary system [11].

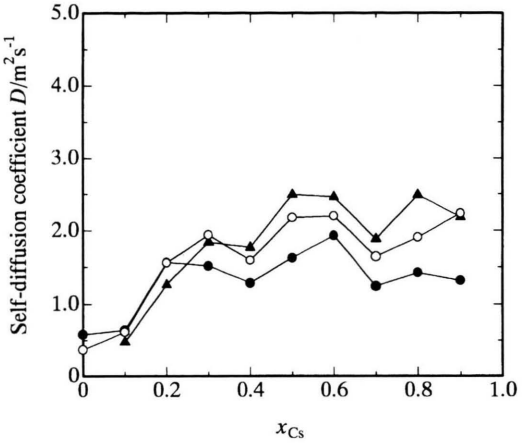


Fig. 3. Relationship between the self-diffusion coefficients and the mole fraction of Cs in molten LiCl-KCl eutectic melts at 673 K, •: $Li^+$, ○: $K^+$, ▲: $Cs^+$.

the average distance between cation and anion within $R_2$ at a given time origin. $\tau$ is the time in which the ion moves from $\langle R(0)\rangle$ to $R_2$. The solid, broken and chain lines are $R_2$ for Li, K and Cs, respectively. The each slope means the SEV for each cation. The orders of the $\nu$'s are as follows:

$$\begin{aligned} &\nu_{Cs} < \nu_K < \nu_{Li}\,(x_{Cs} = 0.10),\\ &\nu_{Cs} \approx \nu_{Li} < \nu_K\,(x_{Cs} = 0.20),\\ &\nu_{Cs} \approx \nu_{Li} \approx \nu_K\,(x_{Cs} = 0.30),\\ &\nu_{Li} < \nu_K < \nu_{Cs}\,(x_{Cs} > 0.40). \end{aligned} \tag{4}$$

The relative differences in the SEV's are calculated from the equation

$$\varepsilon_{\alpha\beta} = \frac{\nu_\alpha - \nu_\beta}{x_{Li}\nu_{Li} + x_K\nu_K} + x_{Cs}\nu_{Cs}. \tag{5}$$

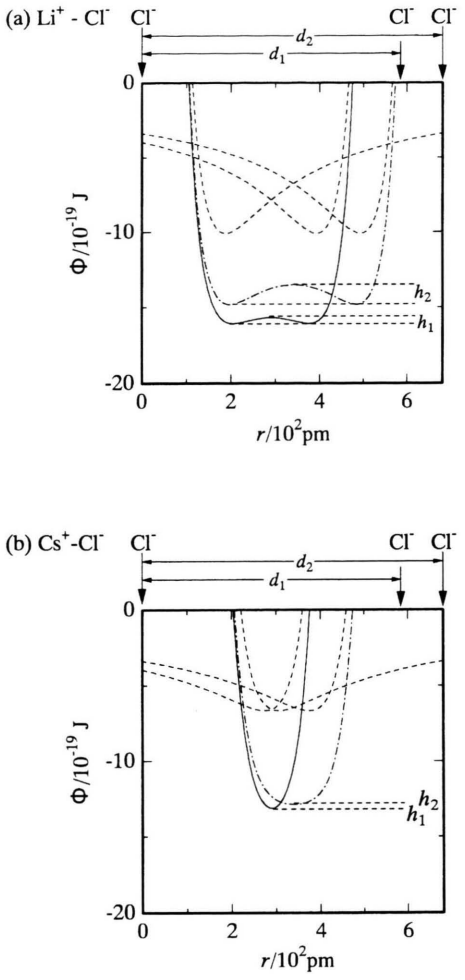


Fig. 4. Potential profiles felt by $Li^+$ and $Cs^+$ ions located near a single $Cl^-$ ion (upper curve of (a) and (b)) and located between two $Cl^-$ ions separated by a distance (a) $d_1$ = 580 pm and (b) $d_2$ = 680 pm (lower curves).

The suffixes $\alpha$ and $\beta$ refer to two ions among $Li^+$, $K^+$ and $Cs^+$, and $x$ is the mole fraction. The obtained relative differences at the corresponding mole fractions are tabulated in Table 3. The calculation of $\varepsilon_{Cs,solv.}$ in the quasi-binary system (Cs, Li-K)Cl, based on [11], allows to compare the results of the quasi-binary system (Cs, Na-K)Cl. This result enables us to conclude that it is more effective to recover concentrated Cs in LiCl-KCl eutectic melts than in NaCl-KCl equimolar mixtures [11].

The self-diffusion coefficients were calculated from the mean square displacements according to the Einstein equation as given in Figure 3. The results obtained with the simulation predict that in this ternary

mixture the order of the self-diffusion coefficients of the cations would be the following:

$$\begin{aligned} &D_{Cs} < D_K \approx D_{Li}\,(x_{Cs} = 0.1),\\ &D_{Cs} < D_{Li} \approx D_K\,(x_{Cs} = 0.2),\\ &D_{Li} < D_{Cs} < D_K\,(x_{Cs} = 0.3),\\ &D_{Li} < D_K < D_{Cs}\,(x_{Cs} > 0.4). \end{aligned} \tag{6}$$

This is consistent with observations on our calculated self-exchange velocities, where the Chemla effect is observed for pairs of Li-K, Li-Cs, and K-Cs.

It can be interpret by the potential for the cations located between two $Cl^-$ ions as presented in Figure 4. These potentials are estimated by combining the pair potentials for $Li^+$-$Cl^-$ (Fig. 4(a)) and $Cs^+$-$Cl^-$ (Fig. 4(b)). Let us consider a one-dimensional motion of the cations leaving the reference $Cl^-$ ion. As the mole fraction of $Cs^+$ increases, the molar volume and the average $Cl^-$-$Cl^-$ distance increases from $d_1$ to $d_2$. Figure 4 shows that the barrier from $h_1$ to $h_2$ becomes higher with increasing molar volume and its rate of increase is very rapid for the $Li^+$ ion. When $d$ is small, the $Cs^+$ ion can move away from the reference $Cl^-$ ion, since the two $Cl^-$ ions separate. At large $d$, the $Li^+$ ion has to wait for a longer time than the $Cs^+$ ion, and $h$ becomes so low that the cation can move away from the reference $Cl^-$ ion. In other words, the $Li^+$-$Cl^-$ pair is more associated and thus the SEV will decrease with increasing $d$, but the decreasing rate is larger for Li than for Cs. Thus, the SEV's of Li and Cs will have a crossing point and the isotherms of two internal mobilities have a Chemla crossing point.

## 4. Conclusion

We investigated the self-exchange velocities and self-diffusion coefficients in molten alkali chlorides from MD simulations. The order of the self-diffusion coefficients calculated from the MD simulation is consistent with the results of the self-exchange velocities in this ternary system. We found that it is more effective to recover concentrated Cs in LiCl-KCl eutectic melts than in NaCl-KCl equimolar mixtures, and that the maximal enrichment degree of Cs estimated from the calculated relative differences of the internal cation mobilities is $x_{Cs} \approx 0.3$ - 0.4 in LiCl-KCl melts.


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