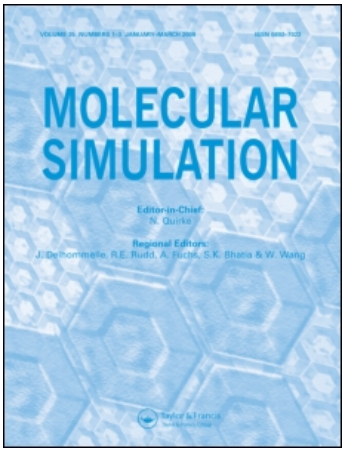

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S. Itoh[a]; T. Matsuzawa[a]; M. Konagai[b]; K. Takahashi[b]
[a] Department of Electronics and Information Sciences, The Nishi-Tokyo University, Yamanashi, Japan [b] Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, Tokyo, Japan

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MOLECULAR DYNAMICS SIMULATION OF A MOLTEN MIXTURE OF LITHIUM BROMIDE AND LITHIUM IODIDE

S. ITOH, T. MATSUZAWA, M. KONAGAI* and K. TAKAHASHI*

Department of Electronics and Information Sciences, The Nishi-Tokyo University Yassawa, Uenohara-chou, Kitatsuru-gun, Yamanashi 409-01, Japan
**Department of Electrical and Electronic Engineering, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152, Japan*

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Molecular dynamics simulation for a 1:5 molar mixture of lithium bromide and lithium iodide was carried out with Born-Mayer-Huggins type pair potential. The self-exchange velocity of the iodide ion is greater than that of the bromide ion although the iodide ion is heavier than the bromide ion. This "anion Chemla effect" is explained from the difference in the barrier height of the potential function which the bromide ion or the iodide ion feels from the lithium ion. The pair distribution functions, the angular correlation functions and the velocity autocorrelation functions are also examined.

KEY WORDS: Molecular dynamics, liquid structure, Chemla effect, molten salt, lithium bromide, lithium iodide

1. INTRODUCTION

In a molten salt mixture composed of two kinds of cations and common anions, the mobility of the larger cation is larger than that of the smaller cation at a certain temperature range. This phenomenon, called the "Chemla effect", has been found for various common anion binary systems [1]. On the other hand, "anion Chemla effect" is found only in several mixtures such as Ag(Cl, NO_3) [1] and Li(Cl, NO_3) [2]. In molten Na(F, Cl) and Na(F, Br), the anion Chemla effect has not been found in the examined range of mixing and temperature [3].

From the microscopic point of view, it is clarified that the internal mobility correlates strongly with the self-exchange velocity (SEV) of unlike ion pairs and the origin of the Chemla effect is mainly due to the difference in the coulombic forces between cation-anion pairs [4,5]. A molecular dynamics study of the anion Chemla effect has been reported for an equimolar molten Li(Cl, Br) mixture at 1000 K. It has been shown that the self-exchange velocity of the Br ion is larger than that of the Cl ion [6].

In this report MD simulation for a 1:5 molar mixture of Li(Br, I) at 1200 K was performed. The result shows that the self-exchange velocity of the I ion is larger than that of the Br ion, and the anion Chemla effect is expected to occur at this mixing ratio and temperature.

Table 1 The parameters employed in the MD simulations.

	Li–Li	*Li–Br*	*Li–I*	*Br–Br*	*Br–I*	*I–I*
A	2.00	1.375	1.375	0.75	0.75	0.75
$c/10^{-79}$ Jm^6	0.073	2.50	3.30	185.0	264.23	378.0
$d/10^{-99}$ Jm^8	0.030	3.30	5.30	423.0	672.55	1060.0

$A = 1 + \frac{Z_i}{n_i} + \frac{Z_j}{n_j}$, $b = 0.338 \times 10^{-19}$ J, $\rho = 41.72 \times 0.92 \times 10^{-8}$ m

$\sigma_{Li} = 81.6$ pm, $\sigma_{Br} = 171.6$ pm, $\sigma_I = 190.7$ pm

2. MOLECULAR DYNAMICS SIMULATION

216 Li^+, 36 Br^- and 180 I^- were placed in the periodic cube. The side length of the unit cell is so assumed that the molar volume of the molten salt mixture follows the additional rule of those molar volumes for the pure salts. In this case the side length L is taken to be 2578.88 pm. The pair potential adopted consisted of the coulombic term, the Born-type repulsive term and two Huggins-Mayer type of the reciprocal terms of the distance, for which the modified Tosi-Fumi parameters were used.

$$V_{ij}(r) = Z_i Z_j e^2/4\pi\varepsilon_0 r + (1 + Z_i/n_i + Z_j/n_j)b \exp[(\sigma_i + \sigma_j - r)/\rho] - c_{ij}/r^6 - d_{ij}/r^8$$

Here Z is an ionic charge number, e the elementary charge, ε_0 the permittivity of vacuum, n the number of the electrons in an outer shell, b a repulsion parameter, σ a value characteristic of an ion size and ρ a softness parameter. The parameter value of ρ was multiplied by 0.92 to the value decided by Tosi-Fumi [7], based on results obtained for the systems (Li, K)Cl [8] and (Li, Na, K)Cl [9] molten salts. The numerical values for the parameters of the potential functions are tabulated in Table 1. For the bromide and iodide ion pair the combination rule presented by Larsen was adopted [10]. In the calculation of the coulombic force, the Ewald method [11] was used. The cut-off distance in the real space was $L/2$, the vector in the reciprocal space was taken up to 27 and the convergence parameter was $\alpha = 5.6/L$. The time step was 4 fs. At the initial stage of the MD simulations, NTV ensemble (1200 K) was settled and the calculations were performed with a slight modification [12] of the Woodcock method [13]. In subsequent calculations, NEV ensemble was postulated and after several thousand time steps of equilibration the collection of the data was started. The data analyses were done with the final 6,000 steps (24 ps). The calculated temperature, pressure and potential energy are 1202.5 K 193 MPa, and -687 kJmol^{-1}, respectively.

3. RESULTS AND DISCUSSION

3.1 Static Properties

Figure 1 represents the pair correlation functions $g_{ij}(r)$ and the characteristic values are summarized Table 2. The first peak of the unlike ion pairs appears at 225 pm and 257 pm for the Li^+-Br^- pair and Li^+-I^- pair, respectively. The peak shape of g_{LiI} is broader than that of g_{LiBr}. It means that the fluctuation of the distance for the Li^+-I^- pair is larger than that for the Li^+-Br^- pair. The roughness of g_{BrBr} is due to the small

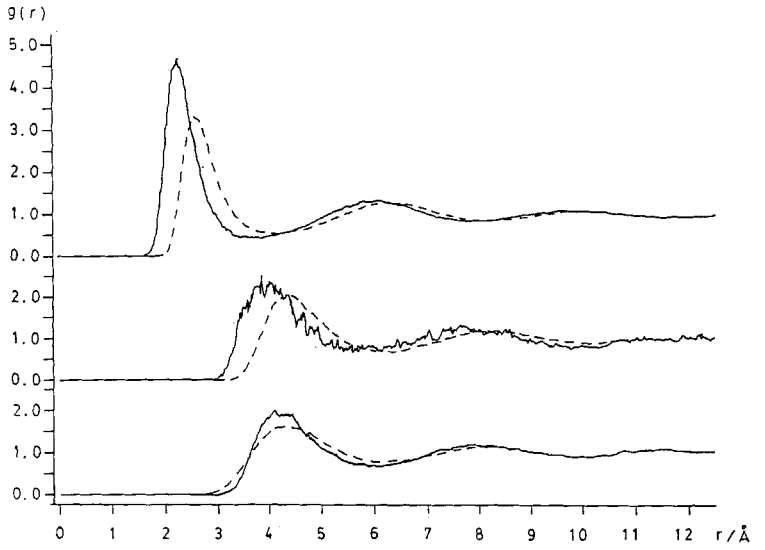

Figure 1 The pair correlation functions g_{ij}, the upper part: – Li^+-Br^-, ---- Li^+-I^-, the middle part: Br^--Br^-, ---- I^--I^-, the bottom part: – Br^--I^-, ---- Li^+-Li^+.

number of particles of the Br ion. The peak profile of g_{LiLi} is rather broad and it is reasonably explained that two kinds of the Li^+-Li^+ pair exist, one type with Br^- as an intermediator, the other with I^- as an intermediator. These six $g(r)$ functions show oscillating profiles.

In Figure 2 the distributions of the coordination numbers of Li^+ around Br^- and I^- within R_2 distances are illustrated, respectively. In both cases, the coordination number 3 is the most predominant one. The average number of the partial coordination number of Li^+ around Br^- is 2.7 and that around I^- is 2.9.

Figure 3 represents the partial angular distribution functions defined as

$$P(\theta) = C\, dn(\theta)/(\sin\theta\, d\theta)$$

where C is the normalization constant taken so that $\int_0^{180} P(\theta)\, d\theta = 1$, and $dn(\theta)$ is the number of ions around opposite signed ion within the distance R_2 between $\theta - \delta\theta/2$ and $\theta + \delta\theta/2$ ($\delta\theta = 1°$). In the case that the center ion is Br^-, the peak position is located around 113° so this indicates that Br^- ions are surrounded by Li^+ ions nearly

Table 2 Characteristic values of the pair correlation functions $g(r)$. R_i, r_{Mi} and r_{mi} give the distance in pm where for the ith time $g(r)$ crosses unity, has a maximum and a minimum, respectively.

	R_1	r_{M1}	$g(r_{M1})$	R_2	r_{m1}	$g(r_{m1})$
Li–Br	189	225	4.64	295	~366	~0.40
Li–I	223	257	3.32	333	~412	0.53
Li–Li	365	432	1.63	539	~617	0.77
Br–Br	~345	~398	~2.41	488	~565	~0.59
Br–I	361	410	~2.13	514	~590	~0.64
I–I	381	436	2.03	538	~632	~0.69

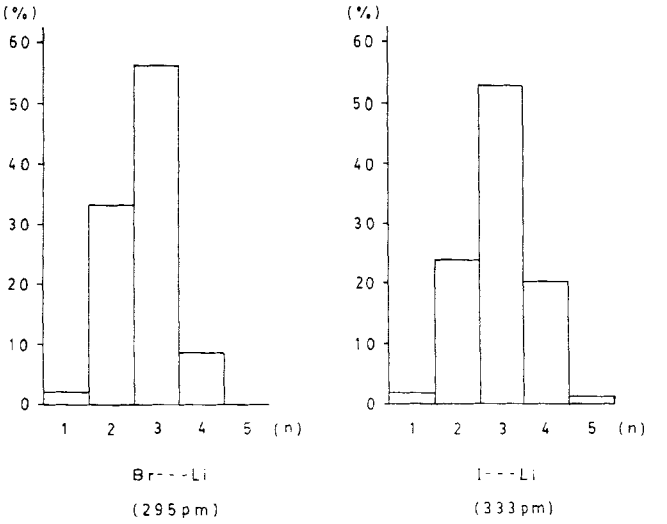

Figure 2 The partial distribution of the coordination number of the opposite charged ions. The value in the parenthesis shows the distance R_2 within which the ion is counted as coordinated ion.

regular tetrahedrally. In the case that the center ion is I^-, the distribution becomes broader than that around the Br^- ion. The peak is located around 101°, so most of the Li^+ ions around I^- ions are considered to have the tetrahedral arrangement. However, the distribution does not diminish drastically as θ decreases, and the ratio with θ less than 90° is considerable. If the ions take the regular octahedral arrangement, two peaks around 90° and 180° will appear [14]. So in the case of the Li^+ ions

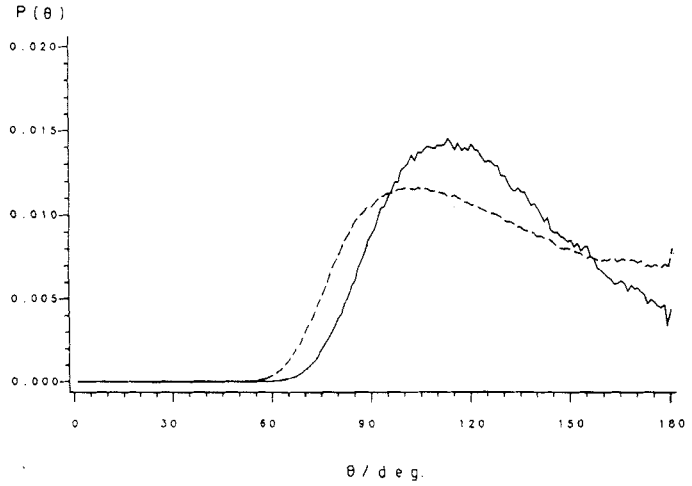

Figure 3 The partial angular distribution function. The solid line for ∠Li–Br–Li and the dashed line for ∠Li–I–Li.

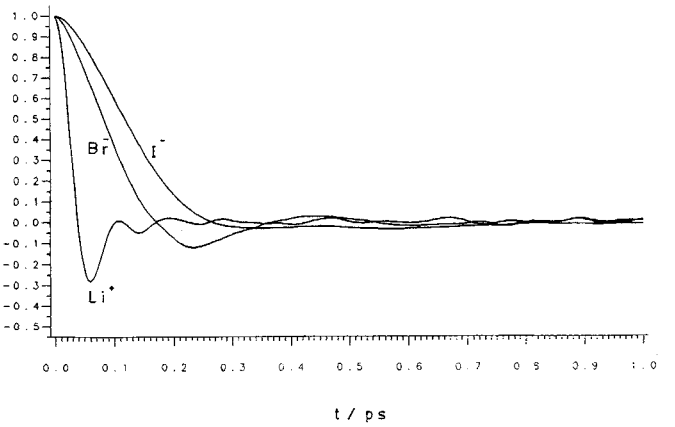

Figure 4 The velocity autocorrelation functions for Li^+, Br^- and I^- ions.

around I^- ions there may exist some variation of coordinated structures, such as the tetrahedral, the pentagonal, and the octahedral.

3.2 Dynamic Properties

The velocity autocorrelation function is defined as

$$Z_i(t) = \frac{\langle v_i(0)\, v_i(t)\rangle}{v_i^2(0)}$$

where v_i is the thermal velocity of species i and $\langle\ \rangle$ denotes the average for i. As seen in Figure 4, the effect of mass on the motion is clearly recognized [15]. The oscillatory behavior becomes important for Li^+, while, the function of I^- resembles the exponential function. The power spectra obtained by Fourier transformation of the velocity autocorrelation functions for three kinds of ions are shown in Figure 5. For Li^+ the distribution of the wave number spreads over a wide range but for I^- the peak is

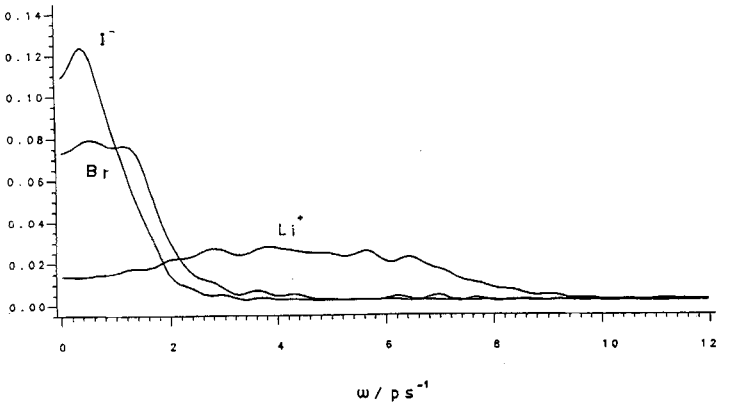

Figure 5 The power spectra for three kinds of ions.

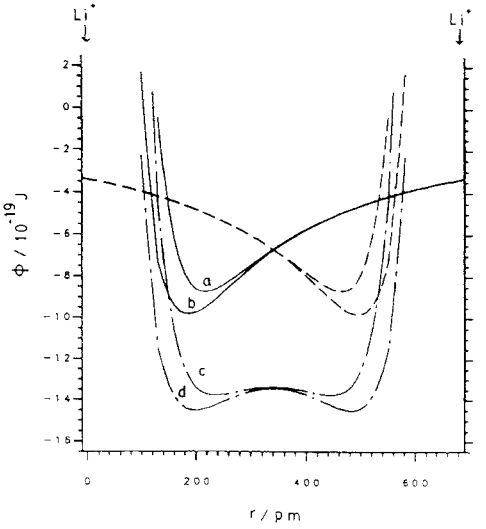

Figure 6 The line *a* represents the potential function felt by I^- from Li^+, which located at $r = 0$. The line *b* shows that for Br^-. The dashed lines show those from Li^+ located at $r = 682$ pm. The lines *c* and *d* indicate the potential profiles for I^- and Br^- located between two Li^+ ions, respectively.

significantly sharper and shifts well towards the low direction. In the power spectrum for Br^- an intermediary profile between those for Li^+ and I^- appears.

The self-exchange velocities of Br^- and I^- with Li^+ is defined by [4]

$$SEV = (R_2 - \overline{R}_2)/\tau$$

where $\overline{R}_2$ is the average distance between Li^+ and Br^- (or I^-) ions located within R_2. The anions in question within the distances R_2 from each Li^+ are marked. As the simulation progresses, the marked anions diffuse and the average distance of the marked ion pairs finally reaches the distance R_2 after a certain time. The average time needed for this process is τ. The self-exchange velocity for Br^- is 148 m/s and that for I^- is 173 m/s. The self-exchange velocity for I^- is greater than that for Br^-. This phenomenon is explained in terms of the potential felt by these anions located collinearly between two Li^+ ions as shown in Figure 6. The distances between two Li^+ ions are taken to be 682 pm, which corresponds to the Li–Li distance for melt of the fictive NaCl-type crystalline structure of the LiBr-LiI mixture. The height of the hump between two minimums for Br^- is larger than that for I^- as shown by lines c and d in Figure 6. This causes the separating motion of Br^- from Li^+ is slower than that of I^-.

In a common cation binary mixture the internal mobility of the larger cation is larger than that of the smaller cation in a certain mixing ratio and temperature range. This phenomenon was first discovered by Chemla in (Li, K)Br system [16] and was named the "Chemla effect" [17]. At a certain composition and temperature the mobilities of the two kinds of cations become equal, and it has been called "Chemla crossing point". As we define the Chemla crossing point as $f(x, T)$ where x is the mole fraction of the component containing the larger ion and T the temperature, $f(x,T)$

shifts towards the lower direction of x on increasing the temperature. The Chemla effect observable region expands at high temperature.

The correlation between the internal mobility and the self-exchange velocity holds not only in pure salt but also in molten salt mixtures [5]. The detailed discussion has already been given in (Li, Rb) Cl [5], (Li, K)Cl [4], (Li, Na, K)Cl [9] and Li(Cl, Br) [6] systems. The mechanism of the movement of the ion is the same whether the ion is cation or anion, although the polarization effect is considered to be more pronounced in the case of the anion. The "anion Chemla effect" is interpreted in the same way as the "Chemla effect" for cations: the larger self-exchange velocity of I^- with respect to that of Br^- is clearly explained in the same analogy as the (Li, K)Cl system [4]. We now appraise whether the Chemla effect occurs or not by calculating the self-exchange velocity of unlike ion pairs. The self-exchange velocity of I^- is greater than that of Br^- in the computer simulated 1:5 molar mixture of Li(Br, I) at 1200 K (see Figure 6), and the anion Chemla effect is therefore predicted to occur in this system.

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