ABSTRACT

Molecular dynamics (MD) simulation of the equimolar mixture of LiCl and LiBr melts has been performed at about 1000 K to evaluate the velocity of separating motion of adjacent unlike ion pairs defined as the self-exchange velocity (SEV). The SEV of Li-Br pairs is greater than that of Li-Cl pairs. This predicts that in this mixture the internal mobility of Br\(^-\) ions would be greater than that of Cl\(^-\) ions, that is, the "anion Chemla effect" will occur. For comparison, MD simulation of pure LiCl and LiBr melts has also been done.

INTRODUCTION

In previous studies, we have measured internal mobilities of cations in various molten binary mixtures with a common anion. In most of the systems the Chemla effect (1, 2) occurs in some concentration range, that is, the mobility of the larger cation is greater than that of the smaller one. This has been interpreted in terms of the difference in the Coulombic forces exerted on large and small cations by the anions.

We have found that in molten alkali chlorides internal mobilities are strongly related with the velocity of the separating motion of neighboring cation and anion defined as the self-exchange velocity (SEV) (3), which can be evaluated by molecular dynamics (MD) simulation. For example, in the molten mixture of (Li, K)Cl the Chemla effect for the internal mobilities (4) has been reproduced by the corresponding SEV's (5).

If the Chemla effect is caused by the difference in the Coulombic forces between two kinds of unlike ion pairs, it is expected that also in a binary mixture with a common cation the anion Chemla effect will occur. Thus,
in the present study the SEV's in the equimolar mixture of LiCl and LiBr melts have been calculated to learn whether the anion Chemla effect in the SEV's occurs. For comparison, the SEV's of neat LiCl and LiBr melts have been calculated. MD simulation of LiBr melt (6) as well as LiCl melt had been performed; however, the SEV of alkali bromide melts had not been studied.

Molecular Dynamics Simulation

For all the systems, 432 ions were taken in the cubic cell. In the case of the equimolar mixture, 216 Li⁺, 108 Cl⁻ and 108 Br⁻ ions were disposed in the cell. The edge length L of the cubes was calculated from the data on the densities (7, 8). The pair potentials of the Born-Mayer-Huggins type were adopted:

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

where $z$ is the charge number, $e$ the elementary charge, $\varepsilon_0$ the permittivity of vacuum, and $A$ the Pauling factor. Parameters $b$, $\sigma$, $\rho$, $c$ and $d$ were taken from those presented for the crystals by Tosi and Fumi (9); for the mixture the combination rule presented by Larsen et al. (10) was employed. The parameters used are given in Table 1. The Ewald method (11) was employed for the calculation of the Coulombic force. The MD-simulations were performed with a constant energy procedure. The step time was 4 fs. The average pressure was 0.24 GPa for LiCl, 0.21 GPa for LiBr and 0.18 GPa for Li(Cl, Br), and the temperatures were 1004 K, 1002 K and 991 K, respectively. After about 3000 time steps for equilibration, the configurations for the following 3000 time steps were employed for various calculations of the properties for each system.

Results and Discussion

Pair Correlation Function

The characteristic values of the pair correlation functions $g(r)$ are given in Table 2. In Fig. 1, $g(r)$ and the running coordination number $n(r)$ are shown for the unlike ion pairs. The positions of the first maximum $R_{M1}$ for $g_{LiCl}$ and $g_{LiBr}$ are almost the same in the pure salts and the mixture, while the peak heights decrease with increasing concentration of LiBr. Similar behavior has been observed in such systems as (Li, Rb)Cl (3). This can be explained as follows: with increasing concentration of LiBr, the average distance between neighboring Li⁺ ions increases, as is seen also from the positions of the first maximum of $g_{LiLi}(r)$ in Table 2, and the halide ions are
more structured with the nearest neighboring Li$^+$ ions by experiencing less interference from other surrounding Li$^+$ ions. This feature distinctively appears also in the self-exchange velocity which will be stated later.

**Angular correlation function**

For further insight into the short range structure, the angular correlation function defined by Eq. (2) was calculated:

$$P_{\pm \pm}(\theta) = C \frac{dn(\theta)}{[\sin \theta \ d\theta]}$$  \hspace{1cm} (2)

where $C$ is the normalization constant taken so that $\int_0^\pi P_{\pm \pm}(\theta) \ d\theta = 1$ and $dn(\theta)$ is the number of the anions around an Li$^+$ ion within distance $R_2$ between $\theta - \Delta \theta/2$ and $\theta + \Delta \theta/2$ ($\Delta \theta = \frac{\pi}{R}$). $R_2$ is the position where $g(r)$ crosses unity for the second time and may be regarded as the end of the nearest neighbor interaction (12). The $P_{\pm \pm}(\theta)$ in the neat salts and in the mixture are shown in Fig. 2. The first peak position is located around $102^\circ$ for $P_{\pm \pm}$ and $P_{\pm \pm}$ in all the cases. This indicates that with high probability each ion is coordinated by the counter-ions nearly regular-tetrahedrally in these melts.

**Self-exchange velocity (SEV)**

The average velocity of separating motion of unlike ion pairs can be expressed in terms of the self-exchange velocity (SEV), $v$, defined by

$$v = \frac{(R_2 - \bar{R}_2)}{\tau},$$  \hspace{1cm} (3)

where $R_2$ is the average distance between unlike ions located within distance $R_2$. The anions within distance $R_2$ from each Li$^+$ ion are marked. With the lapse of time, the marked anions will move from $\bar{R}_2$ to $R_2$. The time needed for this movement is $\tau$. During the same time the loss of the coordinating anions around the cation is compensated by the anions entering this region from the outside.

The SEV's for Cl$^-$-Li$^+$ and Br$^-$-Li$^+$ pairs are given in Table 3. The SEV was calculated for the anions coordinating to totally 43200 Li$^+$ ions for each system. In the mixture the SEV of Cl$^-$-Li$^+$ pairs is greater than that of Br$^-$-Li$^+$ pairs. Thus, the Chemla effect for the SEV occurs.

The SEV's so far calculated by MD simulations with the Tosi-Fumi potentials (9) are plotted against the experimentally obtained internal mobilities in Fig. 3. In these MD simulations the obtained pressures are usually in the order of 0.1 GPa, whereas the internal mobilities taken in Fig. 2 are those at ambient pressure. However, there seems to be strong correlation between $v$ and $b$. The $b$ in pure LiCl is minimally greater than that in pure LiBr at 1000 K, if the data on the conductivities and the den-
sities in Ref. (8) are taken. If the data are taken from another reference (7), this order is reversed. As for the SEV, it is slightly greater in LiCl than in LiBr, as shown in Table 3.

For further insight, the motion of distinct ion pairs is examined. Time evolution of the distances of distinct Cl\(^-\) and Br\(^-\) ions within the respective R\(^2\)'s at t = 0 from a distinct Li\(^+\) ion in the mixture is shown in Fig. 4. This motion can be classified into four processes (4, 13).

(i) The anion which starts within R\(^2\) at t = 0 passes R\(_{\text{ml}}\) for the first time after passing R\(_0\) for the last time at the time t (oscillating motion = O-process); R\(_{\text{ml}}\) is the position of the first minimum of g(r).

(ii) The anion passes R\(^2\) for the last time at the time t = 0 and passes R\(_{\text{ml}}\) for the last time at time t (leaving motion = L-process).

(iii) The cation passes R\(_{\text{ml}}\) at the time t = 0 in the outward direction at the time t = 0 and does not pass R\(^2\) (wandering motion = W-process).

(iv) The cation passes R\(_{\text{ml}}\) in the inward direction at the time t = 0 and passes R\(^2\) for the first time at the time t (coming-back motion = C-process).

The C-process and L-process of Cl\(^-\) and Br\(^-\) ions are compared in the mixture. In Fig. 5 percentage of the anions terminating the O-process for the first time are plotted against time. This figure shows that the O-process of Cl\(^-\) ions is longer than that of Br\(^-\) ions. This is because, at the same number density of Li\(^+\) ions, Cl\(^-\) ions are more associated with the nearest neighboring Li\(^+\) ions than Br\(^-\) ions are, owing to the stronger Coulombic interaction. In other words, Cl\(^-\) ions are more associated with Li\(^+\) ions than Br\(^-\) ions are.

On the other hand, the average velocity of Cl\(^-\) ions in the L-process \(v_L\) is greater than that of Br\(^-\) ions; they are (1399 ± 33) m s\(^{-1}\) and (1326 ± 30) m s\(^{-1}\), respectively, and lie on an empirical equation \(v_L = (0.577 ± 0.005) \times (v_c + v_a)\), where \(v_c = \sqrt{8 R T/\pi M_c}\) and \(v_a = \sqrt{8 R T/\pi M_a}\) (M\(_c\) and M\(_a\): masses of the cation and anion, respectively) (5). In the L-process the velocity is mainly dependent on the masses of cation and anion of interest and temperature (5). Since a Cl\(^-\) ion is lighter than a Br\(^-\) ion, it is reasonable that in the L-process Cl\(^-\) ions are faster than Br\(^-\) ions are.

As the contribution of the O-process is greater than that of the L-process in the present mixture, the SEV of Br\(^-\) ions is greater than that of Cl\(^-\) ions, although in the
L-process the velocity of the former is smaller than that of the latter.

**Self-diffusion coefficient**

The self-diffusion coefficients of the ions, D, have been evaluated from the mean square displacements, which have been taken over 8 ps from different 40 time origins. The evaluated values are given in Table 5 along with the experimental values for LiCl (14). This table shows that D of Cl\(^-\) ions is greater than that of Br\(^-\) ions in the mixture as well as in the pure melts. That is, the Chemla effect does not occur for the self-diffusion coefficients. The self-diffusion coefficient refers to the motion of the ions with reference to their original position, whereas the internal mobility of the anions is related to the motion with reference to their counter-ions. Therefore, the self-diffusion coefficient of the smaller and lighter ions should be generally greater than that of the larger and heavier ones.

Table 5 indicates also that D for Cl\(^-\) and Br\(^-\) ions are greater in the pure melts than in the mixture. This may be explained as follows. The Cl\(^-\) ions are more associated in the mixture than in the pure salt, and therefore D is smaller in the former than in the latter. As for Br\(^-\) ions, these may be more associated in the pure melt than in the pure salt, but the free space is smaller in the former than in the latter. Thus, the effect of free space must be greater than the effect of association for such large ions as Br\(^-\) ions, as far as the motion with reference to their original position is concerned.

In conclusion, the Chemla effect occurs for the SEV in the equimolar mixture of LiCl and LiBr melts. This predicts that the Chemla effect would occur for the mobilities of the two anions. This is to be ascertained experimentally.

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**REFERENCES**

1. J. Périé and M. Chemla, C. R. Acad. Sci. Paris, 250, 3986 (1960).
2. I. Okada, R. Takagi, and K. Kawamura, *Z. Naturforsch.*, 34a, 498 (1979).
3. I. Okada, R. Takagi, and K. Kawamura, *Z. Naturforsch.*, 35a, 493 (1980).
4. A. Lundén and I. Okada, *Z. Naturforsch.*, 41a, 1034 (1986).
5. I. Okada, *Z. Naturforsch.*, 42a, 21 (1987).
6. F. Lantelme and P. Turq, *Mol. Phys.*, 38, 1003 (1979).
7. G. J. Janz, F. W. Dampier, G. R. Lakshminarayanana, P. K. Lorenz, and R. P. T. Tomkins, *Molten Salts: Vol. I*, Electrical Conductance, Density, and Viscosity Data, NSRDS-NBS 15, Nat. Bur. Stand., Washington 1968.
8. G. J. Janz, R. P. T. Tomkins, and C. B. Allen, *Phys. Chem. Ref. Data*, 8, 125 (1979).
9. M. P. Tosi and F. G. Fumi, *J. Phys. Chem. Solids*, 25, 45 (1964).
10. B. Larsen, T. Førland, and K. Singer, *Mol. Phys.*, 26, 1521 (1973).
11. P. P. Ewald, *Ann. Phys.*, 64, 253 (1921).
12. G. Pálinkás, W. O. Riede, and K. Heinzinger, *Z. Naturforsch.*, 32a, 1137 (1977).
13. I. Okada, *Z. Naturforsch.*, 39a, 880 (1984).
14. R. Lenke, W. Uebelhack, and A. Klemm, *Z. Naturforsch.*, 28a, 881 (1973).

Table 1. The parameters used for the MD simulation.

| Parameter | Li-Li | Cl-Cl | Br-Br | Li-Cl | Li-Br | Cl-Br |
|-----------|-------|-------|-------|-------|-------|-------|
| A (pm)    | 2.00  | 0.75  | 0.75  | 1.375 | 1.375 | 0.75  |
| σ (pm)    | 163.2 | 317.0 | 343.2 | 240.1 | 253.2 | 330.1 |
| C (10^-9 J m^6) | 0.073 | 111.0 | 185.0 | 2.00  | 2.50  | 143.0 |
| D (10^-9 J m^6) | 0.030 | 223.0 | 423.0 | 2.40  | 3.30  | 307.1 |

b = 0.338 x 10^-19 J

Table 1b

| System    | /pm | L/pm | Ref. |
|-----------|-----|------|------|
| LiCl      | 34.2| 2187.9| (7)  |
| LiBr      | 35.3| 2345.3| (7)  |
| Li(Cl, Br)| 34.8| 2274.8| (8)  |
### Table 2. Characteristic values of the pair correlation functions $g_{ij}(r)$.

| System     | i   | j   | $R_1$ (pm) | $R_{\text{M1}}$ (pm) | $g(r_{\text{M1}})$ | $R_2$ (pm) | $R_{\text{m1}}$ (pm) | $g(r_{\text{m1}})$ |
|------------|-----|-----|------------|----------------------|---------------------|------------|----------------------|---------------------|
| Li(Cl, Br) | Li  | Cl  | 188        | 219                  | 4.29                | 279        | 353                  | 0.42                |
|            | Li  | Br  | 211        | 241                  | 3.40                | 304        | 367                  | 0.50                |
|            | Li  | Li  | 327        | 385                  | 1.80                | 477        | 553                  | 0.72                |
|            | Cl  | Cl  | 323        | 369                  | 2.19                | 455        | 527                  | 0.62                |
|            | Br  | Br  | 350        | 397                  | 2.13                | 491        | 577                  | 0.65                |
|            | Cl  | Br  | 335        | 381                  | 2.14                | 469        | 551                  | 0.63                |
| LiCl       | Li  | Cl  | 192        | 223                  | 3.72                | 281        | 353                  | 0.46                |
|            | Li  | Li  | 318        | 371                  | 1.82                | 459        | 535                  | 0.69                |
|            | Cl  | Cl  | 324        | 373                  | 2.13                | 455        | 537                  | 0.65                |
| LiBr       | Li  | Br  | 207        | 239                  | 3.78                | 302        | 369                  | 0.47                |
|            | Li  | Li  | 341        | 397                  | 1.79                | 494        | 573                  | 0.70                |
|            | Br  | Br  | 349        | 401                  | 2.14                | 487        | 573                  | 0.63                |

$R_1$ is the position where $g(r)$ crosses unity for the first time.

### Table 3. Self-exchange velocity of neighboring unlike ions at about 1000 K.

| System     | Cl$^-$-Li$^+$ | Br$^-$-Li$^+$ |
|------------|---------------|---------------|
| Li(Cl, Br) | 119 (m s$^{-1}$) | 134 (m s$^{-1}$) |
| LiCl       | 145 (m s$^{-1}$) | ---           |
| LiBr       | ---           | 120 (m s$^{-1}$) |

### Table 4. Self-diffusion coefficients at about 1000 K.

| System     | Li$^+$ | Cl$^-$ | Br$^-$ |
|------------|--------|--------|--------|
| Li(Cl, Br) | 10.5 (10$^{-9}$ cm$^2$ s$^{-1}$) | 7.0 (10$^{-9}$ cm$^2$ s$^{-1}$) | 4.7 (10$^{-9}$ cm$^2$ s$^{-1}$) |
| LiCl       | 9.2 [14.2] (10$^{-9}$ cm$^2$ s$^{-1}$) | 8.2 [7.2] (10$^{-9}$ cm$^2$ s$^{-1}$) | --- |
| LiBr       | 10.0 (10$^{-9}$ cm$^2$ s$^{-1}$) | --- | 6.2 (10$^{-9}$ cm$^2$ s$^{-1}$) |

The values in brackets are the experimentally obtained ones at 1000 K at ambient pressure (14).
Fig. 1a. Pair correlation function $g_{LiCl}(r)$ and running coordination number $n(r)$ of Li$^+$ ions around a Cl$^-$ ion. 
--- : LiCl; ----- : Li(Cl, Br).

Fig. 1b. Pair correlation function $g_{LiBr}(r)$ and running coordination number $n(r)$ of Li$^+$ ions around a Br$^-$ ion. 
--- : LiBr; ----- : Li(Cl, Br).
Fig. 2a. Angular correlation function \( P(\theta) \) for \( \angle \text{Cl-Li-Cl} \). \( \bigcirc \): LiCl; \( \bullet \): Li(Cl, Br).

Fig. 2b. Angular correlation function \( P(\theta) \) for \( \angle \text{Br-Li-Br} \). \( \bigcirc \): LiBr; \( \bullet \): Li(Cl, Br).
Fig. 3. Relationship between $v$ and $b$ in some alkali halides.

Fig. 4. Time evolution of the distances of the anions (located within $R_2$ at $t=0$) from an arbitrary $Li^+$ ion.

Fig. 5. Percentage of the halide ions terminating the $O$-process for the first time.