Self-Diffusion of Sodium and Potassium in Molten Flinak†

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In the previous paper[1], the authors reported the self-diffusion coefficients of fluorine and lithium in molten LiF-NaF-KF (46.5:11.5:42.0 mole%) eutectic mixture (Flinak) with the improved capillary reservoir technique using ^{18}F and ^{6}Li tracers. The diffusion coefficients of fluorine and lithium in molten Flinak are smaller than those of other molten alkali halides, in spite of similar values of D_0 (independent term of temperature) and E_D (activation energy) for diffusion in molten Flinak as those molten alkali halides.

In this note, the self-diffusion coefficients of sodium and potassium in molten Flinak are reported. The diffusion coefficients were measured with the same experimental technique in temperature range of 491–616°C with the use of ^{22}Na and ^{42}K as tracer. **Figure 1** shows the diffusion coefficients of sodium, potassium, fluorine[1] and lithium[1], in molten Flinak. The results can be expressed in term of

$$D = D_0 \exp(-E_D/RT) \qquad (1)$$

, where D denotes the diffusion coefficient (cm^2/sec), D_0 the independent term of temperature, E_D the activation energy (kcal/mole), R the gas constant, and T the absolute temperature, respectively. **Table 1** shows the constants of equation (1) calculated with least square means for fluorine[1], lithium[1], sodium and potassium. The diffusion coefficients of anion and cations in molten Flinak took almost similar values within experimental error.

Table 1 Constants of equation (1) for fluorine, lithium, sodium and potasium in molten Flinak.

Salt	Tracer	$D_0 \times 10^3$ (cm^2/sec)	E_D (kcal/mole)	Temp. range °C	E_D/RT_m
Flinak	^{18}F	1.63	7.23	480-663	5.01
	^{6}Li	3.85	8.88	480-663	6.15
	^{22}Na	4.42	8.70	504-616	6.02
	^{42}K	0.729	6.06	491-613	4.20

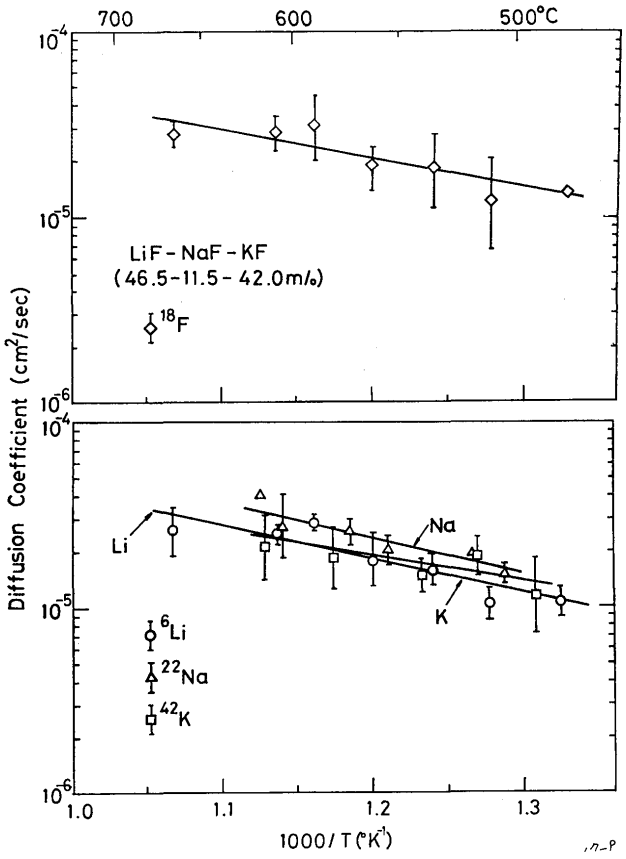

Fig. 1 Self-diffusion coefficients of fluorine, lithium, sodium and potassium in molten Flinak.

If the diffusion phenomena in molten Flinak are governed with jumping and exchanging of anion and cation, it is thought that the diffusion will be affected by size and number of ionic species. In **Table 2**, the values such as ionic fraction, ionic radius and volume ratio of

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Table 2 Values of ionic fraction, ionic radius and volume ratio of anion and cations in molten Flinak.
r_+ and r_- are the ionic radius of cation and anion.

Salt	Ionic fraction	Ionic radius	$(r_+/r_-)^3$
Flinak	F 0.5000	1.36	1.000
	Li 0.2325	0.60	0.086
	Na 0.0575	0.95	0.341
	K 0.2100	1.33	0.935

various anion and cations in molten Flinak are compared. With the comparison of these values and obtained results, it is thought that the diffusion coefficients in molten Flinak are not necessarily influenced by the ionic radii or number of ionic species.

Generally, it can be accepted that each ion in molten Flinak is surrounded by oppositely charged ions. Therefore it can be considered that the jump of individual ion for a rearrangement is controlled with cation-anion electrostatic attraction with the following equation,

$$I = Z^+ Z^- e^2/r^2 \qquad (2)$$

, where Z^+e and Z^-e are charge of cation and anion, r sum of cation and anion radii ($r = r_+ + r_-$). Accordingly, the activation energy E_D for diffusion will be proportion to the cation-anion electrostatic atrraction I, $E_D \propto I$. **Figure 2** shows the comparison of E_D with I in molten

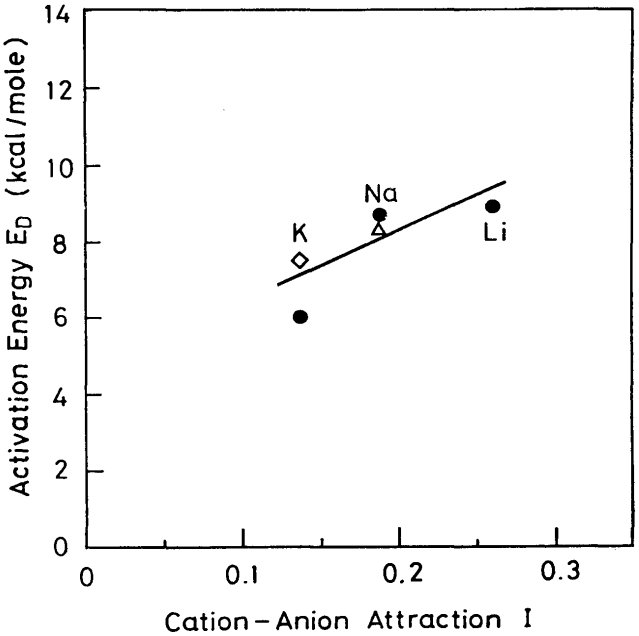

Fig. 2 Comaprison of the activation energy E_D for diffusion with cation-anion electrostatic attraction I in molten Flinak, NaF[2] and KF[2]. ●, Flinak; △, Na in NaF; ◇, K in KF.

Flinak, NaF[2] and KF[2]. It is evident that the value of E_D increases with increasing of I. The size effect of an ion for diffusion generally decreases with increasing of the interaction between anion and cation. It is, therefore, concluded that in molten Flinak the size effect is depressed by the interaction of individual ion, because the observed diffusion coefficients of each ion are almost equal. According to Sjöblom[3], the value of E_D/RT_m, where T_m is the melting point in degree Kelvin, is more than 4.0 for the salts considered as forming complex anions in the metl. As arithmetic mean value of E_D/RT_m of molten Flinak is about 5.3 in table 1, it is anticipated that the interaction between anion and cation in molten Flinak is strong.

Furthermore, there exists the correspondence between diffusion and electrical conductance with the following relation called as Nernst-Einstein equation,

$$D_i = \Lambda_i R T / Z_i F \qquad (3)$$

, where Λ_i denotes the equivalent conductance, Z_i the charge of species i, and F the Faraday constant. **Figure 3** shows the comparison of the observed diffusion coefficients with those calculated from electrical con-

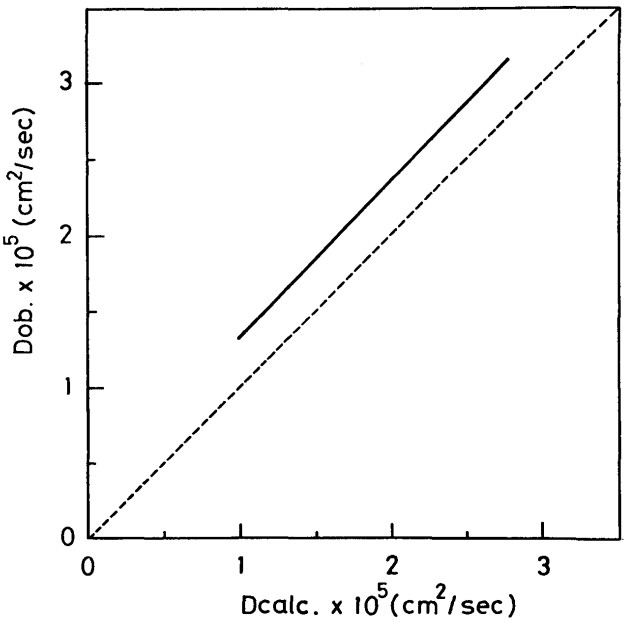

Fig. 3 Comparison of the observed diffusion coefficients with those calculated from electrical conductance[4] in molten Flinak.

ductance[4] according to equation (3). The observed diffusion coefficients take value 20% excess on an average at same temperature. It seems that the diffusion processes without charge transfer contribute in molten Flinak in the same way as other molten alkali halides.

Figures 4 and **5** show the comparison of diffusion coefficients of fluorine, lithium, sodium and potassium in molten Flinak with those of anions and cations in other

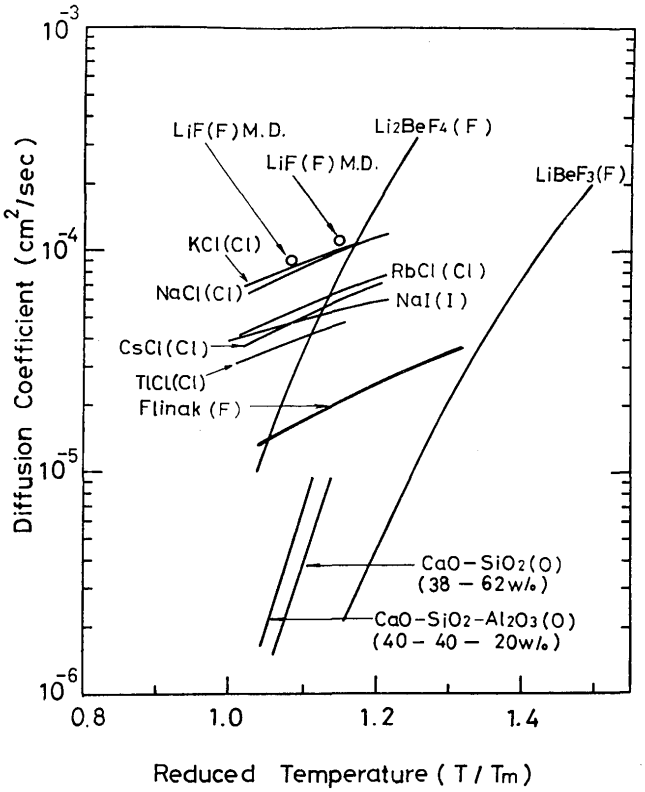

Fig. 4 Comparison of the self-diffusion coefficients of fluorine in molten Flinak with those of anions in other molten alkali halides under the reduced temperature scale T/T_m. M.D. shows the diffusion coefficients calculated by molecular dynamics.

molten alkali halides under the reduced temperature scale T/T_m. It is recognized that the diffusion coefficients of fluorine, lithium, sodium and potassium in molten Flinak are samller than those of anions and cations in other molten alkali halides. These results will support our disccusion of diffusion mechanism in molten Flinak in the previous paper[1].

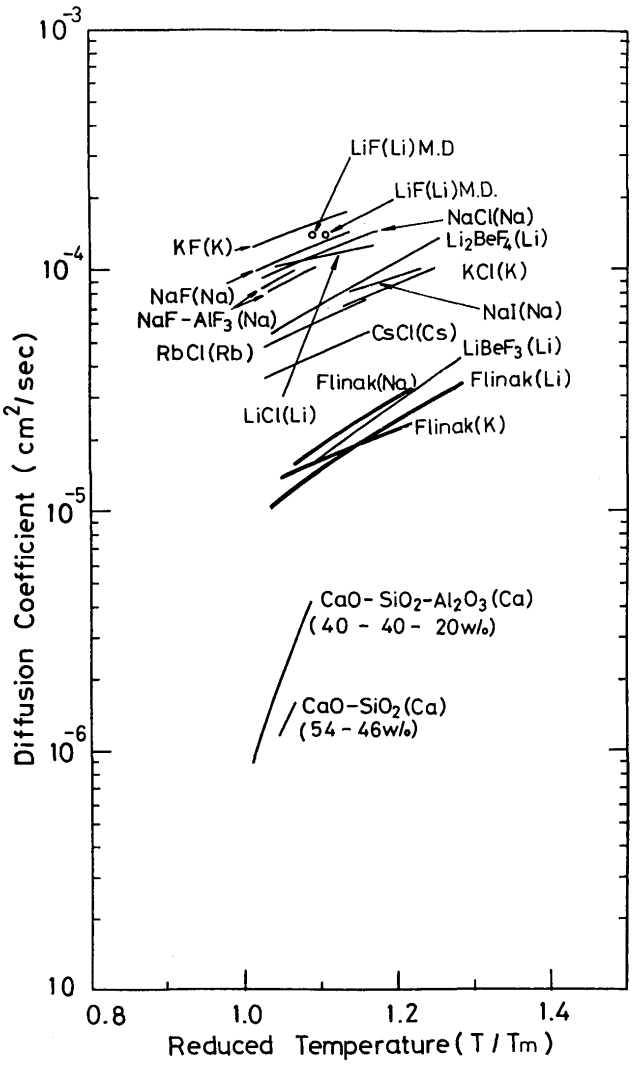

Fig. 5 Comparison of the self-diffusion coefficients of lithium, sodium and potassium in molten Flinak with those of cations in other molten alkali halides under the reduced temperature scale T/T_m. M.D. shows the diffusion coefficients calculated by molecular dynamics.

References

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