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# Self-Diffusion of Fluorine and Lithium in Molten Flinak<sup>†</sup>

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## Abstract

The self-diffusion coefficients of fluorine and lithium in molten LiF-NaF-KF (46.5–11.5–42.0 mole%) eutectic mixture (Flinak) have been measured by means of the capillary reservoir technique, using <sup>18</sup>F or <sup>6</sup>Li as the tracer. The results can be expressed as follows by the Arrhenius equation,

$$D_F = 1.63 \times 10^{-3} \exp(-7230/RT),$$

and

$$D_{Li} = 3.85 \times 10^{-3} \exp(-8880/RT),$$

where  $D$  is expressed in  $\text{cm}^2/\text{sec}^{-1}$ ,  $R$  in  $\text{cal}/\text{mole}\cdot\text{deg}$ , and  $T$  in degrees Kelvin.

## 1. Introduction

Molten LiF-BeF<sub>2</sub> (especially Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub>) and LiF-NaF-KF (46.5–11.5–42.0 mole%) eutectic mixture are useful materials as solvent for fissile (UF<sub>4</sub>) and fertile (ThF<sub>4</sub>) materials or coolants in Molten Salt Breeder Reactor (MSBR).

It will be therefore important to advance understanding of the dynamical structure of molten state and the chemical reaction process in those salts. We have been studying of diffusion behaviour of fluorine<sup>1,2)</sup> and lithium<sup>3)</sup> in molten Li<sub>2</sub>BeF<sub>4</sub> and LiBeF<sub>3</sub>. A study of diffusion behaviour of various ions in molten salts appears to offer one of the most promising means of understanding such transport properties.

In this paper, the diffusion behaviour of fluorine and lithium in molten Flinak was investigated by the capillary reservoir technique.

## 2. Experimental Procedures

The procedures of the experiment were carried out by the capillary reservoir technique.

For the preparation of Flinak, a mixture of LiF, NaF and KF was melt in a platinum crucible under He atmosphere. The chemicals used were as follows: analytical reagent grade LiF, NaF prepared by Merk Co., analytical reagent grade KF prepared by Rare Metallic Co., respectively. The radioactive or stable isotopes were used as tracers. The fluorine radioactive <sup>18</sup>F was prepared using JRR-3 (Japan Research Reactor-3). Highly purified Li<sub>2</sub>CO<sub>3</sub> was used as a

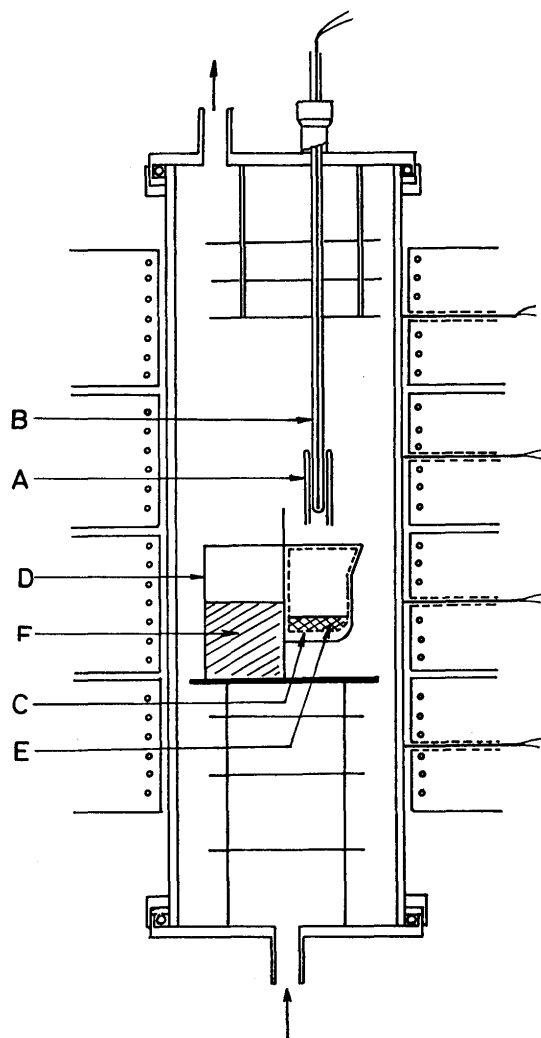


Fig. 1 A: Ni capillaries. B: Ni rod. C: Pt crucible. D: Ni crucible. E: labelled salt. F: non-labelled salt.

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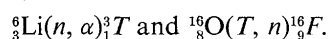
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target materials and the following reactions occurred to produce  $^{18}\text{F}$ .



After irradiation,  $\text{Li}_2\text{CO}_3$  powder was treated with aqueous hydrogen fluoride in a platinum crucible to produce the labelled  $\text{Li}^{18}\text{F}$  deposit. On the other hand, the lithium stable  ${}^6\text{Li}$  was prepared using  $\text{Li}_2\text{CO}_3$  powder which a  ${}^6\text{Li}/{}^7\text{Li}$  abundance ratio of 19 and then  $\text{Li}_2\text{CO}_3$  was treated with aqueous hydrogen in the same way as above mentioned.

The diffusion cell used in previous experiment<sup>1)-3)</sup> was improved in order to avoid the solidification of tracer melt in a capillary before the diffusion run. A schematic diagram of the diffusion cell is shown in Fig. 1. The capillaries (A) which were 1 mm inner diameter and 30–40 mm length were made of Ni. The capillaries whose mouths faced down were wound with Ni wire to be held at the lower end of Ni rod (B). After the labelled salt (E) was placed in a platinum crucible (C) and the non-labelled salt (F) in a Ni crucible (D), the furnace was heated in inert atmosphere of He gas. After melting of these salts, the capillaries above the crucible (C) were filled with the labelled salt by dipping their mouths in the melt under vacuum and then feeding He gas slowly back in the cell. They were raised out of the melt by the movable rod and then immersed into the diffusion crucible (D) after turning round the stainless steel flange. This procedure could prevent the solidification of the labelled

melt in a capillary. The duration of the diffusion run was in the range of 70–80 minutes. The maximum difference in temperature between the top and the bottom of the capillary was about  $0.5^\circ\text{C}$ . After the diffusion run, the capillaries were slowly lifted out of the melt and then removed from the cell. After cleaning the outside of the capillaries, they were cut by a saw at intervals of about two millimeters.

The concentration profiles of tracer  $^{18}\text{F}$  and  ${}^6\text{Li}$  in the capillaries were measured in the same way with  $\gamma$ -ray spectrometer and ion micro mass analyser (HITACH IMA-SS), respectively, as in the previous paper.<sup>1)-3)</sup>

### 3. Results and Discussions

It is considered that the errors in the capillary reservoir technique may arise due to disturbance at the mouth of capillary on immersion and removal of the capillary into/from the mouth salt bath. Therefore, the results which gave the abnormal concentration profile of  $^{18}\text{F}$  or  ${}^6\text{Li}$  were neglected in this study.

Diffusion coefficient  $D$  was calculated by the following equation,

$$C_x = C_0 \operatorname{erf}(x/[2(Dt)^{1/2}]), \quad (1)$$

where  $C_0$  is the initial concentration of  $^{18}\text{F}$  or  ${}^6\text{Li}$ ,  $C_x$  the concentration of  $^{18}\text{F}$  or  ${}^6\text{Li}$  at the distance  $x$  from the boundary diffusion time  $t$ .

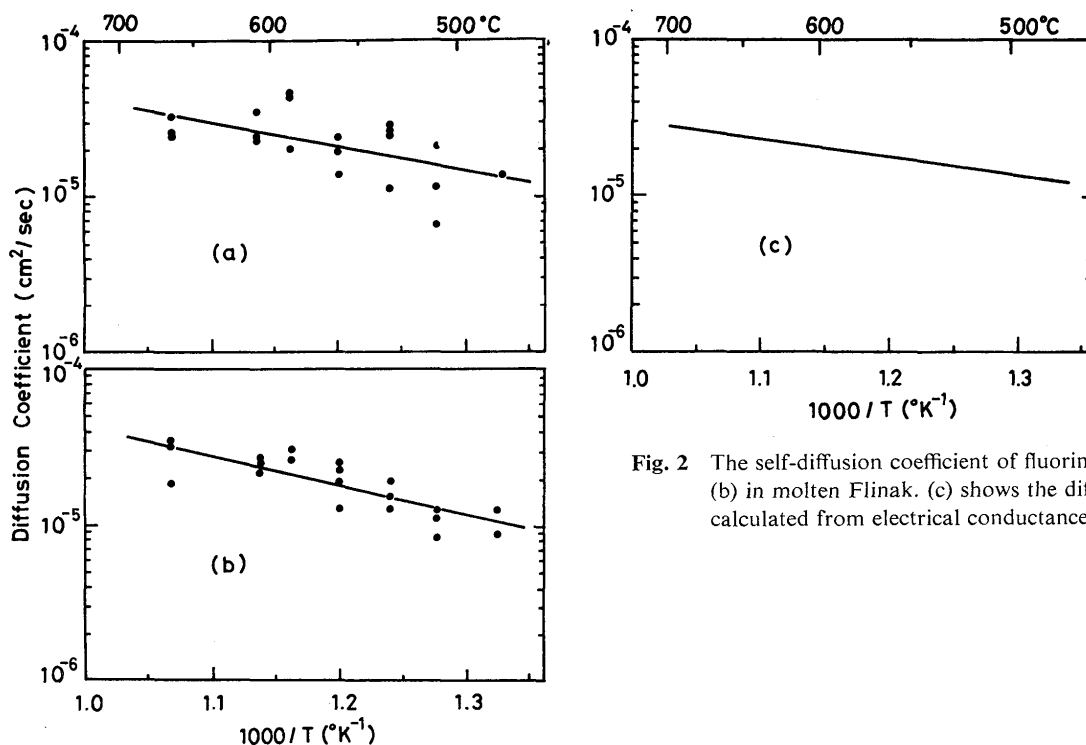


Fig. 2 The self-diffusion coefficient of fluorine (a) and lithium (b) in molten Flinak. (c) shows the diffusion coefficient calculated from electrical conductance.

The results of experimental  $D_F$  and  $D_{Li}$  in molten Flinak are given in Fig. 2(a) and (b), respectively. The diffusion coefficient is written in the form of

$$D = D_0 \exp(-E_D/RT), \quad (2)$$

where  $E_D$  is the activation energy,  $R$  the gas constant and  $T$  the absolute temperature. The following results were obtained by least square from all experimental data,

$$D_F = 1.63 \times 10^{-3} \exp(-7230/RT), \quad (3)$$

and

$$D_{Li} = 3.85 \times 10^{-3} \exp(-8880/RT). \quad (3)$$

It was seen that the diffusion coefficients of fluorine and lithium in molten Flinak showed approximately equal values at the same temperature.

It is necessary to examine the relation between the diffusion behaviours of molten Flinak and other alkali halides, because Flinak is a mixture of simple alkali halide LiF, NaF and KF. Table 1 lists the pre-exponential terms  $D_0$  and activation energy  $E_D$  of anions and cations in some molten alkali halides<sup>(4)-(11)</sup> together with those of present work. As shown in this table, it is seen that  $D_0$  and  $E_D$  of fluorine and lithium in molten Flinak are relatively similar to those of anions and cations in other molten alkali halides. Figs. 3 and 4 show the comparison of the diffusion coefficients of fluorine and lithium in molten Flinak

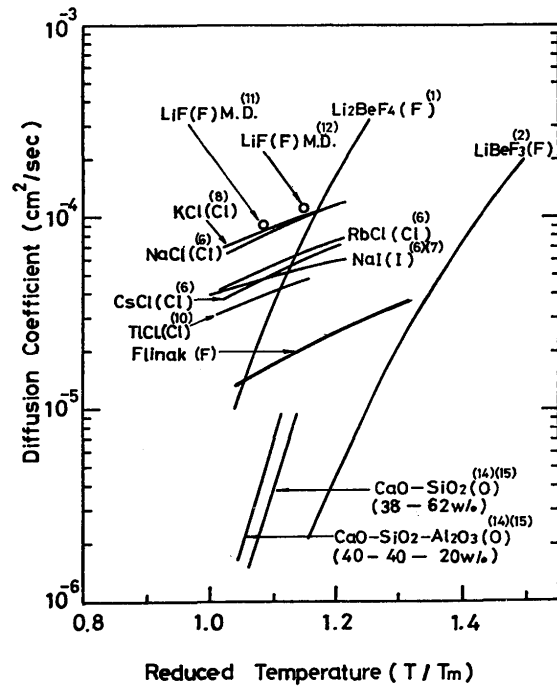


Fig. 3 Comparison of the self-diffusion coefficient of fluorine in molten Flinak with those of anions in other molten alkali halides under the reduced temperature scale  $T/T_m$ . M.D. shows the diffusion coefficient calculated by molecular dynamics.

Table 1 Pre-exponential terms  $D_0$  and activation energies  $E_D$  for self-diffusion of anions and cations in molten Flinak and other alkali halides.

System	Tracer	$D_0 \times 10^3$ (cm <sup>2</sup> /sec)	$E_D$ (Kcal/mole)	Temp. range ( C )	Reference
Flinak	<sup>6</sup> Li	3.85	8880		present work
	<sup>18</sup> F	1.63	7230	460-660	
NaF	<sup>22</sup> Na	3.08-0.06	8700-600	970-1160	(4)
KF	<sup>42</sup> K	2.46-0.06	7500-600	840-1060	
LiCl	Li	1.03	4300	610-760	(5)
NaCl	<sup>22</sup> Na	3.36	7860-110	830-990	(6)
	<sup>36</sup> Cl	3.02	8390-40		
RbCl	<sup>86</sup> Rb	2.51	8010-30	740-880	
	<sup>36</sup> Cl	1.67	7420-70		
CsCl	<sup>134</sup> Cs	1.73	7320-50	668-794	
	<sup>36</sup> Cl	2.46	7820-80		
NaI	<sup>22</sup> Na	0.63	4030-50	670-806	(7)
	<sup>131</sup> I	0.43	4420-60		
KCl	<sup>42</sup> K	1.8	6680	798-983	(8)
NaCl	<sup>22</sup> Na	1.84-0.19	6320-360	830-1005	(9)
	<sup>36</sup> Cl	1.83-0.38	7140-540	829-981	
	<sup>137</sup> Cs	0.72-0.12	4830-320	672-879	
TlCl	<sup>204</sup> Tl	7.3	4540-240	452-526	(10)
	<sup>36</sup> Cl	0.79	4560-460	472-542	
LiF	Li	$D_{Li} = 1.8 \times 10^{-4}$ (cm <sup>2</sup> /sec)		942	M.D. (11)
LiF	F	$D_F = 9.0 \times 10^{-5}$			
LiF	Li	$D_{Li} = 1.36 \times 10^{-4}$		1014	M.D. (12)
LiF	F	$D_F = 1.13 \times 10^{-4}$			

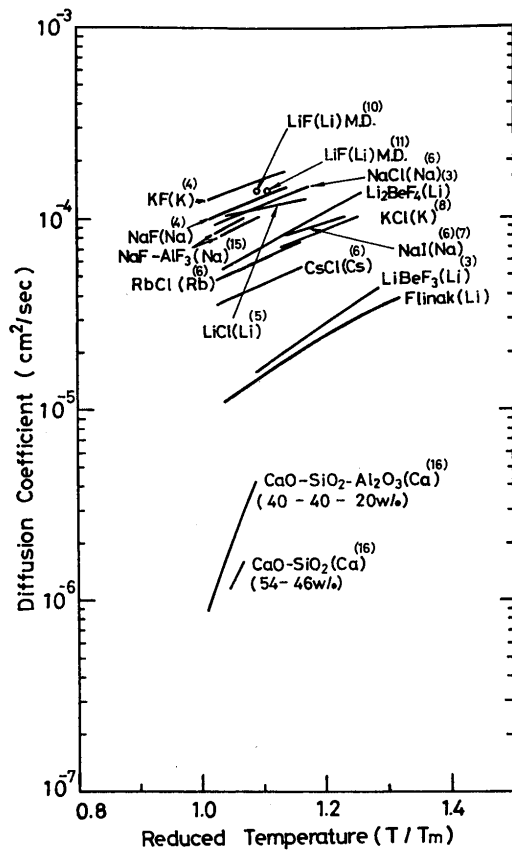


Fig. 4 Comparison of the self-diffusion coefficient of lithium in molten Flinak with those of cations in other molten alkali halides under the reduced temperature scale  $T/T_m$ . M.D. shows the diffusion coefficient calculated by molecular dynamics.

with those of anions and cations in other molten alkali halides<sup>11-17</sup>, respectively, under the reduced temperature scale  $T/T_m$ , where  $T_m$  is the melting point temperature. In spite of the similar values of  $D_0$  and  $E_D$  in molten Flinak to those in other molten alkali halides, it is seen that the diffusion coefficients of fluorine and lithium in molten Flinak are smaller than those of anions and cations in other molten alkali halides.

These phenomena will be corresponded to viscosity and electrical conductance. The comparison of the viscosity coefficients and electrical conductances of molten Flinak<sup>18</sup> and other alkali halides<sup>19,20</sup> are shown in Figs. 5 and 6, respectively, under the reduced temperature scale  $T/T_m$ . It is seen that the viscosity coefficient in molten Flinak is larger than those in other molten alkali halides, while the electrical conductance in molten Flinak is smaller. It is well known that the diffusion coefficient in a liquid is closely related to the viscosity coefficient by the Stokes—Einstein equation (5) and the electrical conductance by the Nernst—Einstein equation (6).

The Stokes—Einstein equation:

$$D_i = kT/a\eta r_i, \quad (5)$$

where  $D_i$  is the diffusion coefficient of a  $r_i$  radius particle moving in a medium having the viscosity

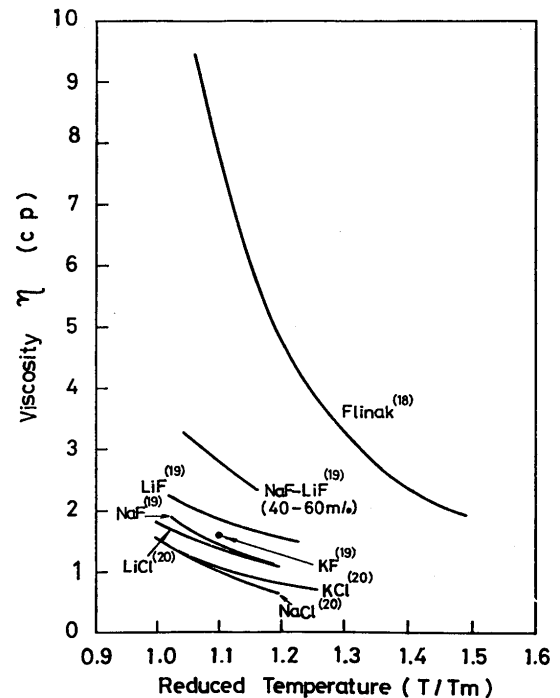


Fig. 5 Comparison of the viscosity coefficients of molten Flinak and other alkali halides under the reduced temperature scale  $T/T_m$ .

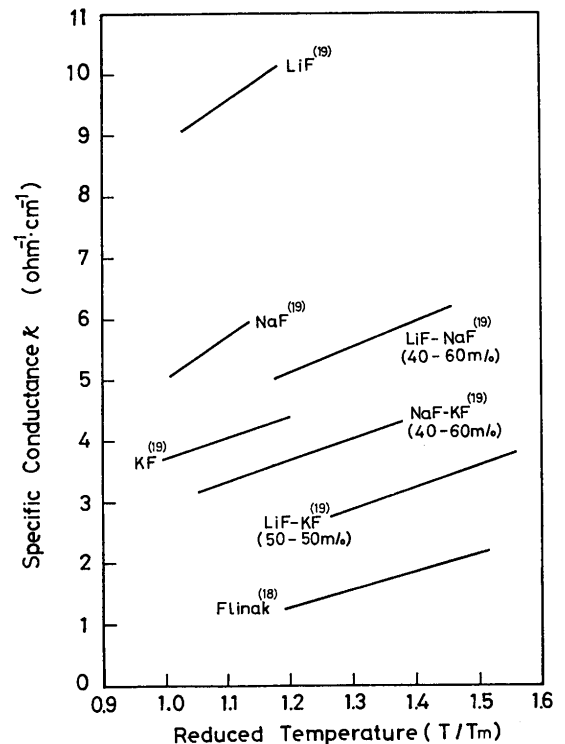


Fig. 6 Comparison of the electrical conductances of molten Flinak and other alkali halides under the reduced temperature scale  $T/T_m$ .

coefficient  $\eta$ ,  $a$  constant,  $k$  the Boltzman constant and  $T$  the absolute temperature.

The Nernst—Einstein equation:

$$D_+ + D_- = RTA^2/F^2, \quad (6)$$

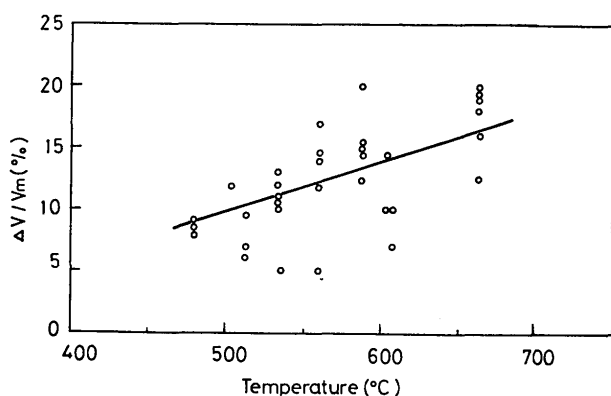
where  $D_+$  and  $D_-$  are the diffusion coefficients of cation and anion, respectively,  $A$  the equivalent conductance. The diffusion coefficient calculated from the latter relation (equation (6)) is shown in Fig. 2(c). As shown in Fig. 2, the value of  $(D_+ + D_-)$  is much larger than the calculated one at same temperature. It therefore seems that the diffusion without charge transfer such as ion pair, neutral coupled vacancy and cluster contributes largely in molten Flinak. Table 2 lists the activation energy for diffusion,

**Table 2** Activation energies of self-diffusion of fluorine and lithium, viscosity and electrical conductance in molten Flinak

Activation Energy (kcal/mole%)	
Diffusion	7.23 (F)
(our results)	8.88 (Li)
Viscosity <sup>(18)</sup>	8.25
Electrical Conductance <sup>(18)</sup>	1.74

viscosity<sup>(18)</sup> and electrical conductance<sup>(18)</sup> in molten Flinak. The activation energy for diffusion is much larger than for electrical conductance and approximately equal to that for viscosity. It is considered from this comparison that in molten Flinak the diffusion process is similar to the viscosity flow. It seems that the interaction between anion and cation is strong and furthermore molten Flinak contains something as cluster in addition to ion pair or neutral coupled vacancy mentioned above.

In alkali halide melts, the volume expansion always takes place and hence the holes are created in those melts. The volume change fraction  $\Delta V/V_m$  (%) in molten Flinak is shown in Fig. 7. The volume change  $\Delta V = V_m - V_s$  between the melt at the observed

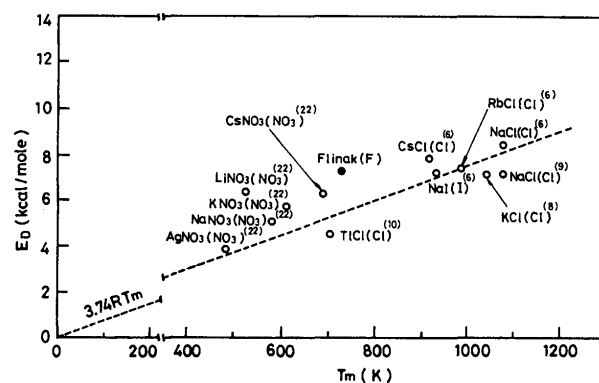


**Fig. 7** Temperature dependence of the fraction  $\Delta V/V_m$ .

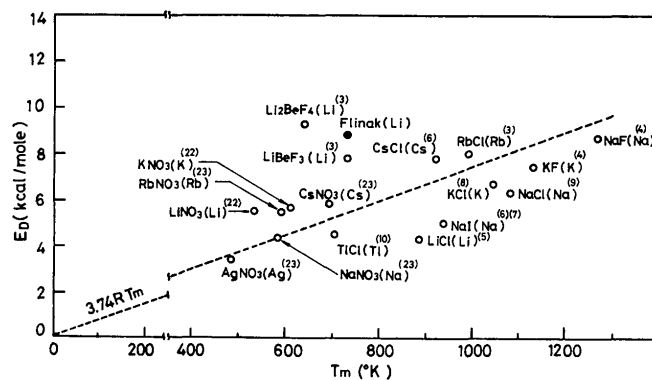
temperature ( $V_m$ ) and solid at room temperature ( $V_s$ ) can be roughly obtained by the distance from the mouth of the capillary where solid line intersects the zero activity. This figure shows that the volume change at the melting point temperature is about 5–10%. This value is smaller than that of other molten alkali halides such as LiF, NaF and KF and similar as that of molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$ . Furthermore, it seems that the diffusion behaviour in this study has not size effect of  $\text{F}^-$  and  $\text{Li}^+$  ionic radius ( $r_{\text{F}^-} = 1.36\text{\AA}$ ,  $r_{\text{Li}^+} = 0.6\text{\AA}$ ) as shown in Fig. 2. It is therefore supported that the contribution of holes to the diffusion of the constituent ions in molten Flinak is relatively smaller than that in other molten alkali halides. The activation energy for diffusion from hole theory<sup>(21)</sup> is given by

$$E_D = 3.74RT_m, \quad (7)$$

where  $T_m$  is the melting point temperature and  $R$  the gas constant. The comparison of observed  $E_D$  with calculated one for various anions and cations in some



**Fig. 8** Comparison of observed activation energy  $E_D$  with calculated values for anions in molten Flinak and some salts. Circles: observed values. Dotted line: calculated values.



**Fig. 9** Comparison of observed activation energy  $E_D$  with calculated values for cations in molten Flinak and some salts. Circles: observed values. Dotted line: calculated values.

molten salts<sup>1)~10),22),23)</sup> and Flinak are shown in **Figs. 8 and 9**. The values of  $E_D$  observed for fluorine and lithium in molten Flinak are larger than the calculated values.

The results in this study indicate that  $D_o$  and  $E_D$  of fluorine and lithium in molten Flinak are relatively similar to those of anions and cations in other molten alkali halides and also the interaction between anion and cation in molten Flinak is strong.

In previous paper<sup>1)~3)</sup>, it was described the result of unusually high self-diffusion coefficients and activation energies of fluorine in molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$ . This phenomena may be caused by the diffusion of HF gas introduced into the treatment of specimen except the rotation of complex beryllate anions suggested by us. If it is so, HF gas will lead to large diffusion coefficient. However, the result of fluorine in molten Flinak suggests that the contribution of HF gas impurity will be very little or not because the diffusion coefficient and activation energy of fluorine in molten Flinak treated in the same way as molten  $\text{Li}_2\text{BeF}_4$  and  $\text{LiBeF}_3$  are not large but rather similar to those of anion in molten alkali halides.

#### Acknowledgement

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