Title	Self-Diffusion of Fluorine and Lithium in Molten Flinak
Author(s)	Iwamoto, Nobuya; Tsunawaki, Yoshiaki; Umesaki, Norimasa et al.
Citation	Transactions of JWRI. 1978, 7(1), p. 5-10
Version Type	VoR
URL	https://doi.org/10.18910/11243
rights	
Note	

Self-Diffusion of Fluorine and Lithium in Molten Flinak†

Nobuya IWAMOTO*, Yoshiaki TSUNAWAKI, Norimasa UMESAKI***,**
Kazuo FURUKAWA** and Hideo OHNO******

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 ^{18}F *or* ^{6}Li *as the tracer. The results can be expressed as follows by the Arrhenius equation,*

$$D_F=1.63\times10^{-3}\exp(-7230/RT),$$

and

$$D_{Li}=3.85\times10^{-3}\exp(-8880/RT),$$

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

1. Introduction

Molten LiF-BeF$_2$ (especially Li$_2$BeF$_4$ and LiBeF$_3$) and LiF-NaF-KF (46.5–11.5–42.0 mole%) eutectic mixture are usefull materials as solvent for fissile (UF$_4$) and fertile (ThF$_4$) 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[1,2] and lithium[3] in molten Li$_2$BeF$_4$ and LiBeF$_3$. 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.

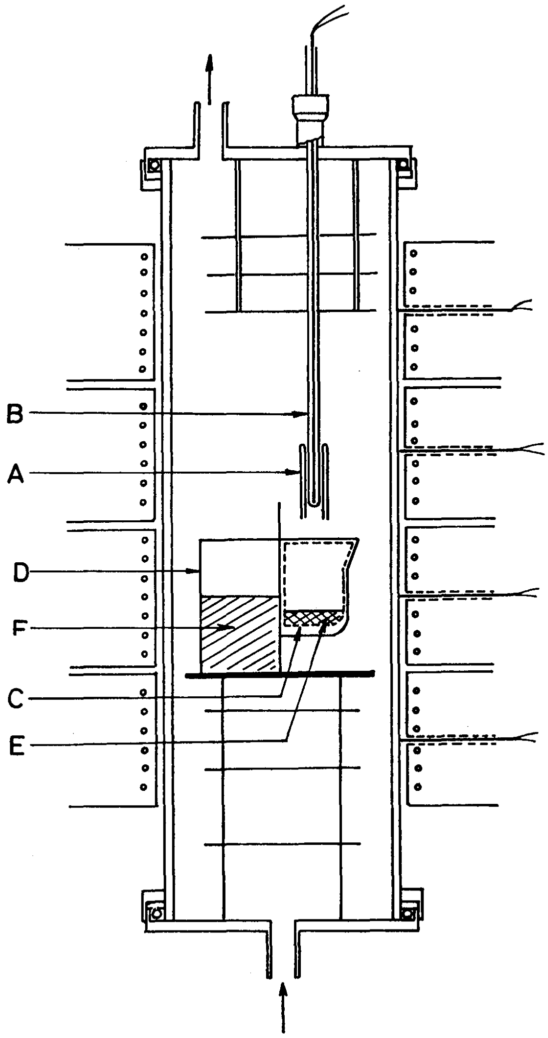

Fig. 1 A: Ni capillaries. B: Ni rod. C: Pt crucible. D: Ni crucible. E: labelled salt. F: non-labelled salt.

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 ^{18}F was prepared using JRR-3 (Japan Research Reactor-3). Highly purified Li$_2$CO$_3$ was used as a

---

† Received on March 31, 1978
* Professor
** Research Instructor
*** Graduate Student, Osaka University
**** Japan Atomic Energy Research Institute

target materials and the following reactions occured to proceduce ^{18}F.

$^{6}_{3}\mathrm{Li}(n, \alpha)^{3}_{1}T$ and $^{16}_{8}\mathrm{O}(T, n)^{16}_{9}F$.

After irradiation, Li_2CO_3 powder was treated with aqueous hydrogen fluorine in a platinum crucible to produce the labelled $Li^{18}F$ deposit. On the other hand, the lithium stable ^{6}Li was prepared using Li_2CO_3 powder which a ^{6}Li/^{7}Li abundance ratio of 19 and then Li_2CO_3 was treated with aqueous hydrogen in the same way as above mentioned.

The diffusion cell used in previous experiment$^{1)-3)}$ 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 innert 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 vaccum 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 °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}F and ^{6}Li in the capillaries were measured in the same way with γ-ray spectrometer and ion micro mass analyser (HITACH IMA-SS), respectively, as in the previous paper.$^{1)-3)}$

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}F or ^{6}Li were neglected in this study.

Diffusion coefficient D was calculated by the following equation,

$$C_x = C_o \, \mathrm{erf}(x/[2(Dt)^{1/2}]), \qquad (1)$$

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

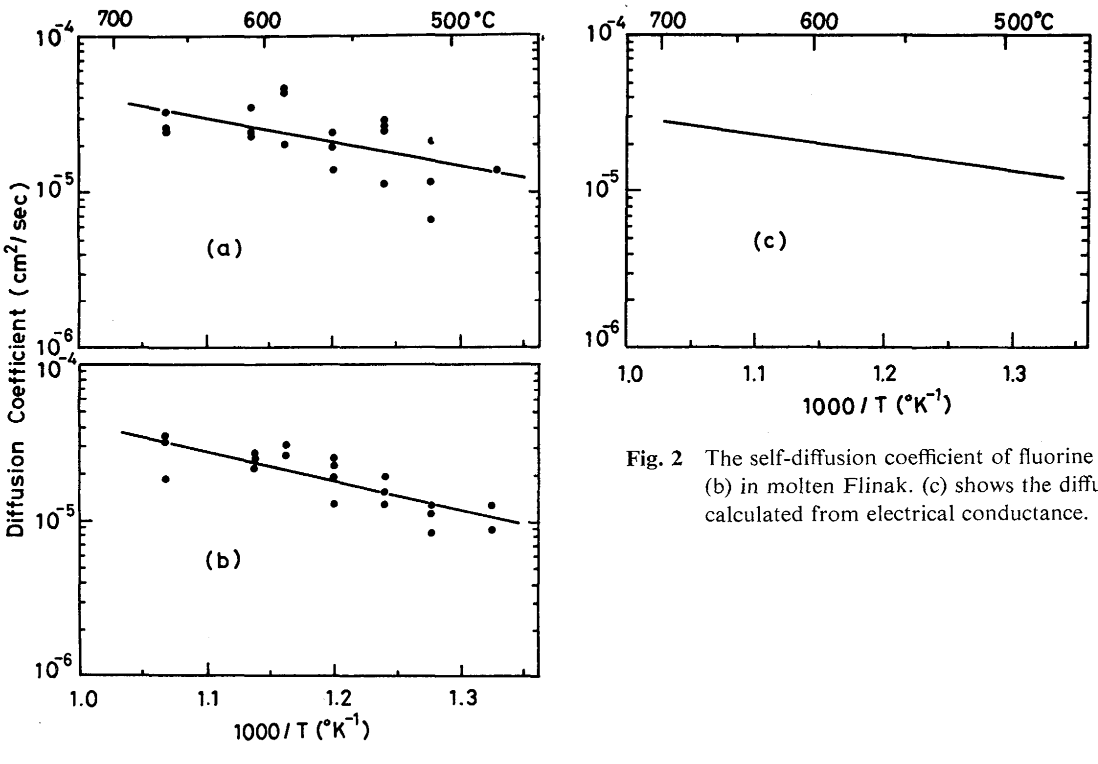

Fig. 2 The self-diffusion coefficient of fluorine (a) and lithium (b) in molten Flinak. (c) shows the diffusion coefficient calculated from electrical conductance.

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

$$D=D_o \exp(-E_D/RT), \qquad (2)$$

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,

$$D_F=1.63\times10^{-3} \exp(-7230/RT), \qquad (3)$$

and

$$D_{Li}=3.85\times10^{-3} \exp(-8880/RT). \qquad (3)$$

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_o and activation energy E_D of anions and cations in some molten alkali halides[4)~11)] together with those of present work. As shown in this table, it is seen 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. **Figs. 3** and **4** show the comparison of the diffusion coefficients of fluorine and lithium in molten Flinak

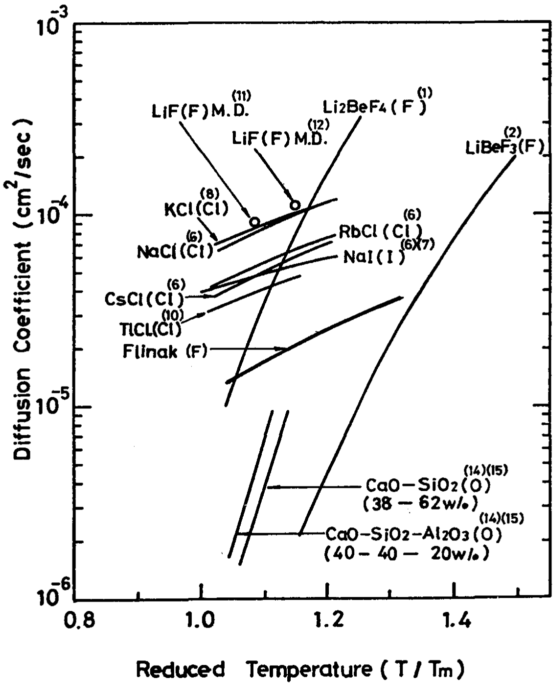

Fig. 3 Comparison of the self-diffusion coefficient of fluorine in molten Flinak with those of anions in other molten alkali halides under the reduced temperature scale T/T_m. M.D. shows the diffusion coefficient calculated by molecular dynamics.

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

System	Tracer	Do×10³ (cm²/sec)	E_D (Kcal/mole)	Temp. range (C)	Reference
Flinak	^{6}Li	3.85	8880		
	^{18}F	1.63	7230	460–660	present work
NaF	^{22}Na	3.08–0.06	8700–600	970–1160	
KF	^{42}K	2.46–0.06	7500–600	840–1060	(4)
LiCl	Li	1.03	4300	610–760	(5)
NaCl	^{22}Na	3.36	7860–110	830–990	(6)
	^{36}Cl	3.02	8390–40		
RbCl	^{86}Rb	2.51	8010–30	740–880	
	^{36}Cl	1.67	7420–70		
CsCl	^{134}Cs	1.73	7320–50	668–794	
	^{36}Cl	2.46	7820–80		
NaI	^{22}Na	0.63	4030–50	670–806	(7)
	^{131}I	0.43	4420–60		
KCl	^{42}K	1.8	6680	798–983	(8)
NaCl	^{22}Na	1.84–0.19	6320–360	830–1005	(9)
	^{36}Cl	1.83–0.38	7140–540	829–981	
	^{137}Cs	0.72–0.12	4830–320	672–879	
TlCl	^{204}Tl	7.3	4540–240	452–526	(10)
	^{36}Cl	0.79	4560–460	472–542	
LiF	Li	$D_{Li}=1.8\times10^{-4}$ (cm²/sec)		942	M.D. (11)
	F	$D_F=9.0\times10^{-5}$			
LiF	Li	$D_{Li}=1.36\times10^{-4}$		1014	M.D. (12)
	F	$D_F=1.13\times10^{-4}$			

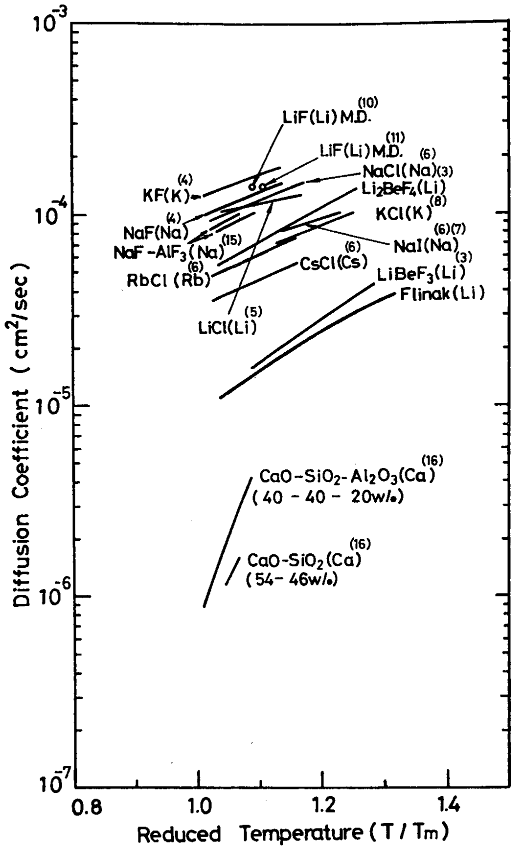

Fig. 4 Comparison of the self-diffusion coefficient of lithium in molten Flinak with those of cations in other molten alkali halides under the reduced temperature scale T/T_m. M.D. shows the diffusion coefficient calculated by molecular dynamics.

with those of anions and cations in other molten alkali halides[1)-17)], 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_o 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[18)] and other alkali halides[19),20)] 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:

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

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

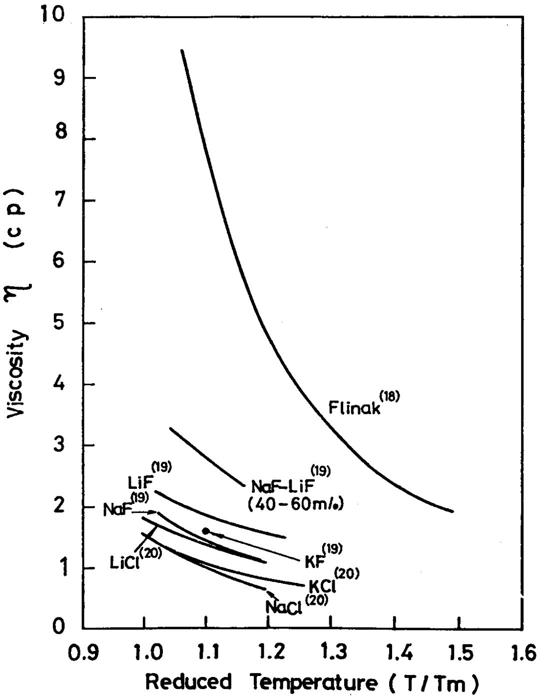

Fig. 5 Comparison of the viscosity coefficients of molten Flinak and other alkali halides under the reduced temperature scale T/T_m.

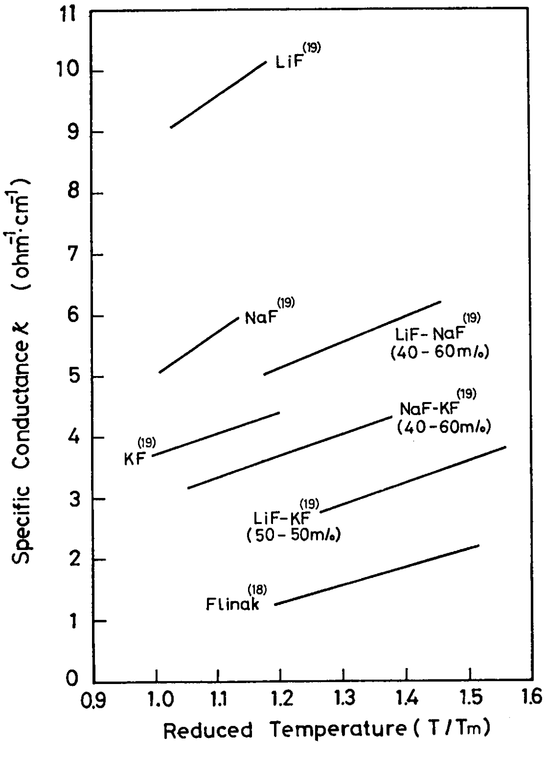

Fig. 6 Comparison of the electrical conductances of molten Flinak and other alkali halides under the reduced temperature scale T/T_m.

coefficient η, a constant, k the Boltzman constant and T the absolute temperature.

The Nernst—Einstein equation:

$$D_{+}+D_{-}=RT\Lambda^{2}/F^{2}, \qquad (6)$$

where D_+ and D_- are the diffusion coefficients of cation and anion, respectively, Λ 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, viscosity[18] and electrical conductance[18] 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 somethig as cluster in addition to ion pair or neutral coupled vacancy mentioned above.

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

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

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 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 Li_2BeF_4 and $LiBeF_3$. Furthermore, it seems that the diffusion behaviour in this study has not size effect of F^- and Li^+ ionic radius ($r_{F^-}=1.36$Å, $r_{Li^+}=0.6$Å) 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[21] is given by

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

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

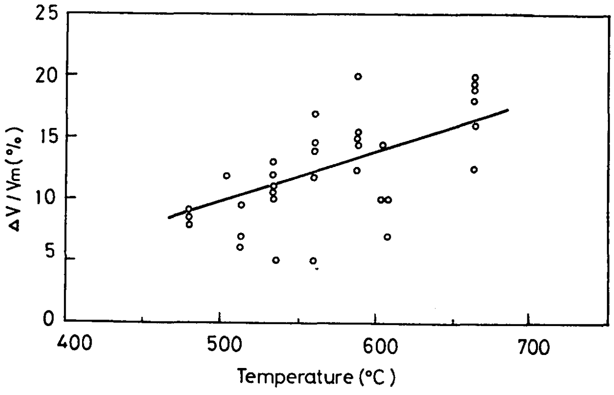

Fig. 7 Temperature dependence of the fraction $\Delta V/V_m$.

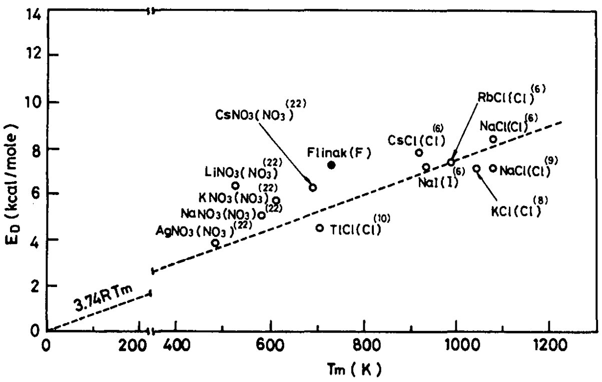

Fig. 8 Comparison of observed activation energy E_D with calculated values for anions in molten Flinak and some salts. Circles: observed values. Dotted line: calculated values.

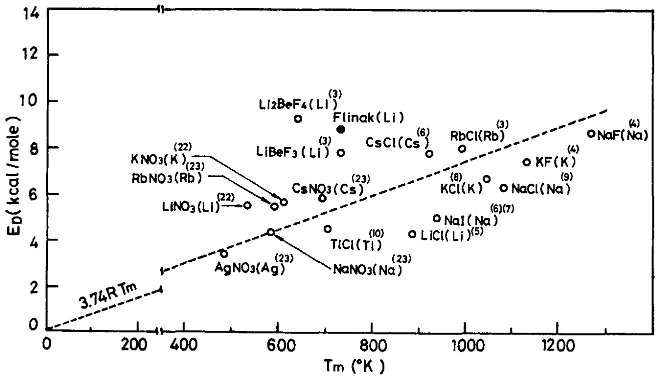

Fig. 9 Comparison of observed activation energy E_D with calculated values for cations in molten Flinak and some salts. Circles: observed values. Dotted line: calculated values.

molten salts[1)~10),22),23)] 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[1)~3)], it was described the result of unusually high self-diffusion coefficients and activation energies of fluorine in molten Li_2BeF_4 and $LiBeF_3$. 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 Li_2BeF_4 and $LiBeF_3$ are not large but rather similar to those of anion in molten alkali halides.

Acknowledgement

This work was partially supported by the Grant-in-Aid from Interdisciplinary Research Institute of Environmental Sciences.

References

1) H. Ohno, Y. Tsunawaki, N. Umesaki, K. Furukawa and N. Iwamoto: J. Japan Inst. Metals, 41 (1977), p. 391, (in Japanese).
2) H. Ohno, Y. Tsunawaki, N. Umesaki, K. Furukawa and N. Iwamoto: J. Chem. Soc. Farad. Trans. I, (to be published).
3) N. Umesaki, Y. Tsunawaki, H. Ohno, N. Iwamoto and K. Furukawa: J. Phys. Chem., (to be published).
4) K. Grjotheim and S. Zuca: Acta Chem. Scand., 32 (1968), p. 531.
5) R. Lenke, W. Uebelank and A. Klemm: Z. Naturforsch, 289 (1973), p. 881.
6) J.O'M. Bockris and G.W. Hooper: Disc. Faraday Soc., 32 (1961), p. 218.
7) S.B. Trickelebank, L. Nanis and J.O'M. Bockris: J. Phys. Chem., 68 (1964), p. 58.
8) J.O'M. Bockris, S.R. Richards and L. Nanis: J. Phys. Chem., 69 (1965), p. 1627.
9) T. Ejima, T. Yamamura and H. Hisamura: J. Japan Inst. Metals, 41 (1977), p. 742, (in Japanese).
10) C. Angel and W. Tomlinson: Trans. Faraday Soc., 61 (1965), p. 2321.
11) A. Rahman, R.H. Fowler and A.H. Narten: J. Chem. Phys., 57 (1972), p. 3010.
12) G. Ciccotti, G. Jacucci and I.R. McDonald: Phys. Rev. A, 13 (1976), p. 426.
13) D. Harari, F. Lantelme and M. Chmla: J. Chem. Phys. Physicochim. Biol., 66 (1969), p. 1286.
14) P.J. Kores and T.B. King: Trans. AIME, 224 (1962), p. 299.
15) Y. Oishi, R. Terai and H. Ueda, "Mass Transport Phenomena in Ceramics", A.R. Cooper and A.H. Heuer, Ed., Plenum Publishing Co., New York, N.Y., p. 297.
16) H. Towers and J. Chipman: Trans. AIME, 209 (1957), p. 769.
17) T. Saito and K. Maruyama: J. Japan Inst. Metals, 21 (1957), p. 728, (in Japanese).
18) S.I. Choen, W.D. Powers and N.D. Greene: ORNL-2150 (1956), p. 22.
19) G.J. Janz, G.L. Gardner, Ursula Krebs and R.P.T. Tomkins: J. Phys. Chem. Ref. Data, 3 (1974), p. 1.
20) G.J. Janz: "Molten Salt Handbook", Academic Press., New York, London, 1967, p. 52.
21) R. Furth: Proc. Cambridge Phil. Soc., 37 (1941), p. 252.
22) A.S. Dworkin, R.B. Escue and E.R. Van Arstdalen: J. Phys. Chem. 64 (1960), p. 872.
23) S. Zuca and M. Constantinescu: Rev. Roumaine Chim., 17 (1972), p. 385.