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Self-Diffusion of Lithium in Molten LiBeF_3 †

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Abstract

The self-diffusion coefficients of lithium in molten LiBeF_3 have been measured with the capillary reservoir technique using ^6Li as a tracer. The self-diffusion coefficients D were calculated from the concentration profiles of ^6Li in a capillary obtained by an ion micro mass analyser. The result can be described with the Arrhenius equation,

$$D = 1.12 \times 10^{-2} \exp(-9310 \pm 3000/RT),$$

where D is expressed in cm^2/sec , R in $\text{cal}/\text{mol-deg}$ and T in degree Kelvin. The self-diffusion coefficients of lithium in molten LiBeF_3 are smaller than those in molten Li_2BeF_4 . On the other hand, the activation energies are quite similar in molten Li_2BeF_4 and LiBeF_3 . These results suggest that lithium ion diffuses through narrow space between the complex anions keeping electrical neutrality.

1. Introduction

Molten alkali fluoroberyllates, especially $\text{LiF}-\text{BeF}_2$ mixture system, are useful materials as solvent for fissile (UF_4) and fertile (ThF_4) materials in Molten Salt Breeder Reactor (MSBR) and as blanket medium of D-T nuclear fusion reactors.^{1,2)} It has also been reported that the corresponding-state principle was established on molten alkali fluoroberyllates and alkaline-earth silicates and their physical properties in molten state, such as ionic packing densities (molar volumes), viscosity coefficients and equivalent conductivities had a simple quantitative relation between these two systems.³⁾

Molten BeF_2 with the network-type structure⁴⁾ of tetrahedral BeF_4 is highly viscous and the breakdown of the network-type structure with addition of alkali fluorides is indicated by the analysis of viscosity,⁵⁾ electrical conductance,⁶⁾ thermal expansivity⁷⁾ and enthalpy of mixing.⁸⁾

Our interest centers on how the diffusion behaviour of constituent ions, in particular the fluorine and lithium ions, in the molten $\text{LiF}-\text{BeF}_2$ system changes with composition of melts, because the diffusion coefficients give important informations to solve the dynamical structure of molten state and the chemical reaction process.

In previous papers,⁹⁻¹¹⁾ we presented self-diffusion coefficients and their temperature dependence for lithium in molten Li_2BeF_4 , and for fluorine in molten Li_2BeF_4 and LiBeF_3 . Their results for fluorine

showed the unusually high diffusion coefficients and activation energies, while those for lithium in molten LiBeF_4 were usually as low as cations in typical molten alkali halides.

In this paper, the self-diffusion coefficients of lithium in molten LiBeF_3 were investigated to get the more precise interpretation of ionic transport properties in molten mixtures of beryllium fluoride with alkali fluorides.

2. Experimental Procedures

All experimental procedures were almost the same as described in the previous paper.¹¹⁾ LiBeF_3 labelled with ^6Li ($^6\text{Li}/^7\text{Li}$ abundance ratio=19) was used as filling into a Ni capillary of which the length was about 30 or 40 mm and the inner diameter was about 1 mm. After the diffusion run for about 50 minutes, the capillary was cut at intervals of about two millimeters. The concentrations of ^6Li and ^7Li at the surface of their sections were measured by ion micro mass analyser (HITACH IMA-SS). The operational condition of ion micro mass analyser was as follows:

primary ion beam	: Ar
ion beam energy	: 5 KeV
beam diameter	: 500 μm

In order to avoid the electrical charging due to the insulating property of LiBeF_3 , electrons from a tungsten filament were showered onto the specimen,

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It was assumed that the ratio of ${}^6\text{Li}^+/({}^6\text{Li}^+ + {}^7\text{Li}^+)$ gave the concentration profile of ${}^6\text{Li}$ in a capillary because the values obtained of ${}^6\text{Li}^+/({}^6\text{Li}^+ + {}^7\text{Li}^+)$ accorded with the natural abundance (0.074) and enriched abundance (0.95) at the mouth of the capillary and the nondiffused portion, respectively.

3. Results

The typical concentration profile of ${}^6\text{Li}$ in a capillary is shown in Fig. 1. Diffusion coefficient D was calculated by the following equation,

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

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

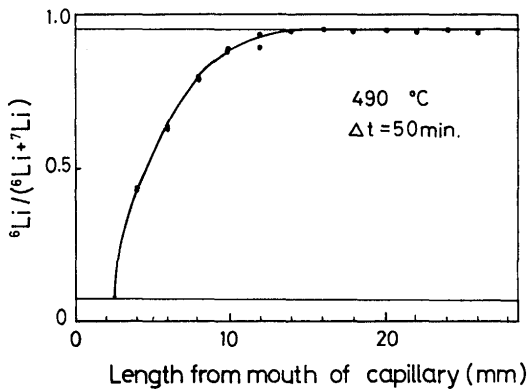


Fig. 1 Distribution of ${}^6\text{Li}$ in a capillary after a diffusion run LiBeF_3 , temperature: 490°C , diffusion time: 50 min., capillary length: 30 mm

The results of the experiments (solid circle) in molten LiBeF_3 are given in Fig. 2. The diffusion coefficients of lithium are written in the form

$$D = D_0 \exp [-E_D(\text{Li})/RT], \quad (2)$$

where $E_D(\text{Li})$ is the activation energy of lithium diffusion, R the gas constant, and T the absolute

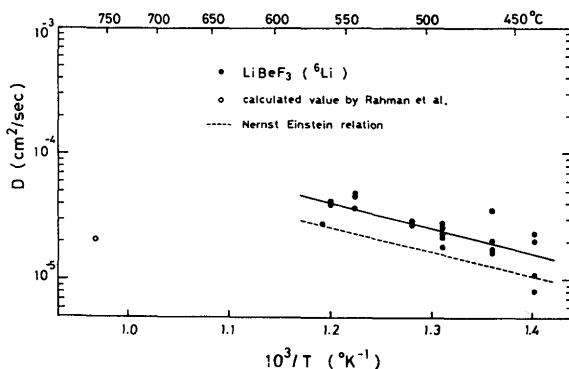


Fig. 2 Diffusion coefficients of lithium (solid line) in LiBeF_3 melt and a calculated value at 1035°K (open circle) by Rahman et al.¹²⁾ Dashed line shows diffusion coefficient calculated from electrical conductivity.

temperature. The following result was obtained by least squares from all experimental data,

$$D = 1.12 \times 10^{-2} \exp (-9310 \pm 3000/RT) \quad (3)$$

The open circle in Fig. 2 shows the diffusion coefficient of lithium in molten LiBeF_3 calculated from molecular dynamics by Rahman et al.¹²⁾

The dashed line in Fig. 2 shows the diffusion coefficient obtained from the electrical conductance of molten LiBeF_3 using Nernst-Einstein relation,¹³⁾

$$D = \sigma KT / (Ze)^2 n, \quad (4)$$

where σ is electrical conductance, K Boltzmann constant, Z charge number of diffusion ion, e electron charge, n number of ions per unit volume, T absolute temperature. The values of σ was after Robbins et al.⁶⁾

4. Discussions

Molten BeF_2 has network-type structure in which tetrahedral BeF_4 units are bridged at corners.⁴⁾ The addition of LiF to molten BeF_2 indicates the breakdown of the network-type structure of BeF_2 ⁵⁾ and it is expected to exist independent anions, such as BeF_4^{2-} and $\text{Be}_2\text{F}_7^{3-}$ in molten Li_2BeF_4 and LiBeF_3 .^{4,14,15)} Unusually high diffusion coefficients and activation energy of fluorine in molten $\text{LiF}-\text{BeF}_2$ mixture seem to be attributed to the movement accompanying both the rotation of large fluoroberyllate complex anions and the exchange of fluorine between neighbouring anions,^{9,10)} as shown in Fig. 3. On the other hand, the comparison of the self-diffusion coefficients of lithium in molten Li_2BeF_4 and LiBeF_3 with those of cations in molten alkali halides and molten silicates under the reduced temperature scale (Fig. 3 in ref. (11)) shows the self-diffusion coefficients and the activation energy of lithium in molten Li_2BeF_4 have the similar behaviour to those of cations in molten alkali halides.

In molten LiBeF_3 , the activation energy of lithium has nearly equal value to that in molten Li_2BeF_4 . But the self-diffusion coefficients of lithium in molten LiBeF_3 are about one third smaller than those in molten Li_2BeF_4 . This will be due to smaller probability of exchange between the neighbouring lithium keeping electrical neutrality because of the small amount of lithium contained in molten LiBeF_3 or the large jumping distance of lithium because of larger complex anions comparing with Li_2BeF_4 system. If the activation process is regarded as the movement of lithium through a narrow space between the complex anions, it seems reasonable that the both activation

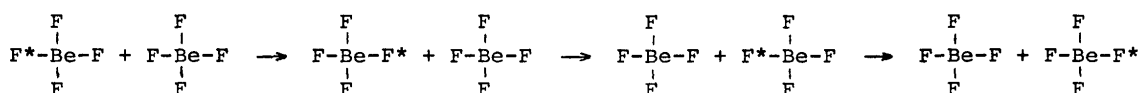


Fig. 3 Schematic diffusion process of fluorine in molten Li₂BeF₄ and LiBeF₃. Asterisk expresses a tracer ion of fluorine.

energies on Li₂BeF₄ and LiBeF₃ show approximately equal value. These phenomena consist with the result of the electrical mobility of lithium in molten LiF-BeF₂.¹⁶⁾ Dotted line in Fig. 2 shows the diffusion coefficient of lithium calculated by equation (4) with the electrical conductance in molten LiBeF₃. The observed diffusion coefficients of lithium are larger than those of calculated one in this molten salts, and the differences are much larger than those in typical molten alkali halides, such as NaCl¹⁷⁾ and NaF.¹⁸⁾

It is noticed in Fig. 2 that the self-diffusion coefficient of lithium in molten LiBeF₃ calculated using molecular dynamic method by Rahman et al.¹²⁾ does not agree with our self-diffusion coefficient extrapolated at 762°C. The observed self-diffusion coefficients of fluorine were not consistent with their calculated one, too. This will be due to that the molecular dynamics calculation of them is not so enough to reflect the exact diffusion mechanism of various elements in molten LiBeF₃ because the model used in the calculation is too small (32 molecules of LiBeF₃) and the periodic boundary condition restricts too much the movement of constituent atoms and ions, especially the rotation of large complex anions such as BeF₄²⁻ and Be₂F₇³⁻ which exist stably in the melt.

In previous papers,^{9,10)} it was reported that the behaviour of oxygen in molten lime-silica-alumina slag^{19,20)} is qualitatively similar to those of fluorine in molten Li₂BeF₄⁹⁾ and LiBeF₃.¹⁰⁾ In order to discuss more precisely the relation of self-diffusion behaviour of various constituent ions of molten fluoroberyllates and molten silicates, it will be necessary to obtain the self-diffusion coefficients of Be in LiF-BeF₂ mixture, Na, F and Be in NaF-BeF₂ mixture and Mg, Si and O in MgO-SiO₂ system.

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