

# Self-Diffusion in Molten Lithium Nitrate

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Z. Naturforsch. **47a**, 1047–1050 (1992); received July 16, 1992

Self-diffusion coefficients of  ${}^7\text{Li}^+$  ions have been measured in molten  $\text{LiNO}_3$  with several compositions of  ${}^6\text{Li}^+$  and  ${}^7\text{Li}^+$  over a temperature range from 537 to 615 K. The NMR spin-echo method with pulsed field gradients was applied. It was found that the self-diffusion coefficient depends on the isotopic composition and shows a maximum at equimolar ratio. At temperatures above 600 K this behaviour disappears.

**Key words:** Molten salts, Self-diffusion, Isotope effect, NMR spin-echo.

## Introduction

It is evident from spectroscopic X-ray [1–3] and neutron diffraction [4–6] measurements that molten lithium nitrate shows a special behaviour among the alkali metal nitrates. This is mainly due to the smaller size and mass of the  $\text{Li}^+$ -ion, its high polarizing power and the stronger cation-anion interactions as compared with other alkali cations. To improve our understanding of molten salt dynamics the transport properties of molten  $\text{LiNO}_3$  are of particular interest, and we deal with self-diffusion in this paper.

There is only one set of experimental data on self-diffusion in molten  $\text{LiNO}_3$  obtained by the tracer capillary method [7] using the stable isotope  ${}^6\text{Li}$  as tracer. Some molecular dynamics simulation studies on molten  $\text{LiNO}_3$  have been published [8–10]. These simulations have been focused upon the dynamics of the nitrate ion by using a rigid-anion [8] and vibrating-anion [9, 10] model of  $\text{LiNO}_3$ . In the simulations performed by Yamaguchi et al. [8] the simulated translational diffusion of  $\text{Li}^+$  was too slow as compared with the experimental one. The simulation result of  $2.93 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$  obtained by Kato et al. [9, 10] for the  $\text{Li}^+$  self-diffusion coefficient in molten  $\text{LiNO}_3$  at 620 K is in very good agreement with tracer measurements [7]. In the last simulations performed by Kato et al. [10] an interionic potential well of varying depth between  $\text{Li}^+$  and oxygen of  $\text{NO}_3^-$  was added to the standard potential (Coulomb plus repulsion) and it was found that the simulated diffusion coefficient strongly depends on this interionic potential. So far,

molecular dynamics simulations on  $\text{LiNO}_3$  are not available in which the mass of the ions was varied. Recently, a structural study by neutron diffraction measurements has been carried out on  $\text{LiNO}_3$  melts by changing the isotopic composition of either the Li or the N nucleus [11]; the intramolecular structure of  $\text{NO}_3^-$  has been determined and a local structure of four nitrate ions around  $\text{Li}^+$  was deduced.

The self-diffusion coefficients measured by isotopic tracer techniques refer to the mutual motion of a tracer in an unmarked diffusion medium and may be influenced by tracer isotope effects, which in the case of small diffusing species such as H, D or Li could be appreciable. The mass dependence of the ion dynamics in molten salts was studied by Lantelme et al. [12] through molecular dynamics experiments on  $\text{LiBr}$  with variable masses of Li, and expressions are derived to represent the mass effect on the self-diffusion coefficients.

In order to obtain a direct experimental evidence of the isotopic mass effect on the diffusive motion in liquids the NMR technique is particularly well suited for self-diffusion measurements. By means of the NMR spin-echo method the  ${}^1\text{H}/{}^2\text{H}$  isotope effect on water diffusion was well established [13, 14], while for the  ${}^6\text{Li}/{}^7\text{Li}$  pair in aqueous solution the isotope effect is found to be negligible [15, 16]. Regarding the isotope effects in molten salts, the  ${}^6\text{Li}/{}^7\text{Li}$  pair is of interest but experiments on this matter were done only on ionic mobilities and not on self-diffusion. The mass effect for electromigration of lithium ions in molten  $\text{LiNO}_3$  was detected [17–19] by measuring the relative difference between the internal mobilities of  ${}^6\text{Li}$  and  ${}^7\text{Li}$ . Information about the isotope effects could be obtained by measuring self-diffusion coefficients of both isotopes

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in  ${}^6\text{LiNO}_3/{}^7\text{LiNO}_3$  over the whole composition range. The comparative measurement of the self-diffusion coefficients of isotopic ions allows to isolate the effect of mass on the diffusive motion since the interaction potentials remain constant. The two stable isotopes  ${}^6\text{Li}$  and  ${}^7\text{Li}$  have spin 1 and 3/2, respectively. It is possible to apply the NMR technique both for  ${}^6\text{Li}$  and  ${}^7\text{Li}$ . In this work the NMR spin-echo method with pulsed magnetic field gradient [20] has been applied to measure the  ${}^7\text{Li}^+$  self-diffusion coefficient  $D$  in  ${}^6\text{LiNO}_3/{}^7\text{LiNO}_3$  at different compositions. Self-diffusion experiments observing  ${}^6\text{Li}$  NMR signals are in progress in our laboratory.

## Experimental

The experiments have been carried out with a home-built probe head observing the  ${}^7\text{Li}$  nucleus at a resonance frequency of 116.64 MHz on a Bruker CXP-300 spectrometer equipped with a superconducting magnet ( $B_0 = 7$  T) having a 89 mm wide gap. Details of the apparatus and the experimental procedure were basically the same as in our previously published work on self-diffusion in molten  $\text{NaNO}_3$  [21]. Some points are briefly described below.

Lithium nitrate with lithium in natural abundance (Aldrich Chemical Co. reagent grade) of 99.9% purity was directly used for the NMR measurements after drying as described below.  ${}^6\text{LiNO}_3$  and  ${}^7\text{LiNO}_3$  were prepared from  ${}^6\text{Li}_2\text{CO}_3$  of 99.5 atom%  ${}^6\text{Li}$  and  ${}^7\text{Li}_2\text{CO}_3$  of 99.9 atom%  ${}^7\text{Li}$ , respectively, both from Isotec Inc., by reaction with  $\text{HNO}_3$ . They were recrystallized twice from aqueous solution.

The samples were contained in quartz cells of 30 mm length, 8 mm outer diameter and 1.5 mm wall-thickness. Since lithium nitrate is very hygroscopic special attention was taken to keep the salt dry. The cells filled with salt corresponding to about 1  $\text{cm}^3$  melt were dried by heating under vacuum for about five hours at temperatures ranging from 350 to 520 K. They were finally heated above the melting temperature and sealed under vacuum to avoid any absorption of water. The sample was allowed to cool down slowly to room temperature in the heating unit. With each sample placed inside the probehead NMR measurements could be repeated as desired without damage of the sample when the heating and cooling process was carefully controlled. The temperature, maintained with  $\pm 0.2$  K throughout the experiments,

was measured near the sample tube by a Pt–Pt/Rh thermocouple.

The  ${}^7\text{Li}$  signal attenuation from the echo maximum  $M(2\tau, g)$  at time  $2\tau$  in the presence of a magnetic field gradient of strength  $g$  was recorded as a function of the gradient pulse length  $\delta$ . The radio frequency 90°-pulse, which was produced by a coil with two windings of silver wire, was 18  $\mu\text{s}$  long. The field gradient was produced by a quadrupolar coil described previously [21]. The time intervals between the 90° and 180° radio frequency pulses,  $\tau$ , and between the gradient pulses,  $\Delta$ , were set to 20 ms. The signal amplitudes from two scans were added for each gradient pulse length using a pulse repetition time of 120 s. The self-diffusion coefficient  $D$  of  ${}^7\text{Li}^+$  having the gyromagnetic ratio  $\gamma$  was calculated from the fit of equation

$$M(2\tau, g) = M(2\tau, g=0) \exp[-\gamma^2 g^2 D \delta^2 (\Delta - \delta/3)] \quad (1)$$

to the echo maximum using 28 signals with  $\delta$  values between 0.5 and 8 ms. To evaluate the diffusion coefficient it is necessary to know the gradient strength  $g$ , which was determined with a substance of known  $D$ . In lack of an established reference sample for molten salts we chose  $\text{NaNO}_3$  for which  $D$  values were obtained by us previously through NMR spin-echo measurements [21]. These values are in good agreement with those from the tracer capillary technique [7]. Furthermore, the resonance frequencies of 79.38 MHz for  ${}^{23}\text{Na}$  and of 116.64 MHz for  ${}^7\text{Li}$  can be observed with the same probe head modified only in the capacity of the resonance circuit.

Gradient calibration was performed under the same experimental conditions with respect to pulse sequence parameters, sample geometry and location, as in the actual experiments. Thus, possible experimental errors due to the presence of background gradients, effects of rise and fall times or those of residual gradients are included in the actual  $g$  value. Before gradient calibration the spin echo shape of molten  $\text{NaNO}_3$  was analysed as a function of  $\delta$ ,  $\tau$ , field gradient current  $I$  and temperature  $T$ . A small correction  $\delta'$ , in the microsecond range, was needed for the time duration of the second pulse gradient in order to obtain a symmetric shape of the spin echo. It is found that this delay depends on  $\tau$  but not on  $I$  and  $T$ , and for  $\tau = 20$  ms the correction term is given by

$$\delta'/\text{s} = 2.67794 (\delta/\text{s})^2 - 1.08692 \times 10^{-3} (\delta/\text{s}) + 1.02495 \times 10^{-6}. \quad (2)$$

Table 1. Self-diffusion coefficient of  ${}^7\text{Li}^+$  in molten  $\text{LiNO}_3$  as function of  ${}^7\text{LiNO}_3$  content and temperature.

Pure ${}^7\text{LiNO}_3$		Natural ${}^7\text{LiNO}_3$ $x_1 = 0.927$		${}^6\text{LiNO}_3(x_1) + {}^7\text{LiNO}_3$ $x_1 = 0.5$		${}^7\text{LiNO}_3(0.3) + {}^6\text{LiNO}_3$ $x_1 = 0.3$	
T/K	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$	T/K	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$	T/K	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$	T/K	$D/10^{-9} \text{ m}^2 \text{ s}^{-1}$
539	1.56	538	1.54	534	1.57	537	1.53
546	1.66	543	1.57	539	1.63	543	1.61
558	1.79	551	1.71	550	1.82	545	1.68
571	2.00	560	1.82	552	1.84	556	1.84
576	2.07	571	2.00	556	1.94	561	1.90
590	2.44	573	2.04	564	2.10	571	2.07
599	2.50	583	2.25	566	2.12	573	2.10
605	2.71	589	2.42	573	2.16	579	2.17
		607	2.75	575	2.21	589	2.39
		613	2.92	576	2.25	590	2.47
				599	2.66	604	2.54
						607	2.70
						615	2.81

The gradient strength  $g$  measured at currents between 3 and 5.5 A and in the temperature range from 593 to 643 K lies between  $0.6726$  and  $1.2331 \text{ Tm}^{-1}$ . Since the value of the specific gradient  $g^* = g/I = 0.2242 \text{ Tm}^{-1} \text{ A}^{-1}$  remains constant with temperature no correction factor was applied. For the value of  $g^*$  used in the present work the error introduced in the calculation of  $D$  is less than 1%. In order to set the repetition time of the spin-echo pulse sequence the spin lattice relaxation time  $T_1$  was also measured by application of the standard  $180^\circ - \tau - 90^\circ$  pulse sequence.  $T_1 = 18.5 \text{ s}$  was found for  ${}^7\text{Li}$  in molten pure  ${}^7\text{LiNO}_3$  at 558 K.

The diffusion measurements were performed from just above the melting point of  $\text{LiNO}_3$  (528 K) over a temperature range of 80 K. The  $D$  values are considered to be accurate to  $\pm 5\%$ . The reproducibility between runs was  $\pm 1\%$ .

## Results

The self-diffusion coefficient of  ${}^7\text{Li}^+$  was measured as function of temperature for four  $\text{LiNO}_3$  melts of the following isotopic compositions: 100%  ${}^7\text{LiNO}_3$ , natural  $\text{LiNO}_3$  which contains 92.7%  ${}^7\text{LiNO}_3$ , equimolar composition and 30%  ${}^7\text{LiNO}_3$ . The results are given in Table 1 and are plotted in Figure 1. Diffusion values are the result of at least three sets of measurements performed in experimental series with both decreasing and increasing temperatures.

It can be seen that the  $D$  values for  ${}^7\text{Li}^+$  are slightly dependent on the isotopic composition and they are larger for the equimolar mixture than for the mixture containing 70%  ${}^6\text{LiNO}_3$ . As the temperature in-

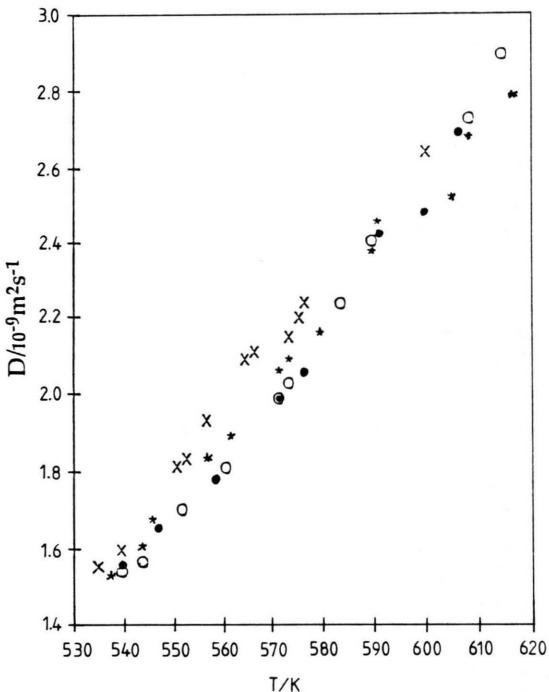


Fig. 1. Self-diffusion coefficients of  ${}^7\text{Li}^+$  in  $\text{LiNO}_3$  melts as function of temperature. ● pure  ${}^7\text{LiNO}_3$ ; ○ natural  $\text{LiNO}_3$ ;  $\times$   ${}^6\text{LiNO}_3(0.5) + {}^7\text{LiNO}_3$ ;  $*$   ${}^7\text{LiNO}_3(0.3) + {}^6\text{LiNO}_3$ .

creases the differences in  $D$  decrease and at temperature above 600 K there is no experimentally significant change of  $D$  in  $\text{LiNO}_3$  with different isotopic composition. Over the range of temperatures at which  $D$  was measured results may be expressed in the form of the Arrhenius equation  $D = A \exp(-E_D/RT)$ . The values of the activation energy  $E_D$  and the preexponential factor  $A$  are given in Table 2.

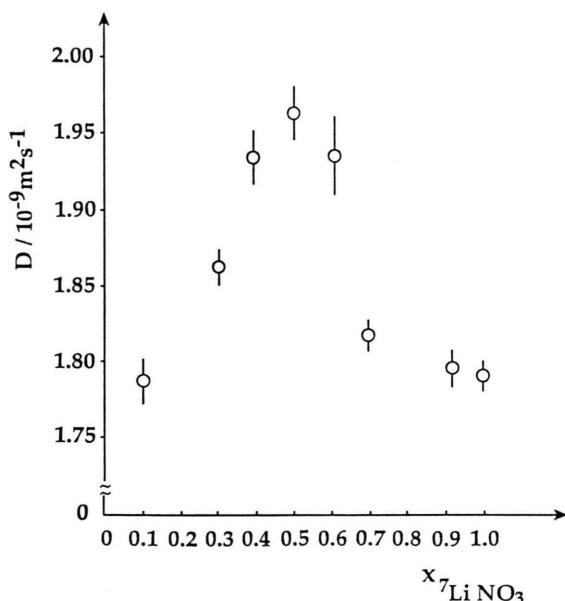


Fig. 2. Self-diffusion coefficients of  ${}^7\text{Li}^+$  in mixture  ${}^7\text{LiNO}_3 + {}^6\text{LiNO}_3$  as a function of  ${}^7\text{LiNO}_3$  composition at 558 K.

In another series of experiments  $D$  was measured at a fixed temperature of 558 K, where the concentration was varied from pure  ${}^7\text{LiNO}_3$  ( $x_1 = 1$ ) to 0.1 mole fraction  ${}^7\text{LiNO}_3$ . As Fig. 2 shows,  $D$  values are found to be larger at mole fractions around  $x_1 = 0.5$ . At  $x_1 = 0.1$  the self-diffusion coefficient has the same value again as in pure  ${}^7\text{LiNO}_3$ .

$D$  depends on isotopic composition in an unexpected way, it does not increase gradually as the concentration in  ${}^6\text{LiNO}_3$  increases. It was expected that due to

Table 2. Arrhenius parameters for  ${}^7\text{Li}^+$  self-diffusion in  $\text{LiNO}_3$  melts.

Melt	Temp. range/K	$E_D / \text{kJ mol}^{-1}$	$A / 10^{-7} \text{m}^2 \text{s}^{-1}$
Pure ${}^7\text{LiNO}_3$	539–605	$22.49 \pm 0.96$	2.32
Natural $\text{LiNO}_3$	538–613	$23.61 \pm 0.69$	2.96
${}^7\text{LiNO}_3(0.5) + {}^6\text{LiNO}_3$	534–599	$20.65 \pm 0.90$	1.68
${}^7\text{LiNO}_3(0.3) + {}^6\text{LiNO}_3$	537–615	$21.28 \pm 0.56$	1.82

the mass difference between the two isotopes the diffusion of  ${}^7\text{Li}^+$  should be favoured in presence of light isotope  ${}^6\text{Li}^+$ , specially at high  ${}^6\text{LiNO}_3$  concentrations. If the system consists of a mixture of  ${}^6\text{Li}^+$  and  ${}^7\text{Li}^+$  isotopes, at any instant the local distribution around any nitrate ion is identical as far as shape and charge are concerned. Also the polarisation of  $\text{NO}_3^-$  by  $\text{Li}^+$  is the same for both  ${}^6\text{Li}$  and  ${}^7\text{Li}$ . There exists only a difference in mass of the lithium ions. Therefore the cause of the observed behaviour is difficult to interpret. Additional data on  ${}^6\text{Li}^+$  will be useful in order to get more information about the relative self-diffusion behaviour of the two lithium isotopes. Therefore, a detailed discussion of the isotope effect on lithium ion diffusion will be postponed. It will be helpful to study the isotopic mass effect also in molecular dynamics simulation.

#### Acknowledgement

Financial support from Deutsche Forschungsgemeinschaft and Fonds der Chemischen Industrie is greatly appreciated.

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