

# Spin Echo Self-Diffusion Measurements in Molten Salts

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An NMR probe head for diffusion measurements in molten salts at temperatures up to 673 K is described. The spin echo technique using pulsed magnetic field gradients was employed. Resulting self-diffusion coefficients of  $\text{Na}^+$  in molten  $\text{NaNO}_3$  in the temperature range 596–670 K are compared with literature data obtained by other methods.

## Introduction

Several methods (electrical, optical, gravimetric, radioactive and stable tracers) have been developed to perform diffusion measurements in molten salts. However, in comparison with other transport properties the agreement between the results is poor, and it is difficult to decide which of the methods is to be preferred.

A critical examination of diffusion data and a review of the experimental techniques is reported by Janz et al. [1]. The capillary method using radioactive tracers [2, 3] has been found to be suitable for a large temperature range (up to 1100 °C), for high pressures and for corrosive molten salts. Its disadvantage is the long diffusion period (hours!) required because convection could interfere.

Another way for measuring the self-diffusion coefficient is by means of nuclear magnetic resonance (NMR) techniques. While the NMR technique has been widely applied to study diffusion processes of normal liquids, solids or colloidal systems, there are only few contributions to molten salts. NMR line-width measurements were employed for some preliminary diffusion investigations in molten LiI [4]. Both pulsed and steady state NMR have been used in studies of ionic crystals up to the melting point [5] and in liquid Li [6, 7].

Among the different NMR techniques the spin echo method employing a pulsed field gradient, as demonstrated for the first time by Stejskal and Tanner [8], permits a direct measurement of self-diffusion, and this has been used by several investigators for a wide variety of systems. To our knowledge no results for

molten salts using this method have been reported in the literature. It is our aim to extend the spin echo self-diffusion method with pulsed field gradients to molten salts.

There are several advantages of the spin echo method. The duration of each run for a diffusion experiment is short (minutes!), the diffusion process can be studied *in situ*, i.e. without disturbing or interrupting the process under study, and there is no need to set up and maintain a concentration gradient. Furthermore an unlimited number of runs can be performed and the repetition of each run is possible. Contrary to other methods, no radioactive tracers or chemical analysis are necessary. Only a small amount of sample (about 1 cm<sup>3</sup>) is needed, so that temperature control is straightforward, and the sample cell can be of rather simple construction. Due to differences in nuclear Larmor frequencies it is possible to measure the self-diffusion coefficient for single species in any complicated system. Finally, all experiments can be entirely performed under computer control.

In this paper we describe in detail an NMR probe head that can be used up to 673 K. Preliminary experimental results for  $\text{Na}^+$  in molten  $\text{NaNO}_3$  as a function of temperature will be given.

We have chosen sodium nitrate because the temperature region for the measurements is easily accessible experimentally. The sodium nucleus gives quite a sensitive resonance signal, and a large number of experimental data on self-diffusion is available in the literature, allowing comparisons between various methods.

## Method of Measurement

In the NMR spin echo method a sample of nuclei is placed in a magnetic field gradient  $\partial B/\partial z$ , applied

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along the static magnetic field  $B_0$ . The spin echo experiment based on a  $90^\circ$ – $\tau$ – $180^\circ$  radio frequency (rf) pulse sequence first described by Hahn [9] is modified by adding the magnetic field gradient either in a steady [10] or pulsed [8] manner. The NMR signal generated at a fixed time  $2\tau$  is the spin echo, its amplitude is observed as function of the applied field gradient.

The presence of the magnetic field gradient causes differences in resonance frequency between nuclear spins of the same species due to their spatial displacements by diffusional processes. The diffusing nuclei will have different precession frequencies, i.e. different Larmor frequencies  $\omega_0$ , which are determined by the applied static magnetic field  $B_0(z)$ , their position in the field gradient  $z\partial B/\partial z$ , and the gyromagnetic ratio  $\gamma$ , specific for each nucleus, through the relation  $\omega_0 = \gamma(B_0 + z\partial B/\partial z)$ . Accordingly, complete refocusing of the magnetization to form the echo is no longer possible and a decrease of the echo amplitude is observed. The variant of the pulsed field gradient experiment [8] is based on incorporation of two identical magnetic field pulses of duration  $\delta$  and strength  $g$  into the basic  $90^\circ$ – $\tau$ – $180^\circ$  spin echo sequence. The first gradient pulse is applied between the  $90^\circ$  and  $180^\circ$  rf pulses and has the effect of labelling the position of individual nuclei within the sample. The second field gradient pulse, identical to the first and occurring a time  $\Delta$  later, is applied between the  $180^\circ$  pulse and the echo. Its role is to monitor any spatial movement of the nuclear spins which occurs during the period  $\Delta$ . The time interval  $\Delta$  between the gradient pulses represents the time during which the diffusion process is being observed. The effect of diffusion on the spin echo appearing at time  $2\tau$  is to decrease the echo amplitude relative to that observed in absence of gradient pulses. The echo attenuation can be taken as a quantitative measure for the precession frequency changes of diffusing nuclei during  $\Delta$  and permits the quantitative evaluation of the self-diffusion coefficient for the observed nucleus. It has been shown [8] that the spin echo amplitude  $M(2\tau, g)$  in the presence of a magnetic field gradient of strength  $g$  and duration  $\delta$  is given by

$$M(2\tau, g) = M(2\tau, 0) \exp \left\{ -\gamma^2 D g^2 \delta^2 \left( \Delta - \frac{\delta}{3} \right) \right\}, \quad (1)$$

where  $M(2\tau, 0)$  refers to the amplitude of the NMR signal including relaxation effects obtained in the absence of the field gradient pulses, and  $\gamma$  is the magnetogyric ratio of the observed nucleus the diffusion coefficient  $D$  of which is to be determined.

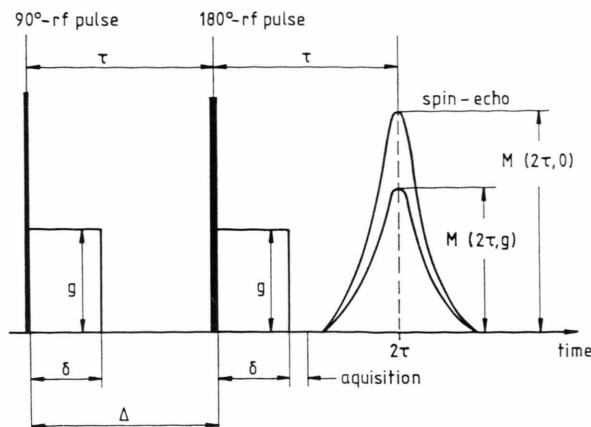


Fig. 1. Pulse sequence for spin echo measurements of self-diffusion.

Practically the echo maximum is measured at time  $2\tau$  for various applied linear magnetic field gradients by keeping the time intervals  $\tau$  between rf pulses and  $\Delta$  between gradient pulses at constant values. Under these conditions, at a given temperature, the attenuation of the echo maximum depends upon the values of  $\delta$  and  $g$ . The pulse sequence applied and the corresponding times are defined in Figure 1. The gradient pulses were turned on immediately after a rf pulse was turned off. The duration of the  $90^\circ$  rf pulse was short (up to 30  $\mu$ s) in comparison to the relatively long gradient pulse (up to 8 ms), so that the rf pulses had a negligible effect on the diffusion. The pulses were programmed and their lengths and phases automatically optimized and controlled by the pulse programmer of the spectrometer. Only the peak height of the echo was then digitized. Automatic data acquisition was used for a series of spin echo signals obtained by varying the gradient pulse duration  $\delta$  for a given  $g$  while the intervals  $\Delta$  and  $\tau$  were kept constant in the course of the experiment. Each experiment was performed with  $\Delta$  fixed to 20 ms and  $\delta$  varying between 0.5 and 8 ms. The interval  $\tau$  between the two rf pulses was set to 20 ms and it coincided practically with  $\Delta$  in the chosen pulse sequence since the rf pulse lengths were negligible compared to the other time intervals. The pulse repetition rate was 2 s.

The value of  $M(2\tau, g)$  was measured for about 30 different values of  $\delta$  at a given  $g$ . Results were then fitted to (1), and  $D$  was extracted. At constant temperature several runs were carried out with about 5 different values of  $g$ , and finally an average value of  $D$  was

obtained. The magnitude of  $g$  was adjusted to such a value that the decrease in echo amplitude was well discernible. The experiments were performed entirely under computer control except for regulation of the gradient current.

## Design of Probe

Our objective has been the design of a probe head for use in high temperature NMR diffusion experiments to be installed in a superconducting magnet ( $B_0 = 7.04$  T) having a 89 mm wide gap. The requirements to observe in the construction were, that the homogeneity and the thermal stability of the magnet should be protected, that a uniform temperature within the sample should be provided and maintained and that variable temperature experiments could be carried out. In all these respects the probe head to be described below proved satisfactory.

The design of Meckl [11] for a probe capable to work at high pressures and ambient temperatures recently developed in our laboratory [12] has been adapted for high temperature measurements. The probe head, which consists of the sample cell, rf coil, and gradient coil, was designed to be located inside a furnace with an outer cooling jacket maintained at room temperature. The furnace diameter of 89 mm corresponds exactly to the gap width of the laboratory magnet. It should be noted that the sample-coil configuration described below is the most efficient way to achieve a satisfactory field gradient uniformity over the sample volume, but on the other hand it creates difficulties when carrying out experiments at high temperatures because the coils become hot when the sample is heated. Consequently the temperature range of the measurements is limited, the upper limit depending critically on the selected material for the coils, especially on their insulation. With the presently used wire for the gradient coils the measurements are limited to a maximum of 700 K.

Another probe design has been previously described by Strange *et al.* [13]. It was used up to 1300 K for diffusion measurements in ionic crystals [5]. In this arrangement the field gradient coil was placed outside the high temperature furnace containing rf coil and sample. This configuration, however, needed much higher current (100 A) to produce the same field gradient as our compact small probe. In addition other characteristics were also worse.

It has been noted [14] that the static magnetic field impairs the uniformity of the field gradient if the magnet gap is not much larger than the cross-section of the gradient coil. This effect was avoided by our setup.

Figure 2 shows the geometrical arrangement of the three magnetic fields, i.e. the static magnetic field  $B_0$  of our cryomagnet in the  $z$ -direction, the magnetic field gradient  $\partial B/\partial z$  aligned parallel to the  $B_0$  direction, and the rf magnetic field  $B_1$  acting perpendicular to both other fields. The  $B_1$  field was produced by an inductive coil consisting of two windings of silver wire with a diameter of 1 mm, which surrounds the sample cell. This coil, which is 10 mm long and 8 mm in diameter, is used both as transmitter of the rf pulses and receiver of the induced NMR signals. The sample of about 1 cm<sup>3</sup> in volume was contained in an L-shaped cylindrical quartz cell of 30 mm length and 8 mm outer diameter in that branch which lies perpendicular to  $B_0$ .

The linear magnetic field gradient was produced at the sample by a cylindrical quadrupole coil with its axis in  $B_1$  field direction. The characteristics and applicability of a quadrupole coil for NMR spin echo diffusion measurements have already been demonstrated [14, 15] and its advantages in comparison to Helmholtz coils are well established. In designing the quadrupole coil some conditions must be observed, i.e. a small coil volume is necessary in order to produce a uniform field gradient across the sample, the time required to establish the current in the coil (the rise time) should be short, current pulses with rise and decay times as short as possible are desirable, and a small inductance to gradient ratio is required. The quadrupole coil is shown schematically in Figure 3.

On the surface of a cylinder from MACOR, which is 30 mm long and has outer and inner diameters of 20 mm and 10 mm, respectively, a copper wire of 0.4 mm diameter was wound parallel to the axis of the cylinder. The windings are grouped in 12 bundles as shown in Figure 3. Each quadrant contains three groups of windings in a 7–10–7 turn configuration. In adjacent quadrants the direction of the current is reversed. The gradient at the center of the coil is given by [14]

$$g = \frac{\partial B}{\partial z} = \frac{\mu_0 I_0}{2 r_0^2}, \quad (2)$$

where  $\mu_0$  is the permeability of vacuum,  $r_0$  the coil radius and  $I_0$  the total current in each quadrant.

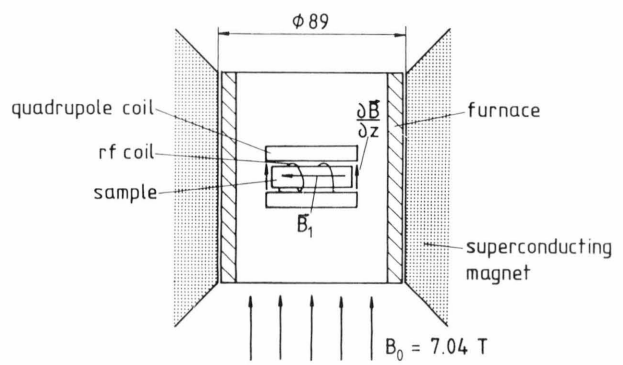


Fig. 2. Schematic diagram of the NMR system used for self-diffusion measurements.

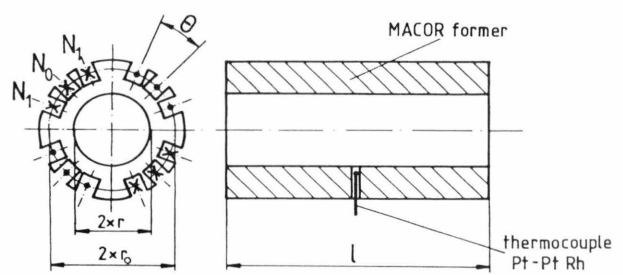


Fig. 3. Cross-section of the quadrupole coil.  $N_1 = 7$ ,  $N_0 = 10$ ,  $\theta = 22.5^\circ$ ,  $l = 30$  mm,  $r_0 = 8$  mm,  $r = 5$  mm.  $\odot$  current up,  $\otimes$  current down.

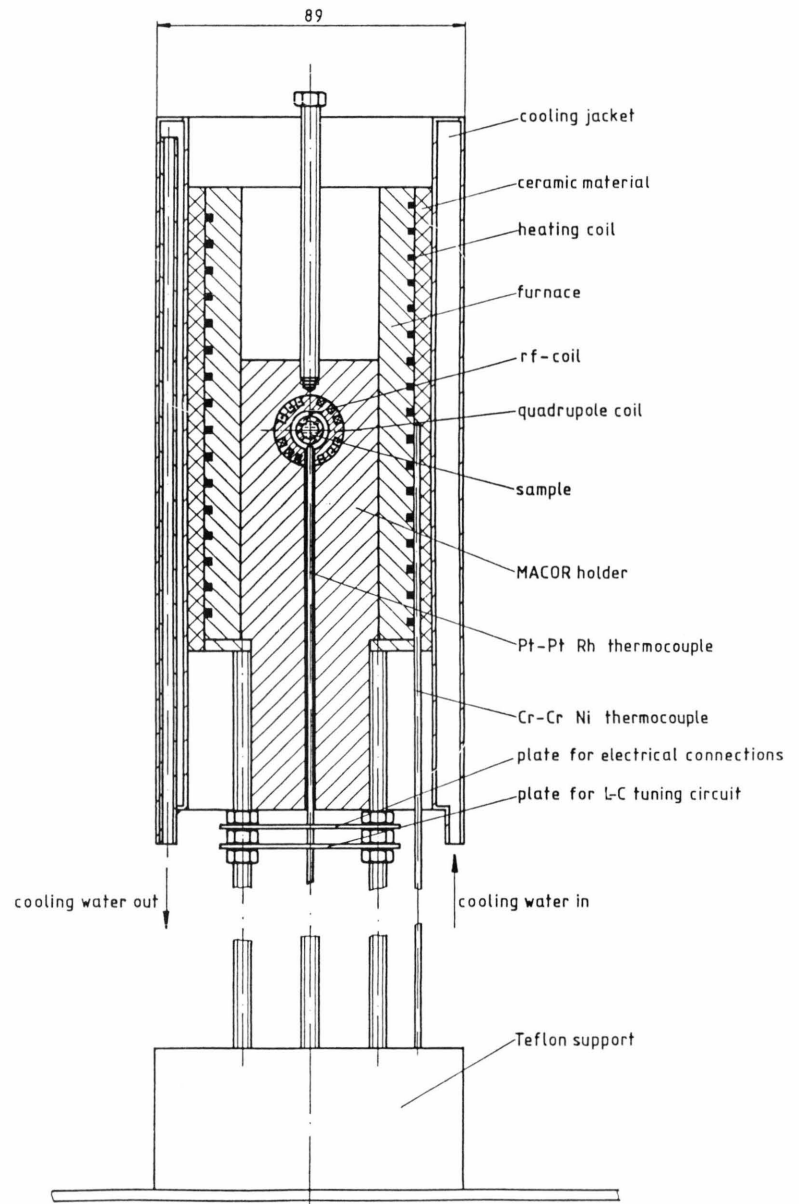


Fig. 4. High temperature probe assembly.



With this distribution of the windings one gets the most satisfactory field gradient uniformity over the probe inside the coil [16].

The value of  $g$  as calculated is  $0.2356 \text{ Tm}^{-1}$  for a current of 1 A. The coil radius was estimated from the profile of the MACOR cylinder. The rise time for the current pulse is usually determined by the inductance  $L$  and the resistance  $R$  of the coil through  $L/R$ . Our coil has values of  $R = 0.8 \Omega$  and  $L = 18 \mu\text{H}$ , thus the rise and decay times of the pulse are about  $20 \mu\text{s}$ . It may be noted that a similar Helmholtz coil gives a much larger value for the time constant, about 2.2 ms [15].

Since in practice the actual coil radius is difficult to measure, an alternative is to calibrate the field gradient. For this purpose a sample with known self-diffusion coefficient is taken and the relation between the gradient  $g$  and current  $I$  is thus obtained. The experimental procedure is the same as that used for the diffusion measurement except that  $g$  rather than  $D$  is the unknown in (1). For determining  $g/I$  we have used self-diffusion data of  $\text{D}_2\text{O}$  as reported by Mills [17]. The pulsed gradient experiments observing the deuterons in  $\text{D}_2\text{O}$  were performed at a resonance frequency of 40.07 MHz. Since the value of  $g$  must be well known for the quantitative evaluation of  $D$ , calibration of the gradient coil was frequently repeated. Minimum duration of the gradient pulse was  $500 \mu\text{s}$ , and magnitudes up to  $1.1 \text{ Tm}^{-1}$  were obtained using up to 5 A of current from the pulse generator. The quadrupole coil was well stabilized with the ceramic material CONTRONIX (type 944) in a MACOR support (see Fig. 4) in order to minimize the effects of acoustic ringing.

Figure 4 shows the block diagram of the NMR probe assembly including the furnace and the electronics. The furnace, consisting of the heating block, thermal insulation and water cooling jacket was 200 mm long and had outer and inner diameters of 89 mm and 45 mm, respectively. The furnace heating was provided by a non-inductive CALOCOAX wire with a resistance of  $3.1 \Omega \text{ m}^{-1}$ , which was wound in opposite directions on an aluminum block. The temperature of the furnace was constant within 0.5 K, as checked with a chromel-alumel thermocouple. At the highest temperature of about 673 K the thermal gradient was less than  $0.5 \text{ K cm}^{-1}$ . The thermal insulation was provided by a ceramic paper wrapped around the heating block. All the internal space of the furnace was occupied by the NMR probe holder made

from MACOR, a glass ceramic with special physical properties that can be used up to 1073 K. The compact arrangement of gradient and sample coils was placed into a 40 mm diameter hole of this MACOR holder, the advantage being that the sample always had the same position with respect to rf and gradient coils and that the whole system was located within the furnace at the same place. Thus the experimental conditions could be better reproduced. The furnace with the NMR probe was mounted to a three-point support that could be moved within the magnet gap, and the position with the best magnetic field homogeneity was chosen. A single L-C tuning circuit was used to adjust the frequencies of 49.06 and 79.38 MHz for the resonances of  $^2\text{H}$  and  $^{23}\text{Na}$ , respectively. The variable capacitors of 6–30 pF in the tuning circuit were located on a plate close to the furnace. A compromise had to be made concerning the distance of the capacitors from the rf coil since heat protection is needed but long leads disturb the tuning; finally the distance chosen was 10 cm.

To produce field gradient pulses with fast rise and decay times a home-made current pulser was used [11]. It contains a transistor (Siemens type BWZ 11), which is capable of switching currents up to 40 A in 250 ns and which has a low forward resistance of  $30 \text{ m}\Omega$ . The current through the pulser was supplied from a variable voltage source and was controlled manually. The gradient coil current was measured by the voltage drop across a  $10 \Omega$  resistor. The output of the current pulser was displayed on an oscilloscope so that the pulse shape and the magnitude could be monitored. The pulser was connected to the output terminals of the spectrometer's pulse programmer and was synchronized to its pulse sequence.

It should be noted that the gradient pulses were arbitrarily set immediately after the  $90^\circ$  and  $180^\circ$  rf pulses (see Figure 1). In this way the extension of the gradient pulses into the  $180^\circ$  rf pulse and the spin-echo respectively, producing irregular echo attenuation could be avoided. Moreover, the actual area of the two gradient pulses defined as the product  $g\delta$  should be identical, i.e. the gradients should be self-refocusing in order to have non-diffusing spins unaffected. In practice this ideal case was not reached. A correction was needed for the time duration of the second gradient pulse, which practically was slightly smaller than the fixed value of  $\delta$ . That was probably the case because during the time  $\tau - \delta$  after the first gradient pulse the capacitors of the current pulser were not com-

pletely loaded. Consequently the signal frequency was slightly changed and the spin echo shape was not accurate. Therefore a correction factor  $\delta'$  of the order of  $\mu\text{s}$  in the second pulse gradient depending on  $\delta$  and  $\tau$  was introduced by adjusting the values  $\delta$  to make the echo symmetric about  $2\tau$ . For  $\tau = 20\text{ ms}$ , the equation describing the correction  $\delta'$  was established as

$$\delta' = 3.0392 \delta^2 + 0.8210 \cdot 10^{-3} \delta + 0.2500 \cdot 10^{-6}.$$

A typical experiment began by tuning the L-C circuit to the resonance frequency of the nucleus under investigation.

When the working temperature was reached, the  $90^\circ$  and  $180^\circ$  pulses were adjusted in amplitude and duration. A duration of 22 to  $30\mu\text{s}$  was typical for a  $90^\circ$  pulse. Then the probe position was adjusted until a satisfactory shape and width of the echo was found. To avoid instability of the echo by interference from the heating coil of the furnace, which might produce additional magnetic fields, the heating current was switched off during application of the pulse sequence. The period of approximately 80 ms is much shorter than the thermal time constant of the furnace, and consequently the sample temperature was not appreciably altered during the measurement. The temperature at the probe was measured by a Pt-Pt/Rh thermocouple to an accuracy of  $\pm 0.2\text{ K}$ . With the system at thermal equilibrium the automatic acquisition of the spin echos began. Determination of the diffusion coefficient was based on a series of about 30 spin echos for a certain value of  $g$  or  $I$  with  $\delta$  varying randomly between 0.5 and 8 ms, the other variables remaining constant. For a given temperature the measurements were repeated at least three times and the reproducibility was about 1 per cent.

## Results and Discussion

NMR measurements observing  $^{23}\text{Na}$  at 79.38 MHz were performed using a Bruker CXP-300 pulse spectrometer. At first the probe was calibrated for the field gradient using self-diffusion coefficients of heavy water [17] and observing the deuteron resonance, because accurate data for molten salts are not available. Thus calibration had to be done in the ambient temperature range. For currents between 2 and 5 A and with values of  $D$  between 291 and 313 K a gradient of  $g = 0.225\text{ Tm}^{-1}\text{ A}^{-1}$  was found. This is in satisfactory agreement with the one calculated theoretically. Calibration runs usually agreed to 0.05 per cent. The

magnitude of  $g$  was checked frequently and no change was observed after measurements at the high temperatures had been done. Therefore this value of the field gradient was taken to be valid also at the high temperatures. Attempts were made to optimize NMR parameters according to the pulse sequence of Figure 1. For that purpose diffusion measurements of  $\text{Na}^+$  in  $\text{NaNO}_3$  above the melting point of 582 K were done with different values for  $\delta$  and  $g$ . Varying the duration of the gradient pulses from 0.5 to 8 ms at constant  $g$  between 0.4 and  $1.1\text{ Tm}^{-1}$  caused the echo amplitude to decrease almost to zero at the largest values of  $\delta$ . The highest gradient strength caused a decrease in echo intensity up to 50 per cent for the smallest value of  $\delta$ .

To set the pulse repetition rate to about  $8T_1$  the spin lattice relaxation time  $T_1$  of  $^{23}\text{Na}$  in the sample of molten  $\text{NaNO}_3$  was determined by application of the  $180^\circ - \tau - 90^\circ$  pulse sequence. The values found for  $T_1$  were 0.048 s at 598 K and 0.054 s at 623 K.

Finally the self-diffusion coefficients of  $\text{Na}^+$  in  $\text{NaNO}_3$  were measured as a function of temperature between 596 and 670 K. The results are given in Table 1. It is possible to fit the data to the Arrhenius equation and we obtain the parameters  $D_0 = 6.62 \cdot 10^{-8}\text{ m}^2\text{ s}^{-1}$  and  $E = 17.43\text{ kJ mol}^{-1}$ .

A considerable amount of data for the self-diffusion coefficient of  $\text{Na}^+$  in molten  $\text{NaNO}_3$  is available in the literature. They were obtained mainly by four techniques: diffusion out of capillary [3, 18–21], diffusion into capillary [22–26], impregnated paper strip [27–29] and porous frit [30].

Table 2 lists the values of  $D$  at 623 K and the Arrhenius constants obtained in this work together with the results reported in the literature. As one can see there is a large scatter of the  $D$  values ranging from  $2.10$  to  $2.70 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$ . However, it may be noted that diffusion out of capillary technique yields the best agreement between different authors. The value of  $2.30 \cdot 10^{-9}\text{ m}^2\text{ s}^{-1}$  obtained by us lies closely to those of the capillary technique.

Even better does the temperature dependence agree, expressed in terms of the Arrhenius equation  $D = D_0 \exp(-E/RT)$ . The activation energy  $E$  derived from our NMR-diffusion coefficients agrees quite well with the values of other authors. From this comparison it follows that the field gradient  $g$  does not appear to be temperature dependent and that the results reported here point to a good performance of the probe head designed in this work.

T/K	598	601	605	623	629	631	651	654	670
$\frac{D}{10^{-9} \text{ m}^2 \text{ s}^{-1}}$	1.92	2.05	2.07	2.30	2.35	2.38	2.63	2.68	2.86

Table 1. Self-diffusion coefficients of  $\text{Na}^+$  in  $\text{NaNO}_3$  at different temperatures.

Technique	$\frac{D}{10^{-9} \text{ m}^2 \text{ s}^{-1}}$	$\frac{D_0}{10^{-7} \text{ m}^2 \text{ s}^{-1}}$	$\frac{E}{\text{kJ mol}^{-1}}$	Reference
NMR spin echo	2.30	0.66	17.43	this work
Diffusion out of capillary	2.33	1.89	20.79	[3, 17]
	2.27			[18, 19, 20]
Diffusion into capillary	2.10			[21]
	2.13		17.99	[22]
	2.14	0.55	17.99	[23]
	2.48	0.80	18.07	[24]
	2.38	1.29*	18.20	[25]
Impregnated paper strip	2.49			[26]
	2.30	0.63	16.99	[27]
	2.73		22.18	[28]
Porous frit	2.32			[29]

Table 2. Self-diffusion coefficients of  $\text{Na}^+$  in  $\text{NaNO}_3$  obtained by different techniques.

\* is actually 0.8 as calculated from given data of authors [26].

## Conclusions

NMR spin echo technique using pulsed gradients was applied for the first time to the measurement of self-diffusion coefficients in molten salts. The performance of the developed NMR probe head has been tested by molten  $\text{NaNO}_3$  at temperatures up to 673 K. Since our NMR results for self-diffusion coefficients of  $\text{Na}^+$  in  $\text{NaNO}_3$  are in good agreement with the most accurate data from other measuring techniques it is reasonable to consider our experimental setup as a suitable one to be used for further experiments.

Diffusion experiments need to be done more extensively and systematically. It would be desirable for example to extend the temperature range. Since the errors in  $D$  arise mainly from uncertainties in the val-

ues of  $g$ , much attention should be paid to its accurate determination.

The NMR probe presented here might also be used to determine other parameters of particular importance such as spin density or relaxation times  $T_1$  and  $T_2$ .

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