Self Diffusion of Liquid ^{6}Li and ^{7}Li as Measured by Nuclear Magnetic Resonance *

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The self-diffusion coefficients of liquid ^{6}Li and ^{7}Li have been measured using NMR spin echo techniques with pulsed gradients. In the experimental procedure, and in the sample preparation, particular attention has been paid to a relative, rather than to an absolute measurement. At 190 °C, the ratio of the self-diffusion coefficients is found to be $D_6(x_6=1)/D_7(x_7=1)=1.09\pm0.06$, in agreement with the square root of the mass ratio $(m_7/m_6)^{1/2}=1.08$. In an atomic mixture of 80% ^{6}Li and 20% ^{7}Li, $D_6(x_6=0.8)/D_7(x_6=0.8)=1.03\pm0.08$ has been obtained.

Measurements of the shear viscosities of the separated isotopes of molten lithium by BAN, RANDALL and MONTGOMERY[1] at the melting point yielded a ratio $\eta_7/\eta_6=1.44$, in contrast to the limiting classical value of 1.08, the square root of the mass ratio. Moreover, LÖWENBERG and LODDING[2] investigated the interdiffusion of ^{6}Li and ^{7}Li in nearly pure lithium-6, as well as in nearly pure lithium-7, and found a ratio of about 1.30 at the melting point. Because of the importance of such results for the fundamental theory of transport phenomena of the liquid state, it seemed to be of major interest to perform a direct measurement of the self-diffusion coefficients of liquid ^{6}Li and ^{7}Li with nuclear magnetic resonance (NMR) methods. Both MURDAY and COTTS[3] and the present authors have carried out experiments of this nature. In order to obtain the ratio of the self diffusion coefficients free from systematic errors, our experiment has been turned as far as possible into a relative measurement.

Apparatus and Performance

NMR spin echo techniques with pulsed field gradients[4] were applied. Both the spectrometer, of conventional design, and the pulsed gradient set-up are homemade. Details of the experimental method have already been given in another context[5]. Figure 1 shows the pulse sequences used for producing the nuclear spin echo and the gradient pulses. The ratio of the echo amplitude M_0 without, and M with gradient pulses is then given by

$$M=M_0\exp\left\{-\gamma^2 D\left[\delta^2(\Delta-\tfrac{1}{3}\delta)\,G^2+\delta\left(2\,\tau^2-\tfrac{2}{3}\,\delta^2-\delta(t_1+t_2)-(t_1{}^2+t_2{}^2)\right)G\,G_0+\tfrac{2}{3}\tau^3\,G_0{}^2\right]-\frac{2\,\tau}{T_2}\right\} \tag{1}$$

(γ is the gyromagnetic ratio of the nuclei, the meaning of the other parameters can be seen from Fig. 1). All measurements were carried out at the

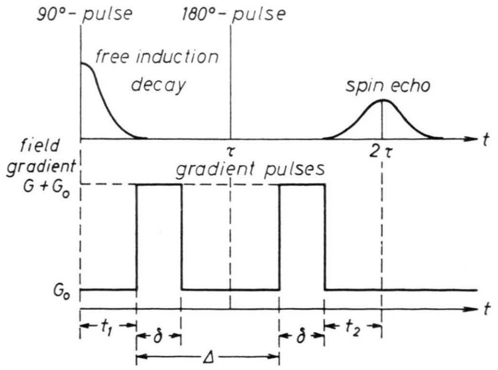

Fig. 1. Pulse sequences used for the measurement of self-diffusion coefficients.

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same frequency of 5.61 MHz, and phase sensitive detection was applied throughout. The gradient pulses were produced by a pair of magnetically opposed rectangular coils in order to obtain a geometry similar to that of the cylindrical sample. The coil arrangement is shown schematically in Fig. 2. The pulsed gradient is longitudinal with respect to the magnetic field H_0. The current through the small sides of the rectangles produces only transverse field components, which do not disturb the measurement. Figure 3 shows a typical example of the nuclear spin echo of ^{6}Li with and without gradient pulses. This is a multi-exposure photograph of the oscilloscope screen in which there is some integration over the noise. Such photographs were used for the measurements. They were preferred to electronic signal averaging, because all fluctuations in the adjustments of the apparatus tend to make the echo smaller. If such fluctuations occur, the values given by an electronic signal averager will therefore always be too small, whereas on a photograph such as Fig. 3 one can select the largest signals for the evaluation.

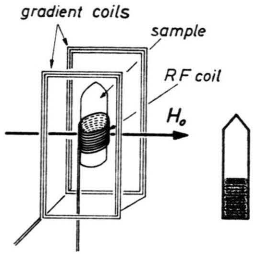

Fig. 2. Coil arrangement (left) and structure of sample (right).

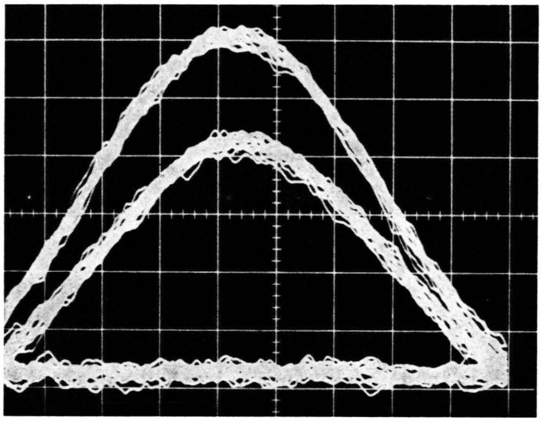

Fig. 3. Nuclear spin echo of ^{6}Li with and without gradient pulses.

Sample Preparation

Enriched lithium metal (95.6 and 99.3% ^{6}Li, main impurities 0.03% Ca, 0.05% Cu, 0.05% Na) and normal lithium metal (7.4% ^{6}Li, main impurities 0.05% Ca, 1% Na) were obtained from Oak Ridge National Laboratory and E. Merck, Darmstadt, respectively.

The application of a radio frequency to metallic lithium requires particles with diameters of the order of the skin depth. At a frequency of about 6 MHz, the sample should therefore consist of spheres with diameters of the order of 100 μm or less. The spheres on the other hand must be large enough to avoid an important restriction of the diffusion within one sphere. After MURDAY and COTTS [6], the factor which corrects the value of D for the effects of the boundaries is 1.1, in the case of a diameter of about 100 μm, but 1.2 at 66 μm. In the present work suspensions of lithium in paraffin oil were used.

To prepare globules of lithium, the molten metal was forced with pressurized argon through a sintered stainless steel filter (Pall Corporation, grade *D*, mean pore size 65 μm, thickness 1.5 mm) into a bath of spectroscopically pure paraffin oil. After cooling, the globules were sorted according to size by means of a separating funnel. Concentrated suspensions were then obtained by removing superflous oil. When left undisturbed on heating, the liquid globules in these suspensions, though touching each other, did not coalesce.

Precautions were taken to avoid systematic errors arising from differences in the particle size, the calibration of the magnetic field gradient, and the segregation of particles. To minimize relative errors, samples of mixtures of lithium globules of differing isotopic compositions and similar diameters were used. The particular properties of these samples can be found in Table 1. x_6 and x_7 are the mole fractions ^{6}Li and ^{7}Li. The error figures of the third column indicate the range of diameters that has been found microscopically.

The sample tubes (Pyrex) had an outer diameter of 15 mm. Within the tube, fractions of the sample are separated by circular mica discs, as can be seen schematically in Fig. 2. The mica was used in order to avoid gravitational demixing of the different globules, which would cause errors due to the inhomogenity of the field gradient.

Using such samples, relative measurements of the ratio of the self-diffusion coefficients, which are more accurate than measurements of D_6 or D_7 alone, could be carried out. The self-diffusion coefficients of ^{6}Li in a lithium-6 environment, and of ^{7}Li in a lithium-7 environment, were thus measured without changing the sample.

Experimental Procedure

The measurements were carried out in the following manner: The sample was heated by a hot air stream to approximately 190 °C. This tempera-

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[6] J. S. MURDAY and R. M. COTTS, J. Chem. Phys. **48**, 4938 [1968].

ture was controlled automatically and kept always constant. It was measured by a thermocouple outside the sample tube. A dummy sample filled with oil was used to measure the temperature inside a sample tube and to correct the reading of the outer thermocouple. Since the ratio of the diffusion coefficients is not as temperature dependent as the coefficients themselves, the absolute value of the temperature is not so important. It was here measured with an accuracy of ±2 °C. It is, however, very important to do the measurements for both diffusion coefficients at exactly the same temperature, and this was the case here, since once the temperature equilibrium was reached, no further change was made in the heater, air-circulation and temperature control systems. The magnetic field was then adjusted to one isotope, e. g. ^{7}Li. The pulse programme was adjusted for a total measuring time 2τ of 10 to 15 ms and this as well as the gradient pulse spacing $\varDelta$ and the gradient pulse width δ were then kept constant in the course of the measurement. The gradient amplitude G was adjusted for a ratio of the echo amplitudes without and with gradient pulses of 1.5 to 2.0. Four photographs similar to Fig. 3 were then taken. After this, the magnetic field and the gradient amplitude were changed to the other isotope, e. g. ^{6}Li. The change in the gradient amplitude was effected by changing the supply voltage of the transistor switch (which switched the gradient current) in order to maintain the pulse shape constant. This was in all cases nearly rectangular. Thus, no correction was applied for the rise and fall times of the gradient pulses. The error caused by this was very small ($<1\%$) and was the same for both isotopes. Then again four photographs were taken. The mean values of the echo amplitude ratios of these two sets of photographs were used to compute the ratio of the diffusion coefficients according to (1) taking into account only the first term on the right side. The ratio of the diffusion coefficients is given by

$$\frac{D_6}{D_7} = \frac{\gamma_7^2\, G_7^2 \log (M_0/M)_6}{\gamma_6^2\, G_6^2 \log (M_0/M)_7} \tag{2}$$

The whole measurement is thus reduced to relative measurements of the echo amplitudes with and without gradient pulses and to a relative measurement of the gradient amplitude, which was also made at the osciloscope using the voltage pulse produced by the gradient current in a precision resistor of 0.1 Ω. Thus, no calibration error of the gradient coils or of the oscilloscope enters into the ratio of the diffusion coefficients.

Results

The mean values of the uncorrected self-diffusion coefficients, as obtained with the first term of Eq. (1), are listed in Table 1. More significant are the ratios of the two diffusion coefficients. Without paying regard to systematic errors and corrections, which will be discussed further below, these turn out to be:

$$D_6(x_6=0.956)/D_7(x_7=0.926) = 1.05 \pm 0.03 \quad \text{(sample I)},$$

$$D_6(x_6=0.993)/D_7(x_7=0.926) = 1.08 \pm 0.03 \quad \text{(sample II)},$$

and $D_6(x_6=0.8)/D_7(x_6=0.8) = 1.02 \pm 0.05$ (sample III),

respectively. Each of these data is the mean value of 13 measurements. The errors are the sums of the mean square error and the personal error. The personal error in evaluating noisy photographs was assumed to be less than 1.5%. In fact, the mean value and the mean square eror of two persons evaluating the same set of measurements were practically the same, although there were deviations in

Table 1. Properties of the samples and experimental results. The absolute values of D_6 and D_7 are uncorrected data; no special care had been taken as far as the absolute calibration is concerned.

Sample	Composition	Particle Diameter (μm)	t (°C)	$D_6 \cdot 10^5$ (cm^2/s) uncorrected	$D_7 \cdot 10^5$ (cm^2/s) uncorrected	D_6/D_7 corrected
I	80% globules (x_6=0.956) 20% globules (x_7=0.926)	70±20	188	6.96	6.65	1.07±0.06
II	80% globules (x_6=0.993) 20% globules (x_7=0.926)	105±35	190	7.66	7.09	1.09±0.06
III	100% globules (x_6=0.8)	70±20	188	6.83	6.71	1.03±0.08

single measurements. The larger error in sample III is due to a smaller signal to noise ratio.

There remain, however, three types of systematic errors, which are not completely compensated for in the course of our measurement. The first arises from the second term of Eq. (1) because there are rather large background gradients in such an inhomogeneous sample. This error was calculated by MURDAY and COTTS[3] to be approximately 7% for the self-diffusion coefficients. It should be about equal for ^{7}Li and ^{6}Li. So we assume that the error in the ratio caused by this effect is not larger than 2%.

The second systematic error comes from the fact that diffusion takes place in small spheres rather than in an unbounded medium. This error has already been mentioned. It was treated in detail by MURDAY and COTTS[6], and in our case it is about 10% for the absolute diffusion coefficient of one isotope. Because of the somewhat larger diffusion coefficient, the error is about 1% larger for ^{6}Li. For this, the measured ratio has only to be corrected by +1%.

A third error arises from the fact that the globules in our samples were not pure ^{6}Li and ^{7}Li. Thus, in either signal a small contribution from the other globules was present. This does not affect the ^{6}Li measurement because the 7.4% ^{6}Li in the natural lithium globules is only 1.5% of the total sample which contained about 80% ^{6}Li. The 4.4% ^{7}Li in the enriched ^{6}Li globules of sample I, however, amount to 3.5% of the total sample and this has to be compared to only 20% natural lithium globules. As a result of this effect, the ^{7}Li diffusion coefficient obtained from sample I is about 1% too large and the ratio 1% too small.

Thus, the total correction to the ratio is estimated to be +2% in sample I and +1% in sample II. Because of the uncertainty of these corrections, an additional error of ±1% was attributed to the corrected values in Table 1.

Discussion

Considering the present state of experimental information and the smallness of the isotope effects, for simplicity and for physical reasons, the following assumptions are justified:

1) D_6, D_7 and D (the mutual diffusion coefficient) depend linearly on x_7,
2) D_6 and D_7 decrease or remain constant with rising x_7, and
3) $D_6 - D_7$ does not depend on x_7.

Bearing in mind that $D_6(x_7=1) = D(x_7=1)$ and $D_7(x_6=1) = D(x_6=1)$, a picture as shown in the lower part of Fig. 4 must qualitatively be correct.

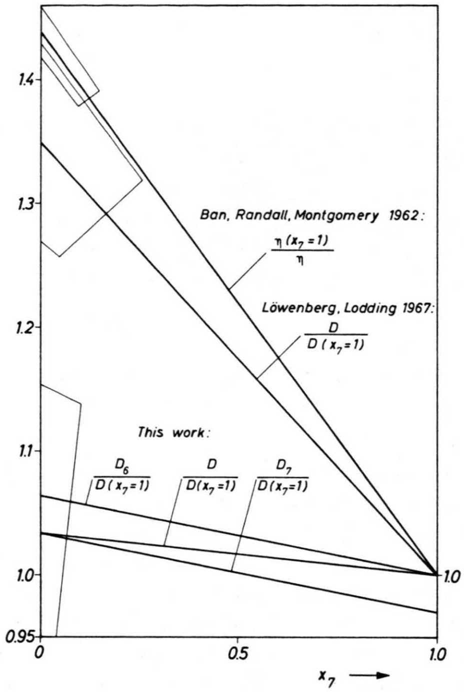

Fig. 4. Isotope effects in liquid lithium at the melting point as measured by BAN, RANDALL and MONTGOMERY[1], LÖWENBERG and LODDING[2], and in this work. η viscosity. D, D_6, and D_7 mutual and self-diffusion coefficients, respectively. x_7 mole fraction of ^{7}Li. Error margins of $\eta(x_7=1)/\eta$ and $D/D(x_7=1)$, as given in [1] and [2] and as resulting from this work, are indicated on the left hand side of the figure. The discrepancy between [2] and this work is evident.

Quantitatively, because of the result on sample III, $(D_6 - D_7)/D(x_7=1)$ has been taken to be 0.03 in this picture. Furthermore, in accordance with the result on sample II,

$$[D_6(x_6=1) - D_7(x_7=0.926)]/D_7(x_7=1)$$

has been taken to be 0.09. In the figure, therefore,

$$[D_6(x_6=1) - D_7(x_7=1)]/D_7(x_7=1) = 0.094 .$$

Also indicated in Fig. 4 are the experimental results of BAN, RANDALL and MONTGOMERY[1] and of LÖWENBERG and LODDING[2].

Our results are in accordance with classical mechanics. The weak dependance of the mutual diffusion coefficient on the mole fraction parallels the behaviour recently observed in gaseous H_2-D_2[7]. Our findings are at variance with the results of LÖWENBERG and LODDING[2], and also, indirectly, with those of BAN, RANDALL and MONTGOMERY[1]. For the explanation of the latter results large quantum effects have to be surmised.

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