

Temperature-dependent self-diffusion coefficients of water and six selected molecular liquids for calibration in accurate ^1H NMR PFG measurements

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Received 3rd July 2000, Accepted 30th August 2000

First published as an Advance Article on the web 3rd October 2000

Pulsed magnetic field gradient (PFG) NMR is today a routine method for the determination of self-diffusion coefficients, D . However, a remaining goal is the improvement of the precision of the method. The best procedure for the determination of accurate diffusion coefficients by PFG NMR is a calibration with a sample of precisely known D -value. In continuation of our previous work on calibration at 25 °C (M. Holz and H. Weingärtner, *J. Magn. Reson.*, 1991, **92**, 115) we present reference data as a function of temperature. Since H_2O plays an outstanding role as liquid and as primary standard, we carefully measured self-diffusion coefficients of water by ^1H PFG NMR in the temperature range from +5 to +55 °C and added literature data obtained from tracer methods in the range between 0 and +100 °C. This comparatively large collection of data could then be fitted to a Speedy–Angell power law, showing the excellent congruence of the results of two completely different methods and proofing the certainty of the absolute values for water. In this manner reliable primary standard values with error limits of <1% were obtained, allowing us to adapt the temperature of the standard water to the sample temperature of interest. We further give ^1H PFG NMR self-diffusion reference data in the range from +5 to +55 °C for six easily accessible solvents, which we propose as secondary calibration standards, namely cyclohexane, dioxane, dodecane, DMSO, tetradecane and pentanol, covering a large range of absolute D -values and allowing us to match in addition the absolute D -values of calibration sample and sample under investigation. Furthermore, the gained accurate self-diffusion data are suited for an elaborate check of theoretical approaches in the physics of molecular liquids.

Introduction

The measurement of temperature-dependent self-diffusion coefficients, D , by pulsed magnetic field gradient (PFG) NMR has gained a rapidly increasing importance during the last few years. There are two main reasons, namely (i) the increasing interest in dynamical quantities of fluid systems and their activation parameters¹ and (ii) the possible use of self-diffusion coefficients for the indirect measurement of local temperatures (temperature mapping) in magnetic resonance imaging (MRI) experiments.² The main advantages of PFG NMR diffusion methods over conventional isotopic tracer methods are: fast measurements, small sample volumes, determination of “true” self-diffusion coefficients (which are not influenced by interfering isotope effects) and an easy application to a wide pressure and temperature range. However, up to now tracer methods can be regarded as more accurate than PFG NMR methods and therefore the improvement of the precision of PFG NMR measurements is still an important aim. The best and thus most applied procedure for the determination of highly accurate diffusion coefficients by PFG NMR is a calibration using a sample with precisely known D -value and therefore the achievable accuracy in a given experiment is closely connected with the quality and suitability of the data of standard samples. Therefore, in the laboratory of one of the present authors (M.H.) the question of suited standard samples has been investigated in the past and a calibration scheme for PFG experiments at 25 °C with NMR of ^1H and eight further nuclides has been proposed,³ which meanwhile

seems to be accepted in the literature. (For details with respect to the calibration problems and the proposed procedure, see ref. 3.) Now, in continuation of this previous work,³ we thought it worthwhile to acquire, at least for ^1H NMR, temperature-dependent reference data in order to enable an improvement of the accuracy of *temperature-dependent* PFG self-diffusion measurements. The reason for that lies in our long standing experience that highly accurate measurements of D , that means those with an error limit <1%, require that at least two experimental conditions should be fulfilled, namely first that the calibration measurement with the standard sample should be performed at the same temperature as with the sample of interest and second that the absolute D -value of standard sample and sample of interest should not differ too strongly. (We mention here that for older NMR instruments, where sometimes the receiver linearity is not good enough, a third condition might be important, namely that the absolute signal intensities of reference sample and sample of interest should not differ markedly.) The background for all these conditions is simply that in the *ideal* case no change of experimental conditions, as *e.g.* position and geometry (volume) of the sample, and of instrumental parameter settings, as *e.g.* receiver gain, gradient strengths, gradient pulse distances *etc.*, should be made when the reference sample is exchanged against the sample under investigation. Thus, for example, it can be easily realised that a temperature change between the two measurements changes the experimental conditions *e.g.* by possible thermal influences on rf- and gradient circuits located within the probe head. When

Table 1 Experimental self-diffusion coefficients, D_{exp} , for water (H_2O) as a function of the temperature

T /°C	$D_{\text{exp}}/10^{-9} \text{ m}^2 \text{ s}^{-1}$			D_{fit}^a / $10^{-9} \text{ m}^2 \text{ s}^{-1}$	Max. difference ^b (%)
	(This work)	(Ref. 5)	(Ref. 6)		
0			1.129	1.099	2.7
1		1.149		1.138	0.9
4		1.276		1.261	1.1
5		1.313		1.303	0.7
10			1.536	1.525	0.7
15	1.766	1.777		1.765	0.6
20	2.025		2.022	2.023	0.1
25	2.299	2.299	2.296	2.299	0.1
30	2.597		2.590	2.594	0.1
35	2.895	2.919		2.907	0.4
40	3.222		3.240	3.238	0.5
45	3.601	3.575		3.588	0.4
50	3.983		3.968	3.956	0.7
56	4.444			4.423	0.5
60			4.772	4.748	0.5
70			5.646	5.615	0.5
80			6.582	6.557	0.4
90			7.578	7.574	0.1
100			8.623	8.667	0.5

^a D_{fit} are the recommended reference values for water as primary standard and are obtained by a fit to eqn. (1) with the parameters given in the text. ^b Maximum differences (%) between the fit values and experimental values.

with strong gradients strong non-linearity of the gradients occurs then even the thermal expansion of the sample might introduce errors.

Table 2 Experimental results for the self-diffusion coefficients measured for six liquids at different temperatures

Standard liquid	T /°C	$D_{\text{exp}}/10^{-9} \text{ m}^2 \text{ s}^{-1}$	$D_{\text{fit}}^a/10^{-9} \text{ m}^2 \text{ s}^{-1}$	Difference ^b (%) ^b
Cyclohexane	15	1.170	1.172	0.2
	25	1.424	1.419	0.3
	35	1.694	1.698	0.2
	45	2.010	2.009	0.1
	55	2.352	2.352	0
Dioxane	15	0.899	0.898	0.1
	25	1.089	1.091	0.2
	35	1.305	1.309	0.3
	45	1.561	1.553	0.5
	55	1.820	1.823	0.2
Dodecane	5	0.544	0.545	0.2
	15	0.670	0.670	0
	25	0.814	0.811	0.4
	35	0.969	0.971	0.2
	45	1.153	1.149	0.3
DMSO	55	1.340	1.345	0.4
	25	0.730	0.731	0.1
	35	0.889	0.890	0.1
	45	1.069	1.067	0.2
	55	1.264	1.266	0.2
Tetradecane	15	0.418	0.419	0.2
	25	0.520	0.521	0.2
	35	0.642	0.639	0.5
	45	0.776	0.773	0.4
	55	0.920	0.925	0.5
Pentanol	5	0.143	0.143	0
	15	0.205	0.205	0
	25	0.286	0.287	0.3
	35	0.391	0.394	0.8
	45	0.532	0.529	0.6
	55	0.700	0.699	0.1

^a D_{fit} are the recommended secondary reference values and were obtained by a fit to eqn. (2), using the parameters given in Table 3. ^b Deviation (%) between the fit value and experimental value.

We also want to point out that for quantitative clinical MRI measurements of self-diffusion coefficients *in vivo*, quality control test liquids with exactly known D -values are required. Consequently, our reference data can also serve for this purpose. (In this connection we point out that a collection of self-diffusion data, in a small temperature range from +15 to +30 °C, with typical error limits of $\pm 2\%$, has been published very recently by Tofts *et. al.*⁴)

Finally, it should be emphasised, that precisely known self-diffusion coefficients and their temperature-dependence, as gained in the present work, have their own relevance in the physics of molecular liquids, since they can serve *e.g.* for an elaborate check of theoretical approaches. This is in particular true for water, a liquid of unique importance.

Experimental

¹H NMR self-diffusion measurements were performed applying the common pulsed gradient NMR spin-echo (PGFSE) technique. Measurements on water have been performed at 300 MHz with a Bruker AM 300 instrument, equipped with a computer controlled PFG unit (Ing. Büro Wühlrl, Regensburg). The other six liquids were measured at 20 MHz on a Minispec PC 120 coupled with a commercial PFG unit, both from Bruker.

The liquids, which shall serve as calibration standards, were of highest purity commercially available, which will be specified in the following. Cyclohexane and DMSO were of 99.9% HPLC grade and anhydrous dioxane of 99.8%, all three solvents purchased from Aldrich. Dodecane (min. 99.5% for GC), tetradecane (min. 99.9% for GC) and pentanol (99.9%) were from Riedel-de Haën. All substances were then used without further purification. Purified H_2O was prepared using Milli-Q Plus from Millipore.

In order to ensure a stable and temperature gradient-free thermostating of the samples, we used a direct liquid cooling of the sample cell by pumping a temperature-controlled hydrogen-free liquid (Galden D20, Ausimont, Milan) through the probe head. We used a thermostat RML6 from Lauda with a temperature accuracy better than ± 0.1 °C. We checked the temperature inside the probe head continuously and at the sample position at the beginning and at the end of every measurement by a platinum thermometer. When measuring the water self-diffusion coefficients we additionally thermostated the whole 300 MHz probe head by pumping a liquid with the desired temperature through the cooling system of the gradient coil.

The self-diffusion coefficients of our primary standard were obtained in the following way. First we calibrated our gradient using at 25 °C the D -value previously obtained by the tracer method⁵ and by NMR,³ namely $D = 2.299 \pm 0.005 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$. Then we made absolute measurements with this gradient calibration at different temperatures in the range 15 to 56 °C. Since our NMR results agreed within an error limit of $< \pm 0.8\%$ with tracer results of Mills⁵ or Easteal *et al.*⁶ we could conclude that in our specially designed NMR probe no temperature dependence of the gradient coil constant occurred in the temperature range investigated.

The values of the self-diffusion coefficients D of the seven liquids of interest cover *e.g.* at 25 °C a range from $2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for the basic reference water to $0.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ for pentanol. As outlined in the Introduction the most precise experimental data are obtained when the diffusion coefficient of the liquid of interest is relatively close to the diffusion coefficient of the reference liquid. For this reason we applied for our temperature-dependent diffusion measurements of secondary standards the following procedure. At every single temperature we first measured the diffusion coefficients for cyclohexane and dioxane relative to the primary standard water, since their D -values are closest to that of water. In a

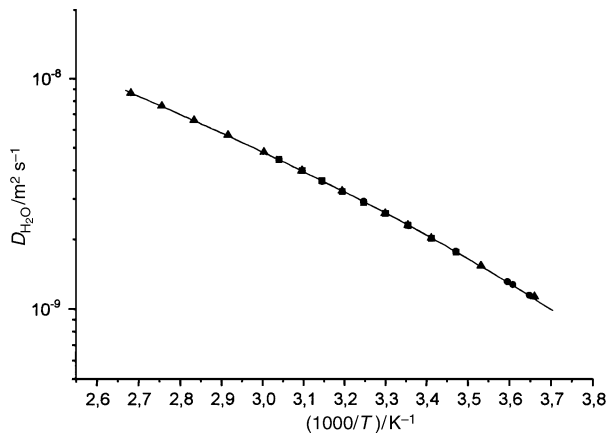


Fig. 1 Arrhenius plot of experimental self-diffusion coefficients for H₂O from isotopic tracer method [(●), ref. 5 and (▲), ref. 6] and from PFG NMR measurements [(■), this paper]. The fit curve represents a Speedy–Angell power-law approach [eqn. (1)] with the parameters given in the text.

kind of “step-by-step calibration” at constant temperature dioxane was then used as reference liquid for dodecane and DMSO and later DMSO was used as reference for tetradecane and pentanol.

All experimental values for the single solvents at the different temperatures reported in Table 1 (our water data) and Table 2 are averaged values of series of at least six independent measurements. The experimental error of the single measurement did not exceed 1%.

Results and discussion

As discussed in our previous paper,³ reliable H₂O self-diffusion data at 25 °C and a few other temperatures, obtained by tracer diffusion studies using the diaphragm cell, have been reported by Mills.⁵ At 25 °C, where we had previously measured the self-diffusion coefficient of water by PFG NMR, we could establish an agreement between the results of the two completely different methods within the error limits of ≤1%,³ demonstrating the reliability of the *absolute* value. Thus, we take the result of the tracer experiment of $D = 2.299 \pm 0.005 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ as the “best” value for water at this temperature.

In Table 1 our experimental self-diffusion coefficients of H₂O at various temperatures are given together with tracer results from refs. 5 and 6. From Fig. 1 it can be realised that the temperature behaviour is of “non-Arrhenius” nature, a fact which is known from the literature and which holds also for other transport quantities of water.^{7–9} Therefore we tried to fit the common set of experimental data in Table 1 to the Vogel–Tamann–Fulcher (VTF) equation and to the Speedy–Angell power-law approach.⁹ It turned out that the data fitted much better a Speedy–Angell power-law, which has the following form:¹⁰

D = D₀[(T/T_S) – 1]^γ (1)

Table 3 Coefficients of eqn. (2) for the calculation of the self-diffusion coefficients of six secondary standards. The activation energies, E_a, for self-diffusion in the different liquids are also given

	C ₁	C ₂	E _a /kJ mol ^{–1}
Cyclohexane	5.8765	–1.6477	13.7
Dioxane	5.7064	–1.6754	13.9
Dodecane	5.3193	–1.6483	13.7
DMSO	5.6991	–1.7927	14.9
Tetradecane	5.6286	–1.8726	15.6
Pentanol	8.4847	–2.9018	24.1

In Fig. 1 the fit curve (obtained by an unconstrained fit) is shown and in Table 1 the maximum difference between the fitted and experimental data is given, reflecting that, with exception of the value at 0 °C, an excellent description of the experimental data can be given. The values D_{fit} in Table 1 are thus the recommended reference data. The fit parameters, which can be used for the calculation of self-diffusion coefficients of the primary standard water in the temperature range between 0 and 100 °C with an error limit of ≤1% are:

D₀ = (1.635 × 10^{–8} ± 2.242 × 10^{–11}) m² s^{–1},

T_S = (215.05 ± 1.20) K

and

γ = 2.063 ± 0.051.

We also point out that the excellent agreement between the results of the isotopic tracer method and the NMR results mean, that now, at least in the range from +5 to +55 °C, we can be sure to possess accurate and reliable *absolute* values for the water diffusion coefficient, since any falsification by unknown method-inherent systematic errors can be excluded.

The experimental temperature-dependent self-diffusion coefficients of the secondary standards are given in Table 2. Since these liquids show an Arrhenius behaviour in the temperature range investigated, the self-diffusion data have been fitted with the least-squares method to the following function:

ln(D × 10⁹/m² s^{–1}) = C₁ + C₂[1000/(T/K)] (2)

and the coefficients C₁ and C₂ for the six solvents investigated are reported in Table 3. From the values of maximum difference between experimental and fitted values, given in Table 2, we can recognise the achieved high relative accuracy for the data sets, which we recommend as secondary standards for temperature-dependent self-diffusion measurements by NMR. E_a, the activation energies for the diffusion process, occurring in the Arrhenius law: $D = A \exp(-E_a/RT)$ are also given in Table 3 for the six liquids.

In conclusion we can state, that the reference data sets derived in the present paper allow, in the given temperature range, a matching of the calibration with respect to the temperature and to the absolute value of the diffusion coefficient of interest, thus reducing major sources of uncertainty in PFG NMR measurements to error limits in the sub-1% range.

Acknowledgements

The authors thank the Research Council of Italy, CNR (International Contract No. 98.01780.03) and the Ministry of University and of Scientific and Technological Research (Cofin. MURST 97 CFSIB) for financial support.

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