Self-Diffusion in Normal and Heavy Water in the Range 1–45°

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Self-diffusion coefficients of tritiated water in normal (H_2O) and heavy water (D_2O) have been measured over the temperature range 1-45°. The diaphragm-cell technique was used and the results are considered to be probably accurate to ±0.2%. The data of Longsworth[1,2] for HDO diffusion in both H_2O and D_2O in conjunction with the tritiated water values measured here have been used to calculate the self-diffusion coefficients of pure normal water (H_2O–H_2O) and pure heavy water (D_2O–D_2O). These coefficients have been tabulated and compared with molecular dynamics and nmr data.

Introduction

One hesitates to report yet another set of data for self-diffusion in liquid water. The fact remains that present values for tritiated water (HTO) in normal water (H_2O) over a temperature range are sparse and inaccurate and even at 25° vary from 2.2 to 2.6 × 10^{-9} m^2 sec^{-1}. There are similar variations in respect to HDO, $H_2{}^{18}O$ and also to pure H_2O self-diffusion as determined by nmr methods. The serious discrepancies between these various sets of data have been discussed extensively in recent reviews.[3-5] In the last of these,[5] it was pointed out that probably the only reliable data of good precision were those of Longsworth[2] for HDO in H_2O and D_2O. However, two sets of values, both by capillary methods, for tritiated water in normal water at 25° those of Devell[3] and Jones, Monk, and Rowlands[6] were considered to be reliable within their limits of error, each of ~2%. It was considered necessary therefore to confirm the value at 25° to better precision using diaphragm cells and to extend the measurements over the temperature range 1-45°.

Measurements have also been made of the self-diffusion of tritiated water in pure D_2O. The motivation here was to try and gain more insight into the mass dependence of the self-diffusion rates of the various isotopic forms of water. In particular, in order to compare isotopic diffusion data with those determined by the nmr spin echo method, one needs to extrapolate from isotopic data to the value for pure water.[7] The availability of Longsworth's accurate optical data[2] of the mutual diffusion of light and heavy water allows such an estimate to be made. Finally, it is hoped that the extrapolated values for pure water reported here will provide calibration points for the nmr method and so bring self-diffusion data obtained by this technique into better agreement with those from isotopic work.

Experimental Section

The normal water used in these experiments was distilled and passed through an ion-exchange column at a fast rate. It was then heated to boiling and vigorously degassed on a water pump. The specific conductance measured with a Jones-Dike bridge was 0.85 × 10^{-6} ohm^{-1} cm^{-1}. Heavy water (99.7 atom % D) was obtained from Merck Sharp and Dohme, Canada, and tritiated water from the Radiochemical Centre, Amersham, England. Both of these were used without further purification.

The magnetically stirred diaphragm cell method as developed originally by Stokes[8] was used in these determinations. The solvent-filled technique in which tracer is added to the top compartment was used throughout. Details of the apparatus and general procedure are given in a recent publication.[9] Additional precautions arising from work with organic solvents,[10] in particular the thermostating of the cells during sampling, were also incorporated. The counting techniques were based on the method outlined in ref 9. It was found that the usual dioxane-based scintillator solutions were not stable enough to give the precision required for these studies. A solution containing 750 ml of toluene, 300 ml of ethanol, and 9 g of butyl-BPD scintillator gave excellent results, however.

Analysis of Errors

As the isotopic extrapolations used later in this paper involve the use of small differences between diffusion coefficient values, a discussion of error limits is necessary.

The diaphragm cell was calibrated using the system 0.5 *M* KCl diffusing into water for which accurate Gouy data are available.[9] The cell compartment concentrations were determined by measuring their conductance with a Jones-Dike bridge which gives analyses accurate to ±0.01%. Duplicate calibration runs usually agreed to 0.05%. As the cell had a platinum sinter and Teflon-coated stirrers no correction for a wear factor was necessary.

(1) L. G. Longsworth, *J. Phys. Chem.*, **58**, 770 (1954).
(2) L. G. Longsworth, *J. Phys. Chem.*, **64**, 1914 (1960).
(3) L. Devell, *Acta Chem. Scand.*, **16**, 2177 (1962).
(4) H. R. Pruppacher, *J. Chem. Phys.*, **56**, 101 (1972).
(5) R. Mills, *Ber. Bunsenges Phys. Chem.*, **75**, 195 (1971).
(6) J. R. Jones, D. L. G. Rowlands, and C. B. Monk, *Trans. Faraday Soc.*, **61**, 1384 (1965).
(7) Some explanation is needed as to what is meant by "the self-diffusion coefficient for pure water." A diffusion coefficient is defined relative to a gradient of some kind. In a tracer experiment it would be a gradient of radioactivity but in the absence of a tracer it becomes a little more difficult. In an assemblage of identical molecules one can, however, conceptually identify a certain number of them and then a gradient of identified molecules exists. The essential point is that the process of identification must not change any of the chemical or physical properties of the molecules. In practice a molecular dynamics "experiment" does this insofar as the momentum and space coordinates of all the molecules are known at any time. It is also very closely approached in an nmr experiment where the only gradient present is related to the phase of nuclear magnetic moments present in the molecules which will not sensibly affect their rate of diffusion.
(8) R. H. Stokes, *J. Amer. Chem. Soc.*, **72**, 763 (1950).
(9) R. Mills and L. A. Woolf, "The Diaphragm Cell," DRU Report RR1, A.N.U. Press, Canberra, 1968.
(10) A. F. Collings and R. Mills, *Trans. Faraday Soc.*, **66**, 2761 (1970).

When tracers are used analytical errors are somewhat greater. The liquid-scintillation counting apparatus has been described in detail in ref 9. All samples for counting are prepared by accurate weight dilution. Each sample is counted simultaneously by two independent counter systems and any appreciable difference between the two results gives an indication of malfunction in one of the electronic components. Normally agreement between the two counters is ±0.1%. More than 10^6 counts are recorded on all samples so that statistical counting error is expected to be <±0.1%. The top compartment solution is diluted by weight to give the same counting rate as the bottom to avoid coincidence errors. Other procedures automatically correct for drift in the photomultipliers and amplifiers in the time between analyses of the two compartments. Overall reproducibility between tracer runs is ±0.2%.

One serious source of error was found, however, in relation to the radioactive tritiated water. In the first 20 or so runs, at several temperatures, the measured diffusion coefficients showed a slight linear increase with time. This effect appears to be due to the high specific activity of the tracer. Tritiated water is readily available at very high specific activities and there is a natural tendency to use high counting rates with consequent low backgrounds. When the specific activity used in the above runs was reduced by a factor of 30, the time variation disappeared and the reproducibility was excellent. It is well known that the recoils of disintegrating tritium atoms can affect molecules in their vicinity and this effect is in fact the basis of the Wilzbach method of tritium labeling. It would appear in the diffusion case that high activities cause some alteration to the water structure although more work needs to be done to specify this more closely. The effect may have contributed to previous anomalous results for tritiated water.

The cells were immersed in a well stirred water thermostat, and temperature fluctuations were measured continuously for all runs with a recording platinum resistance thermometer. In the range 1-35° these fluctuations were not greater than ±0.002° and at 45° not greater than ±0.01°. Absolute temperatures as measured with calibrated calorimeter thermometers and the platinum resistance thermometer are probably correct to ±0.005°.

At a given temperature runs were repeated at least three times for normal water runs and twice for all heavy water runs. The overall reproducibility as shown in Table I was at least of order ±0.2%. There always remains of course the possibility of some unrecognized systematic error.

Results

In Table I are listed the self-diffusion coefficients measured in this work together with Longsworth's extrapolated values for HDO in both normal and heavy water. An asterisk denotes that the species is present effectively in trace amounts.

Before discussing the data in more detail a few comments should be made as to the tracer species present in these experiments. It is obvious that due to the ionization of water there will be rapid exchange between hydrogen, deuterium, and tritium ions. Thus if a small amount of D_2O is introduced into a large volume of H_2O, the only two species virtually present will be HDO and H_2O and similarly for other combinations. In Longsworth's mutual diffusion work on H_2O-D_2O mixtures the limiting mutual diffusion coefficients (obtained by extrapolation) refer to the diffusion of vanishingly small amounts of HDO in H_2O and D_2O at each end of the concentration scale. This fact does not seem to have been appreciated by some authors (see, *e.g.*, Eisenberg and Kauzmann,[11] pp 218-219). Theory indicates[12,13] that these limiting mutual coefficients should be identical with the tracer or self-diffusion coefficients of HDO in these solvents and this equivalence has been borne out by experiment for similar systems. For this reason our tracer coefficients obtained with HTO are directly comparable with Longsworth's data. Another important consequence of this exchange process is that when tritiated water is added to D_2O, the effective tracer species is DTO*. It should be added that tritiated water is not obtained in a pure state but is in trace quantities in normal water. However, the amount of normal water accompanying the tritiated water which is added to the D_2O in the diffusion cell is very small (<0.02 mol %) and has a negligible effect. For a 50 mol % H_2O-D_2O solution, the tracer is an equimolar mixture of DTO* and HTO*.

Comparison with all previous results for tritiated water would serve no useful purpose. However, it may be noted that the two values previously considered most reliable by Mills[5] for HTO in H_2O at 25° were those of Devell[3] (2.25) and Jones, Rowlands, and Monk[6] (2.22) and the average of these is practically the same as the value shown in Table I. Their combined error limits of ±3% obviously lessen the significance of this agreement. The value of 2.029 in the last column is for an equimolar HTO*-DTO* mixture diffusing in a 50/50 mol % H_2O-D_2O solution. This value is almost half-way between the corresponding tracer values for pure H_2O and D_2O and supports Longsworth's conclusion[2] that there are no unusual properties connected with solutions of this composition. It will be observed in Table I that, as might have been expected from mass considerations, the HTO values in H_2O and the DTO values in D_2O are consistently lower than the corresponding HDO ones. These systematic differences are tabulated as percentages in Table II. In all cases the data for HDO are from Longsworth.[2] The parentheses enclose solvents; tracer species either have an asterisk or are subscripted.

Column 2 presents the differences observed when changing from H_2O to D_2O as solvent for the tritiated species used in this work whereas column 3 differences are for the same solvent change but for Longsworth's HDO values. The parallelism between the two sets of data over the three temperatures is quite remarkable. It is even better than it seems because the tritiated tracer changes from HTO to DTO when in D_2O and the mass increase of one unit would slightly increase the differences in column 2. In columns 4 and 5, the differences in diffusion rate between HTO* and HDO* in H_2O and between HDO* and DTO* in D_2O are tabulated and again considering the small differences involved, the data are very consistent.

An analysis of the information contained in Table II now allows calculation of the self-diffusion coefficients of pure normal water[7] (H_2O in H_2O) and also of pure heavy water (D_2O in D_2O). In the first place it can be deduced from columns 2 and 3 that over the range 5 to 45°, HDO and HTO react similarly in changing from one solvent

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(11) D. Eisenberg and W. Kauzmann, "The Structure and Properties of Water," Clarendon Press, Oxford, 1969, pp 218-219.

(12) R. J. Bearman, *J. Phys. Chem.*, **65**, 1961 (1961).

(13) D. W. McCall and D. C. Douglass, *J. Phys. Chem.*, **71**, 987 (1967).

TABLE I: Self-Diffusion of Isotopic Species of Water

	HTO^*-H_2O	$HDO^*-H_2O^a$	DTO^*-D_2O	$HDO^*-D_2O^a$	$\left.\begin{matrix}HTO^*\\DTO^*\end{matrix}\right\}$ / 50 mol % D_2O-H_2O
Temp, °C			$D^* \times 10^9$ m^2 sec^{-1}		
1	1.113 ± 0.002	1.128			
4	1.236 ± 0.003				
5	1.272 ± 0.002	1.295	1.001 ± 0.001	1.034	
15	1.724 ± 0.003				
25	2.236 ± 0.004	2.272	1.849 ± 0.001	1.902	2.029
35	2.838 ± 0.002				
45	3.474 ± 0.003	3.532	2.939 ± 0.005	3.027	

[a] Longsworth's data[1,2] (precision ±0.1%).

TABLE II: Differences in Diffusion Rate Due to Isotopic Mass

	$\frac{[D^*(H_2O) - D^*(D_2O)] \times 10^2}{D^*(H_2O)}$		$\frac{[D^*_{HDO} - D^*_{HTO}] \times 10^2}{D^*_{HDO}}$	$\frac{[D^*_{HDO} - D^*_{DTO}] \times 10^2}{D^*_{HDO}}$
Temp, °C	$HTO^* - DTO^*$	HDO^*	(H_2O)	(D_2O)
5	21.4%	20.2%	1.8%	3.2%
25	17.3	16.3	1.6	2.8
45	15.4	14.3	1.6	2.9

TABLE III: Calculated Self-Diffusion Coefficients of H_2O and D_2O

Temp, °C	$D^* \times 10^9$ m^2 sec^{-1}, H_2O-H_2O	$D^* \times 10^9$ m^2 sec^{-1}, D_2O-D_2O
1	1.149	
4	1.276	
5	1.313	1.015
15	1.777	
25	2.299	1.872
35	2.919	
45	3.575	2.979

(H_2O) to another (D_2O) and the mass effects are carried over in almost exact proportion. Therefore it is reasonable to assume that changes in diffusion rate arising from mass differences between isotopic species in solvent D_2O should be equally applicable to the change in solvent H_2O. In column 5 of Table II, there is tabulated the percentage change in diffusion rate in the solvent D_2O between molecules of mass 21 (DTO) and mass 19 (HDO), a difference of 2 mass units. Now for the solvent H_2O, we have measured diffusion coefficients for molecules of mass 20 (HTO) and what we are trying to calculate are values for molecules of mass 18 (H_2O), again a difference of 2 mass units. Therefore increasing our measured values for HTO by the percentages given in column 5 should give the corresponding values for self-diffusion in pure water, (H_2O in H_2O). Similarly self-diffusion in pure heavy water (D_2O in D_2O) can be obtained by decreasing Longsworth's HDO in D_2O values by the percentages given in clumn 4 which correspond to a mass change of one unit in H_2O. The coefficients so obtained should be accurate to a few tenths of a per cent and are listed in Table III. For values other than 5, 25, and 45°, averaged percentages have been used.

An Arrhenius plot (log *D* vs. $1/T$) for both sets of data is given in Figure 1. If activation energy theories are applicable to diffusion in liquids one would expect a linear relation among the points; instead there is a gentle curvature in both sets. However, without implying that the activation approach is valid one can give experimental activation energies for the temperature regions 1–15° and 15–45° as these data are useful to workers in the biological sciences and other areas. For H_2O, $E_A = 4.7$ kcal/mol (1–15°) and 4.2 kcal/mol (15–45°) and for D_2O, $E_A = 5.0$ kcal/mol (1–15°) and 4.5 kcal/mol (15–45°).

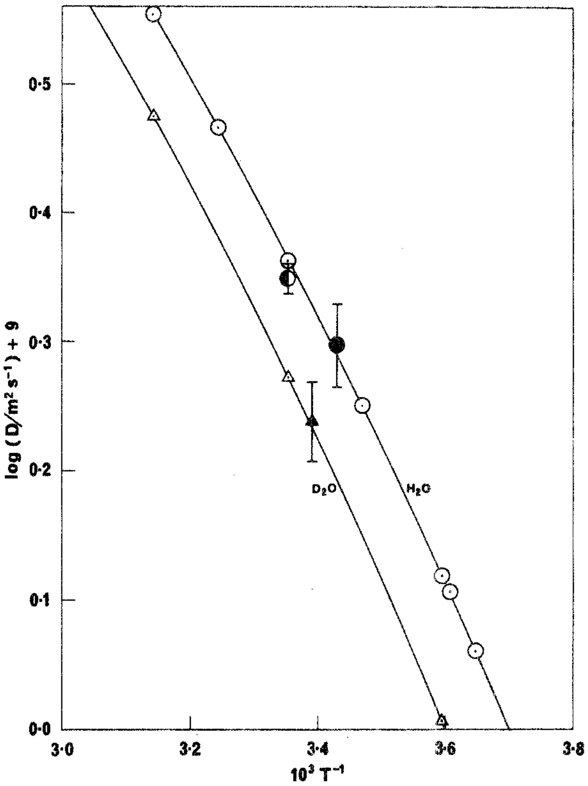

Figure 1. Arrhenius plot of log *D* vs. $1/T$ of the self-diffusion coefficients of pure H_2O (○) and pure D_2O (△); (●,▲), nmr values of Murday and Cotts;[15] (◐), nmr value of O'Reilly and Peterson.[16]

The only comparisons that can be made with the data in Table III are as has been implied earlier, with molecular dynamics and nmr results where the identification process has virtually no effect on physical or chemical properties. A molecular dynamics study of liquid water has recently been reported by Rahman and Stillinger.[14] At a temperature of 34.3° they obtain a figure of 4.2×10^{-9} m^2 sec^{-1} for the self-diffusion coefficient of water which can be compared with our value at that temperature of 2.84. Although the discrepancy is large, the technique of computer simulation of the properties of complex liquids such as water is in its infancy. It might be hoped indeed that feedback from our results into the calculations may eventually help to refine the simulation techniques.

In nmr studies, up until a year or two ago, there was a wide scatter of results for the self-diffusion of liquid water at 25°. These values ranged from 2.13 to 2.51×10^{-9} m^2 sec^{-1} (see, *e.g.*, ref 5). More recently, Murday and Cotts[15] have reported a value of $1.98 \pm 0.14 \times 10^{-9}$ m^2 sec^{-1} at 18.4° and O'Reilly and Peterson[16] $2.23 \pm 0.06 \times 10^{-9}$ m^2 sec^{-1} at 25.0°. For D_2O, Murday and Cotts[15] have determined also a value of $1.73 \pm 0.12 \times 10^{-9}$ m^2 sec^{-1} at 21.7°. These values have been included in our Figure 1 and it is seen that within their limits of error there is satisfactory agreement. The actual reproducibility of nmr results can be of the order of ±0.5% and the large errors quoted in nmr data therefore appear to be due to uncertainties in the machine calibration factor. It might be more practical now to obtain this calibration factor by direct comparison with the data presented in Table III.

So far in this discussion we have been using experimental considerations only to obtain these self-diffusion coefficients. It will be realized that for both H_2O and D_2O, we now have original and derived experimental data for the diffusion of three isotopic forms of water over a considerable temperature range. There is the possibility therefore that the functional form of the mass dependence can be determined. This functional relationship does not appear to be a simple square root of the mass dependence and it seems probable that the differing interaction potentials of the various isotopic species are also involved. This problem is undergoing further study.

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(14) A. Rahman and F. H. Stillinger, *J. Chem. Phys.*, **55**, 3336 (1971).

(15) J. S. Murday and R. M. Cotts, *J. Chem. Phys.*, **53**, 4724 (1970).

(16) D. E. O'Reilly and E. M. Peterson, *J. Chem. Phys.*, **55**, 2155 (1971).

The Limiting Equivalent Conductance of Perchloric Acid in 0.9914 Mole Fraction *N*-Methylacetamide (NMA) at 40°

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At 40.00° and in 0.9914 mole fraction NMA, Λ values for perchloric acid were determined over a range of concentrations of the acid. Λ_0 was obtained from the Λ values using the methods of Kohlrausch, Fuoss and Kraus, and Shedlovsky. The Λ_0 values obtained by the three methods were in excellent agreement and, if the limiting equivalent ionic conductances recorded in the literature are applicable to anhydrous NMA, indicate little or no Grothuss conductance in NMA, and no formation of hydrated entities with ions of perchloric acid which were of different mobilities than the ion entities existing in pure NMA.

Shedlovsky[1] noted in his studies of hydrochloric acid in the water-methanol system that a remarkable drop occurred in the equivalent conductance at infinite dilution when trace amounts of water were added to the pure methanol solvent. Similar decreases were found by Goldenberg and Amis[2,3] for perchloric acid in water-ethanol and water-methanol solvents. The reasons for such sharp decreases are usually ascribed to a breaking up of the Grothuss conduction chains in the alcohols and the formation of H_3O^+ and $H_9O_4^+$ which move as entities through the solution. The highly hydrogen bonded nature of *N*-methylacetamide suggests that it could be a good solvent to test whether a proton jump mechanism is general for strong acids in hydrogen bonded solvents rather than just for water or low molecular weight alkyl alcohols. Dawson, Newell, and McCreary[4] have suggested that the proton does not move by a unique method in formamide.

Experimental Section

The conductance measurements were made at 0.5, 1.0, 2.0, 5.0, and 10.0 kHz and extrapolated to infinite frequency. The conductance apparatus and methods were

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(1) T. Shedlovsky, "The Structure of Electrolytic Solutions," W. J. Hamer, Ed., Wiley, New York, N. Y., 1959.

(2) N. Goldenberg and E. S. Amis, *Z. Phys. Chem. (Frankfurt am Main)*, **30**, 65 (1961).

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