

Viscosity of Deuterium Oxide and Water in the Range 5° to 125° C

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Measurements of the absolute viscosity of deuterium oxide of 99.5 percent purity and of water were made over the range 5° to 125° C. It is estimated that these determinations are accurate within 0.1 percent in relation to the value 1.0050 centipoise for the viscosity of water at 20° C. The work also included determinations of the density of deuterium oxide over the range 90° to 125° C. Values for the viscosity and density of 100-percent deuterium oxide were obtained by linear extrapolations. The ratio of the viscosity of deuterium oxide to that of water at the same temperature was found to be 1.3052 at 5° C. This ratio decreased at a diminishing rate with increase in temperature to a value of 1.1456 at 125° C.

I. Introduction

The work reported here was undertaken to provide accurate data over a wide temperature range. The work was undertaken as two separate projects. The first project covered viscosity measurements with a Bingham viscometer [1]¹ over the range 5° to 95° C. The second project extended the temperature range above the boiling points of water and deuterium oxide, and it was necessary to operate the viscometer under pressure in order to prevent boiling of the test liquids. An Ostwald viscometer was selected for this project as being more readily adaptable to this type of operation.

II. Materials

The distilled water was obtained from a laboratory still of commercial type.

The deuterium oxide was obtained from the Atomic Energy Commission and was said to be of 99.56 mole percent purity. A portion of this material was used as received for the first project. Subsequently, it was learned through tests on other portions that the specific conductance was somewhat higher than for pure water, indicating that the impurities present probably included traces of inorganic salts. Mass-spectrograph analysis indicated the presence of approximately 0.9

¹ Figures in brackets indicate the literature references at the end of this paper.

mole percent of O¹⁸ in the oxygen of the material. A sample of distilled water was found to contain approximately 0.2 mole percent of O¹⁸. The concentration of O¹⁷ in the D₂O was slightly higher than in the distilled water.

The material used in the second part of the work was subjected to a simple distillation under reduced pressure, and without boiling, to reduce or eliminate any inorganic impurities. The center fraction, representing 80 to 85 percent of the original volume, was selected for the viscosity measurements. The density of this fraction was found to be 1.10465 ± 0.00003 g/ml at 25° C. Calculations based on Longworth's equation [2] using the numerical coefficients of Voskuyl [3] for the relation between density and mole fraction of D₂O, and corrected for abnormal O¹⁸ and O¹⁷ content, indicated that the mole fraction of D in the hydrogen was 99.53 mole percent. Similarly, calculations using the density of the sample as received, i. e., 1.10469 ± 0.00003 g/ml at 25° C, indicated that the concentration of D in the hydrogen of the original material was 99.57 mole percent.

III. Work with Bingham Viscometer in the Range 5° to 95° C

The Bingham viscometer [1] used was designed for low-viscosity liquids. The capillary was 12.3 cm long, and its diameter was approximately 0.022

cm. The volume of flow was 5.07 cm.³ With this type of instrument, flow is caused by air pressure applied to one arm of the instrument. The pressure applied was measured with a mercury manometer. It is estimated that the corrected values for pressure causing flow were accurate within ± 0.05 percent.

In calibration tests and in viscosity measurements, times of flow were determined only for flow into the measuring bulb, the walls of which had been previously wetted and allowed to drain. Drainage times were approximately proportional to the viscosity of the liquid. In this way, error due to reduction in effective capacity of the bulb by the film of liquid on its walls was substantially eliminated. The working volume of liquid in this instrument is not highly critical, but it was adjusted at or near the test temperature when required.

Calibration of the Bingham viscometer was based on the usual equation

$$\eta = Cpt - C'\rho/t,$$

in which C and C' are instrumental constants, η is the absolute viscosity of the liquid, p the pressure causing flow, t the time of flow, and ρ is the density of the liquid. By observing the flow time for water at 20° C with several different values for p , data were obtained for evaluating C and C' by use of the usual pt versus $1/t$ plot. In this way, the calibration of the viscometer is made to rest entirely on the value assigned to the viscosity of water at 20° C. The viscosity of water at 20° C was assigned the value 1.0050² centipoises.

Test runs with water were made also at 5°, 40°, 60°, 80°, and 95° C to obtain comparative data on the viscosity of water and also to ascertain whether evaporation losses would cause serious error. Clear indications of slight losses by evaporation were observed, but the effects on the viscosity values were not significant.

A single filling of the viscometer with D₂O was used for observations of the flow time at 20°, 5°, 40°, 60°, 80°, and 95° C in the order named. As a check on possible contamination of the D₂O during these observations, the volume of charge

² The value 1.005 centipoises has been used for many years at this Bureau as the basis for calibration of viscometers. The more recent value, 1.002 centipoises of Coe and Godfrey [11] has not been used because of its tentative nature, although results thus far obtained by J. F. Swindells in a continuation of their work indicate that the true value is in the neighborhood of 1.002 centipoises. Pending completion of Swindells' work, continued use of the value 1.005 seems desirable.

was readjusted at room temperature and two runs made at 20° C for comparison with results of the initial runs at this temperature. This comparison indicated that the effect of any contamination was considerably less than the estimated accuracy of the determinations.

With the Bingham viscometer, the density of the liquid is of only minor importance. Values for the density of water were obtained from published data [4]. Data on the density of D₂O at temperatures below 50° C were in substantial agreement with those of Chang and Chien [5]. Values for density at 60°, 80°, and 95° C were obtained by extrapolation.

IV. Work With Ostwald Viscometer in the Range 90° to 125° C

The Ostwald viscometer was specially designed to provide for use of a capillary with "square-cut" ends and to minimize the effect of surface tension. The capillary was about 40 cm long, and its diameter was approximately 0.04 cm. The mean corrected time of flow for 10.31 cm³ of water at 20° C was 1620.13 sec, the hydrostatic head at mean time being 40.2 cm. The instrument was used with equal pressure applied to both arms to prevent boiling of the test liquid. Accurate values for the pressure were not required, and a Bourdon type pressure gage was used.

In this instrument, flow is caused by the hydrostatic pressure of the test liquid and is dependent on the density of the liquid, the volume of charge, and the dimensions of the instrument. The volume of charge was measured at room temperature with a special pipette. Corrections were applied to the observed time of flow to compensate for variations in the volume of charge caused by variations in room temperature and temperature of test.

The density of the D₂O at the test temperature was determined by use of a simple dilatometer that had been calibrated with water. The dilatometer was calibrated and used with an internal air pressure of 35 psi gage to prevent boiling.

For Ostwald type instruments the equation expressing the relation between η , ρ , and t is written

$$\frac{\eta}{\rho} = At - \frac{B}{t},$$

in which A and B are the instrumental constants,

and the other symbols have the same significance as in eq 1. Determination of the values of the constants was made in the usual way by determining t for water at several temperatures for which η and ρ were known and constructing a Higgins diagram. In both the calibration and use of this instrument, flow times were corrected for the effect of the air column in the receiving arm and to a standard temperature, 20° C, with respect to volume of charge.

Distilled water was used at 20°, 40°, 60°, and 80° C in the calibration of this viscometer. The viscosity of water at 20° C was assigned the value 1.0050 centipoises, and the values for viscosity at the other temperatures were those determined with the Bingham viscometer and reported in table 1.

TABLE 1. Absolute viscosity

Temperature ° C	Ordinary water Centipoises	Deuterium oxide		
		99.53 mole percent Centipoises	99.57 mole percent Centipoises	100 mole percent ^a Centipoises
5	1.5230	-----	1.9858	1.9878
20	^b 1.0050	-----	1.2503	1.2514
40	0.6551	-----	0.7866	0.7872
60	.4679	-----	.5509	.5513
80	.3558	-----	.4138	.4141
90	.3158	0.3656	-----	.3658
95	.2985	-----	.3452	.3454
100	.2830	.3263	-----	.3265
110	.2557	.2939	-----	.2941
120	.2328	.2668	-----	.2669
125	.2227	.2550	-----	.2551
20°	-----	-----	^c 1.2501	-----

^a Extrapolated values not corrected for abnormal O¹⁸ content.

^b Assigned value used as basis for calibration of instruments.

^c Check for comparison with initial determination at 20° C to indicate possible extent of contamination.

Test runs were made with water at the higher temperatures and pressures to test the method and apparatus and to obtain comparative data on water at these temperatures. Usually observations at several temperatures were made on each filling, and for several fillings the temperature was returned to its initial value for final observations, which by comparison with the initial observations served as an indication of the possible maximum error (0.05%) due to loss of charge through evaporation.

Most runs were made by using an applied pressure of 35 psi gage. Although it was not antici-

pated that pressure of this magnitude would have significant effect on the viscosity of water due to air solubility or distortion of the viscometer, this was verified by data obtained in runs at 20° and 80° C at both atmospheric pressure and with an applied pressure of 35 psi. Since the agreement between data obtained under the two pressure conditions was within the experimental accuracy, no effect of pressure was observed.

A single filling of the instrument with D₂O was used for observations at 90°, 100°, 110°, 120°, and 125° C.

In both parts of the work, the temperature of the viscometer was controlled with an oil bath whose temperature was regulated to within approximately ±0.01 deg for the Bingham viscometer and to within approximately ±0.02 deg for the Ostwald viscometer.

Temperatures were measured with mercury-in-glass thermometers that had been calibrated in place with a platinum resistance thermometer.

Times of flow were measured with a manually controlled electric timer operating on a specially controlled constant-frequency circuit. It is estimated that time measurements were accurate within ±0.02 percent.

After the completion of the work with water, the viscometers were cleaned with chromic-acid cleaning solution, washed with distilled water, and dried with a current of dry air.

In all the work with D₂O, a drying tube charged with Drierite was used in the pressure line to protect the D₂O from contamination with water vapor in the compressed air.

V. Results

Values obtained for the absolute viscosity of ordinary water and of deuterium oxide are given in table 1. As no data on the viscosity of D₂O¹⁸ are available, no correction for abnormal O¹⁸ content was attempted in the simple linear extrapolation used to obtain the values for D₂O of 100-percent purity with respect to D content.

Ratios of the viscosity of water and of deuterium oxide at various temperatures to the viscosity of water at 20° C are given in table 2. Values for the relative viscosity of water derived from values for absolute viscosity published in International Critical Tables [6] are included in table 2 for comparison. This table also includes values for the

ratio of the viscosity of deuterium oxide at various temperatures to the viscosity of water at the same temperatures. Table 3 contains values for the density of deuterium oxide that were determined at various temperatures in the range 90° to 125° C. Values for the density of 100-percent deuterium oxide, with normal and abnormal O¹⁸ content were obtained by linear extrapolations based on the assumption that the O¹⁸ and O¹⁷ compounds have the same molar volumes as the O¹⁶ compounds.

TABLE 2. *Relative viscosity*

Temperature ° C	Relative to water at 20° C		Relative to water at <i>t</i> °	
	Water		Deuterium oxide, 100 percent ^b	Deuterium oxide, 100 percent ^b
	Authors	ICT ^a		
5.....	1.5154	1.5057	1.9779	1.3052
20.....	1.0000	1.0000	1.2452	1.2452
40.....	0.6518	0.6480	0.7833	1.2017
60.....	.4656	.4658	.5485	1.1782
80.....	.3541	.3539	.4120	1.1637
90.....	.3142	.3139	.3640	1.1583
95.....	.2970	.2968	.3437	1.1570
100.....	.2816	.2815	.3250	1.1538
110.....	.2544	.254	.2927	1.1504
120.....	.2316	.230	.2656	1.1467
125.....	.2216	-----	.2538	1.1456

^a Derived from values for absolute viscosity published in International Critical Tables [6].

^b Extrapolated values not corrected for abnormal O¹⁸ content.

TABLE 3. *Density of deuterium oxide*

Temperature ° C	Deuterium oxide		
	99.53 mole percent	100 percent ^a	100 percent ^b
90.....	<i>g/cm</i> ³ 1.0711	<i>g/cm</i> ³ 1.0716	<i>g/cm</i> ³ 1.0708
100.....	1.0633	1.0638	1.0630
110.....	1.0549	1.0554	1.0547
120.....	1.0461	1.0466	1.0459
125.....	1.0416	1.0421	1.0414

^a With 0.7 mole percent excess O¹⁸.

^b With normal O¹⁸ content.

VI. Discussion

The values for the absolute viscosity of deuterium oxide given in table 1 are based on the average of three or four determinations of the flow time at each temperature. The spread between the observed flow times at any one

temperature was less than 0.1 percent and less than 0.05 percent for observations at 40° C and higher temperatures. One observation at 125° C was discarded because it departed from the mean of four other determinations by 0.12 percent. However, inclusion of this discarded observation would have changed the viscosity value at 125° C by only 0.0001 centipoise.

The limit of possible error of the determined values given in table 1 is believed to be about 0.25 percent in relation to the value 1.0050 centipoise for the viscosity of water at 20° C. The root mean square of the estimated maximum values for the various individual errors involved is 0.1 percent. The extrapolations to obtain values for the viscosity of D₂O of 100-percent purity neglected the effect on viscosity of the abnormal O¹⁸ and O¹⁷ content, since no data were available on the effect on viscosity of abnormal amounts of these oxygen isotopes.

Data obtained with both instruments over the entire temperature range are shown graphically in figure 1. It will be noted that the data for D₂O obtained with both instruments fall on one smooth curve. The same is true for the data on water.

However, some irregularities, notably at 95° C, will be noted on figure 2, which shows the variation of relative viscosity, η_t^i , with temperature. Points representing the results obtained by other investigators are included for comparison.

Only Lewis and MacDonald [7] have reported viscosity values over a range of temperatures. They observed that the relation between temperature and η_t^i was approximately linear over the range 5° to 35° C; however, our results indicate an appreciable curvature in the relation in this temperature range. The agreement between their values and the curve representing our results is within the estimated accuracy of their data (0.5%), except at 35° C where their value is 1.0 percent lower than the curve and even a little lower than the present value determined at 40° C.

Taylor and Selwood [8] reported the same value as Lewis and MacDonald for the viscosity of D₂O at 20° C. This value is 0.3 percent higher than that obtained here.

Baker and La Mer [9] and Jones and Fornwalt [10] reported values for the relative viscosity of D₂O at 25° C only. Baker and La Mer's value

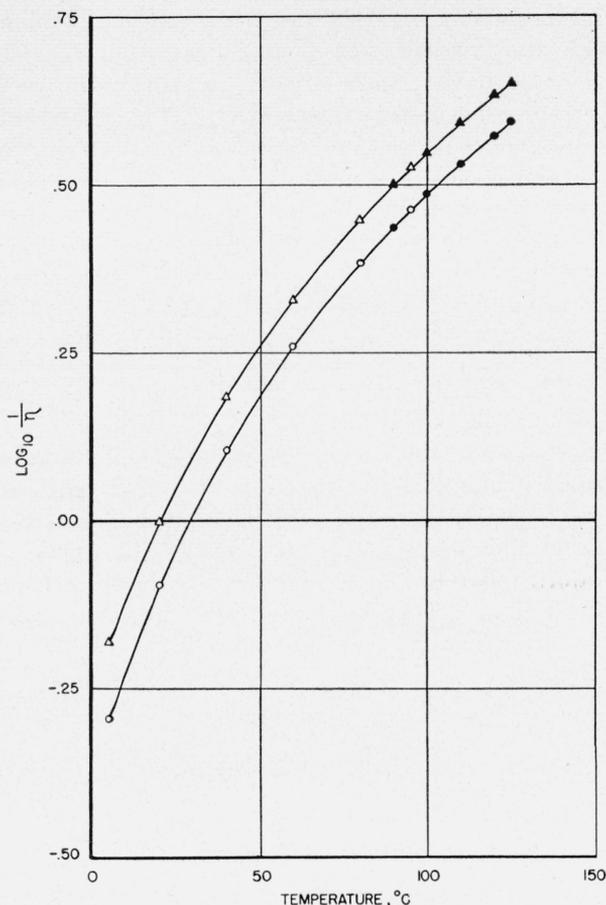


FIGURE 1. Relation between temperature and logarithm of reciprocal viscosity for deuterium oxide and water, showing consistency of results obtained with the two types of instruments.

Bingham viscometer: Δ , water; \circ , deuterium oxide. Ostwald viscometer: \blacktriangle , water; \bullet , deuterium oxide.

agreed with that of Lewis and MacDonald and was only 0.05 percent higher than our curve. However, the value reported by Jones and Fornwalt appears to be the most accurate and is 0.12 percent lower than our curve. Part of this difference between our value and that of Jones and Fornwalt may be due to the abnormal O^{18} content of our sample.

This comparison with published data is shown more accurately in table 4, which contains interpolated values for η'_i at 10° , 15° , 25° , 30° , and 35° C that were calculated from our observed values at 5° , 20° , and 40° C. The interpolated

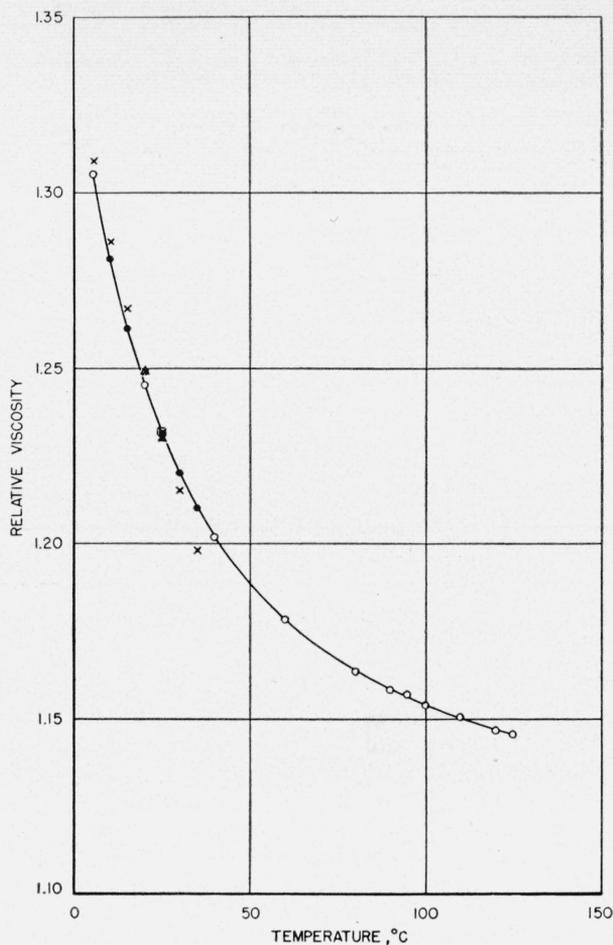


FIGURE 2. Ratio of viscosity of deuterium oxide to the viscosity of water at the same temperature.

\circ , Hardy and Cottingham; \bullet , calculated interpolation; \times , Lewis and MacDonald; Δ , Taylor and Selwood; \square , Baker and Lamer; \blacktriangle , Jones and Fornwalt.

values were obtained by use of the following relations to compute values for the absolute viscosity of D_2O and water at the desired temperatures: For D_2O

$$\log_{10} \eta = \frac{1301}{930.349 + 7.8061(t-20) + 0.000833(t-20)^2} - 3.30103.$$

For water

$$\log_{10} \eta = \frac{1301}{998.333 + 8.1855(t-20) + 0.00585(t-20)^2} - 3.30103.$$

TABLE 4. *Relative viscosity, η_r^t*

Ratio of the viscosity of D₂O to that of water at the same temperature. Comparison with published data.

Temperature	Hardy and Cottington ^a	Lewis and MacDon-ald, 1933	Taylor and Sel-wood, 1934	Baker and La Mer, 1935	Jones and Fornwalt, 1936
° C					
5	1.3052	1.309	-----	-----	-----
10	(1.2813)	1.286	-----	-----	-----
15	(1.2615)	1.267	-----	-----	-----
20	1.2452	1.249	^b 1.249	-----	-----
25	^c (1.2314)	1.232	-----	1.232	1.22996
30	(1.2198)	1.215	-----	-----	-----
35	(1.2100)	1.198	-----	-----	-----
40	1.2017	-----	-----	-----	-----

^a Values in parenthesis are interpolated.

^b Derived from their reported value of 12.6 millipoises for absolute viscosity, using the ICT value for viscosity of H₂O, i. e., 1.0087 centipoise.

^c This value is 0.12% higher than reported by Jones and Fornwalt. This may be due to the abnormally high O¹⁸ content of our sample.

The values for relative viscosity of water at 5° and 40° C derived from the ICT values are believed to be too low by amounts several times greater than 0.1 percent, the estimated accuracy of the ICT values between 5° and 40° C. The value reported here for 5° C is the mean of the values obtained with the two types of viscometers, i. e., 1.5155 with the Bingham and 1.5153 with the Ostwald. Our value at 40° C confirms the value 0.6518 reported by Coe and Godfrey [11] for the same temperature. The agreement with ICT values at other temperatures is within the estimated accuracy (0.5 to 1.0%) given for the ICT values above 40° C.

Unusual accuracy in determining the density of D₂O was not attempted. The values reported in table 3 are believed to be accurate to 0.0002 g/cm³, or a little better.

VII. Summary

Data are presented on the viscosity of deuterium oxide and water over the temperature range 5° to 125° C, and on the density of deuterium oxide in the range 90° to 125° C. Observations were made on deuterium oxide having more than 99.5

mole percent of D in the hydrogen, and values for the viscosity of deuterium oxide of 100-percent purity with respect to deuterium were obtained by linear extrapolation. The deuterium oxide contained 0.7 mole percent more O¹⁸ in the oxygen than the laboratory distilled water. The O¹⁷ concentration also was slightly higher than normal. No correction of the viscosity data was made to compensate for the abnormal content of the heavy oxygen isotopes.

The authors acknowledge the advice and assistance of J. F. Swindells of the Bureau staff in designing the special Ostwald viscometer and in performing part of the work of calibrating both viscometers. The cooperation and assistance of other members of the Bureau staff in supplying information on the composition of the deuterium oxide is acknowledged also. Credit is due the Atomic Energy Commission for financial support of the work.

VIII. References

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