Viscosity of Gaseous D_2O at High Pressures*

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Viscosity of D_2O in the gaseous region up to 400°C and 300 bar was measured with the aid of a capillary viscometer. Existence of a negative pressure gradient at subcritical temperature was experimentally and quantitatively confirmed. Measured results of the viscosity on five isotherms were correlated into a simple empirical equation.

1. Introduction

On the viscosity of steam (H_2O), a negative pressure effect, namely, a negative gradient of isotherms against pressure was first discovered in 1960 by a group at Brown University⁽¹⁾⁽²⁾. Although similar effect of this interesting phenomenon has been expected also for isotopes of H_2O , no experimental evidence for gaseous D_2O has been reported. Present paper describes experimental results on the viscosity of gaseous D_2O in the temperature range 200–400°C where a negative pressure effect is significant. Knowledge of this kind of phenomena is not only interesting from the scientific view point, but also is essential to correlate precise properties of D_2O and to use them for various engineering purposes including nuclear power engineering.

Measuring method of present study was the capillary method. The apparatus was a closed-circuit capillary viscometer modified from the one previously used for measurements of D_2O in the liquid and dense-gas region of up to 500°C and 800 bar⁽³⁾.

2. Nomenclature

C	capillary constant	cm ⁴
L	length of capillary	mm
m	kinetic energy correction factor	
P	pressure	bar
Q	volumetric flow rate	cm ³ /s
r	radius of capillary	mm
t	temperature	°C
Δt	temperature difference	°C
α	thermal expansion coefficient	
ρ	density	g/cm ³
η	viscosity	Pa·s (10 ⁻⁷ Pa·s = 1cP)

3. Existing data on D_2O

At present three former investigations on the viscosity of gaseous D_2O at high temperatures, all at 1 atm or lower,

are known. In 1953 Rowlinson⁽⁴⁾ measured it in the temperature range 80–132°C with the aid of a capillary viscometer. Precision of his measurement was 1%. In this study his main interest lay in the viscosity ratio of D_2O to H_2O . Extensive measurements in the range 225–1450°C and at atmospheric pressure were carried out by Bonilla and co-workers⁽⁵⁾. They used a capillary viscometer which was used also for measurement of H_2O . Recent critical reviews⁽⁶⁾⁽⁷⁾ showed that data by Bonilla on H_2O were systematically lower by 4% than other recent measurements. This means that their results of D_2O might also have systematic deviations of similar magnitude. The most recent measurement of the viscosity of gaseous D_2O was reported by Timrot & co-workers⁽⁸⁾ in 1973. They used the oscillating disk method and claimed the precision of about 0.4%. All three measurements mentioned above are at or below atmospheric pressure, and no data are available at higher pressures.

When data on D_2O under high pressure are needed in various applications including nuclear power engineering, the only practical way presently available is estimating it with the aid of the simple similarity theory between H_2O and D_2O molecules. Experimental data will be useful also for testing the limit of this kind of similarity calculations.

4. Experimental apparatus

Schematic outline of experimental setup is shown in Figure 1. It is similar to the one used for liquid region measurement⁽³⁾ except additional parts 4 to fix the positions of liquid-gas interfaces. The method was a closed-circuit transpiration method. The capillary made of platinum-rhodium alloy had a length of 500 mm and an inner diameter of 0.32 mm. The test fluid flows from one side of high pressure injector 5 and returns to the other side of the injector, after flowing through capillary 1. Temperature was measured with a platinum resistance thermometer in the thermostat bath A which was controlled to constant temperature within $\pm 0.05^\circ\text{C}$.

The pressure drop over the length of the capillary was measured with a mercury manometer which consisted of two high-pressure windows 2, mercury traps 3, a valve 6

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and a cathetometer. The manometer was placed in the thermostatic bath B. Injector 5 for constant flow rate had a plunger and two cylinders, and its temperature was controlled by circulating water from thermostat 6 by pump 7. The flow rate was measured with an electric counter of the revolution speed and a stopwatch.

The test fluid was filled from bottle 8 after evacuating the whole system with vacuum pump 17, and pressurized with high pressure pump 15. Care was taken to prevent the contamination of D_2O with air during filling. The pressure was measured with bourdon-tube gauge 9 and deadweight pressure gauge through separators 10 and 11 which contained mercury.

The test section is shown in Figure 2. The platinum-rhodium capillary 1 was fixed in high-pressure vessel 2 which had four connecting pipes, two for manometer system and two for circulation system. In the case of such gases as H_2O and D_2O , the liquid-gas interfaces in connecting pipes often cause serious troubles in measurements of flow rate and pressure drop. In the present study, the interfaces were fixed at stationary position with the aid of a heating-cooling system.

Fig.1 Experimental set-up

Fig.2 Test section

5. Calculations

Viscosity was calculated with the aid of Hagen-Poiseuille equation modified for compressible fluid:

$$\eta = \frac{\pi C}{8QL} \frac{P_1^2 - P_2^2}{2P} \left(1 + \frac{4\zeta}{r} \right) \frac{(1+\alpha\Delta t)^4}{1+\alpha\Delta t} - \frac{8QL}{8\pi L} \frac{m+1 \ln(P_1/P_2)}{1+\alpha\Delta t} \quad (1)$$

where suffixes 1 and 2 denote the inlet and the outlet of the capillary. The kinetic energy correction factor m was assumed as 1.12. Since the second term in Equation (1) was only 1 % or less of the first term, the variation of m did not cause a sensible error. The slip correction factor ζ was calculated with a semi-empirical equation by Knudsen;

$$\zeta = 0.81 \frac{8\eta}{3} \sqrt{\frac{2}{\pi SP}} \quad (2)$$

In Equation (1), the constant C corresponds to r^4 in Hagen-Poiseuille equation. The capillary constant C was calibrated against the viscosity of water at 50 °C. Measured values at higher pressures were extrapolated to atmospheric pressure and

then the constant C was determined using the reference value:

$$\eta = 5473.7 \times 10^{-7} \text{ Pa}\cdot\text{s} \quad (\text{water, } 50^\circ\text{C and } 1 \text{ atm})$$

which was selected after the critical evaluation of existing data on water. The calibrated value of the constant C was:

$$C = 6.9664 \times 10^{-8} (\text{cm}^4) \quad \text{at } 20^\circ\text{C}$$

where the thermal expansion coefficient of the material was assumed as $1.02 \times 10^{-5} / ^\circ\text{C}$.

Table 1 Measured viscosity of D₂O

t °C	P bar	ρ 10 ³ g/cm ³	η 10 ⁻⁷ Pa·s (poise)	ν 10 ⁴ cm ² /s
199.99	5.90	0.0311	165.2	5.321
200.03	5.90	0.0311	163.6	5.267
200.05	5.92	0.0311	165.5	5.318
200.00	10.77	0.0584	163.7	2.802
200.04	10.77	0.0584	161.9	2.773
249.65	10.79	0.0517	182.1	3.521
249.66	10.79	0.0517	184.1	3.558
249.68	30.32	0.1596	180.3	1.130
249.68	30.34	0.1597	179.4	1.123
300.02	10.79	0.0466	203.1	4.361
300.07	10.79	0.0466	203.2	4.362
300.01	40.12	0.1895	201.4	1.063
300.03	40.12	0.1895	200.4	1.058
300.01	74.40	0.4104	196.0	0.478
300.04	74.41	0.4104	195.8	0.477
350.03	10.77	0.0425	226.7	5.339
350.03	10.81	0.0426	226.8	5.325
349.98	49.94	0.2136	225.1	1.054
350.00	49.95	0.2137	226.3	1.059
349.98	98.91	0.4877	224.3	0.460
349.99	98.91	0.4877	223.7	0.459
350.00	147.87	0.9334	227.0	0.243
349.98	147.88	0.9338	225.0	0.241
399.94	10.85	0.0394	250.4	6.357
399.99	10.86	0.0394	249.0	6.318
399.98	10.87	0.0395	250.2	6.342
399.88	49.96	0.1922	248.6	1.294
400.10	49.96	0.1921	248.9	1.296
400.01	98.90	0.4151	247.0	0.595
400.04	98.90	0.4151	249.0	0.600
399.90	147.87	0.6948	252.0	0.363
400.03	147.88	0.6945	252.8	0.364
399.93	196.84	1.0814	258.1	0.239
400.01	196.84	1.0806	258.1	0.239

Fig. 3 Viscosity of gaseous D₂O

In the calculation of the volumetric flow rate Q , the density data were needed. At present no reliable equation of state for D₂O covering a wide range of temperatures and pressures is available. In the present study the density of D₂O was calculated with the aid of the corresponding-states principle using the equation of state for steam⁽⁹⁾. In order to confirm the density data of procedure, results were compared with recent experimental PVT data. Agreements between calculated density and experimental density data by Tsederberg and co-workers⁽¹⁰⁾ were mostly 0.1 % or less in gaseous region below 400 °C. This accuracy is satisfactory when it is compared with that of viscosity measurement.

6. Estimation of experimental error

Experimental error can be estimated from errors of individual factors in equation(1). Error in the capillary constant C was estimated to be 0.15 % con-

sidering the error in the reference viscosity of water at 50 °C. Error in the volumetric flow rate Q was up to 0.74 % due to the uncertainty in the calculated density. Errors in the capillary length L , the thermal expansion coefficient α and the kinetic energy correction factor m were 0.02 %, 0.01 % and 0.08 % respectively. Maximum error in pressure drop $\Delta P = P_1 - P_2$ was about 0.05 % depending on the magnitude of ΔP .

The maximum error in final viscosity data is therefore 1.5 %, while the mean square error is 0.9 %. Actual deviation of each data from smoothed curve is smaller. The largest source of error lies in density calculations and this can be made less with better equation of state for gaseous D₂O in future.

Each data listed in the Table 1 is the average of two or more measurements repeated at same temperature and pressure, which did not deviate more than 0.7 % from the average.

Purity of the D₂O sample was 99.8 mol %.

Reynolds number in the measurements was always less than 310, while the critical Reynolds number for present capillary was about 400. So all measurements were performed with laminar flow condition.

7. Results and comparison

Measurements were carried out along five isotherms, namely 200 °C, 250 °C, 350 °C and 400 °C, at pressures up to 300 bar.

The following equation was correlated in order to calculate the viscosity of gaseous D₂O.

$$\eta = \eta_0 + AP + BP^2 \quad (3)$$

$$\begin{aligned} \eta_0 &= 902.5 + 3.675t + 8 \times 10^{-4}t^2 \\ A &= -10.108 + 3.8 \times 10^{-2}t \\ &\quad - 0.348 \times 10^{-4}t^2 \\ B &= 688t^{-2} \end{aligned}$$

where η_0 is the viscosity in the ideal gas state. Units are: η [10^{-8} Pa·s], P [bar] and t [°C]. The equation is valid in the temperature range 100 - 500 °C and at pressure up to 300 bar or saturation pressure.

Measured results are given in Table 1. In Figure 3 the gradient of isotherms is negative at subcritical temperatures. Simple comparison with H₂O shows that the negative pressure effect on the viscosity of D₂O vapor is similar to that on H₂O vapor. The gradient changes its sign from negative to positive at about 400 °C. Comparison at atmospheric pressure are made in Figure 4. Present data agree with those by Timrot⁽⁸⁾ but are higher by 2 - 4 % than those by Bonilla⁽⁵⁾. As explained in the earlier section, Bonilla's data on H₂O are also lower than most of other recent measurements. Viscosity ratio of D₂O to H₂O at atmospheric pressure is about 1.04 which differs from the simple theoretical prediction of 1.05.

This means that a simple theoretical estimation with similarity of isotopes is not enough to know the viscosity with pre-

cision of about 1 % or better, although the general behaviors of D₂O are quite similar to those of H₂O.

Relation of present results in gaseous region with previous results in liquid region can be seen in Figure 5 in which our data as well as Rivkin's data⁽¹¹⁾⁽¹²⁾ in liquid and dense-gas region are shown. The viscosity data calculated with the aid of equation (3) are listed in Table 2. In the case of many gases, the residual viscosity - can be expressed as a function of density only. This simple law does not hold for D₂O in the range of present

Fig.5 Viscosity of D₂O

Fig. 4 Viscosity of D₂O at 1 atm

Fig.6 Tendency of isotherm against density

Table 2 Viscosity of D₂O (calculated with the aid of Equation(3))

		10 ⁻⁸ Pa·s									
T (°C)	P (bar)	100	150	200	250	300	350	375	400	450	500
1		1271.4	1466.6	1665.6	1868.5	2075.2	2285.7	2392.4	2500.0	2718.2	2940.2
10		1218.3	1422.9	1632.2	1844.5	2059.4	2276.6	2386.1	2496.2	2718.0	2942.2
25		1154.6	1361.1	1582.7	1808.6	2035.8	2263.5	2377.4	2491.3	2719.0	2946.5
50		1117.2	1288.6	1517.5	1759.6	2004.1	2247.2	2367.8	2487.4	2724.0	2956.5
75		1165.8	1254.4	1473.7	1724.4	1982.0	2238.0	2364.3	2489.0	2733.0	2969.9
100		1300.4	1258.4	1451.5	1703.0	1969.4	2235.8	2366.9	2495.9	2746.7	2986.7
125		1521.0	1300.7	1450.7	1695.4	1966.4	2240.6	2375.6	2508.2	2764.5	3007.0
150		1827.6	1381.1	1471.5	1701.5	1973.0	2252.5	2390.4	2525.8	2786.4	3030.7
175		2220.2	1499.8	1513.7	1721.3	1989.1	2271.3	2411.4	2548.9	2812.7	3057.9
200		2698.8	1656.7	1577.5	1755.0	2014.8	2297.2	2438.5	2577.3	2843.2	3088.5
250		3914.0	2085.1	1769.5	1863.5	2094.8	2370.0	2511.0	2650.2	2916.8	3160.0
300		5473.2	2666.4	2047.5	2027.1	2213.0	2470.9	2607.9	2744.7	3007.5	3245.3

measurements. An example of the tendency against density is given at 400 °C in Figure 6.

8. Concluding remarks

Present study shows the behavior of the viscosity of D₂O in the gaseous region of up to 400 °C and 300 bar, where no former measurements are found among literatures. Existence of a negative pressure effect on gaseous D₂O was for the first time experimentally confirmed. With results in liquid region⁽¹⁾, present series of measurements quantitatively shows the behavior of the viscosity of D₂O over an extensive range of temperatures and pressures.

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