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Density and Viscosity of Deuterium Oxide Solutions from 5–70°C

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The density and viscosity of deuterium oxide solutions have been measured from 5–70°C. The density measurements were made by a magnetic float technique, and the viscosity measurements were made using a modified Cannon-Ubbelohde viscometer with a semiautomatic optical viscometer reader. The results are briefly discussed and compared to the results obtained by other scientists.

In recent years various workers (13, 14, 16, 18) have studied the differences between the thermodynamic and transport properties of deuterium oxide, D₂O, and normal water, H₂O. Many studies (1, 5) have also been made on the differences between electrolyte and nonelectrolyte solutions of D₂O and H₂O. The results of most studies (1, 13, 16, 18) indicate that D₂O solutions are more structured than H₂O solutions at the same temperature.

This study of the density and viscosity of D₂O solutions was made to provide precise thermodynamic and transport data that may prove useful in elucidating the causes of the structural differences between D₂O and H₂O as a function of temperature.

EXPERIMENTAL

The two samples of D₂O used in this study were obtained from Bio-Rad Chemical Co. and were used without further purification. Although both samples were supplied as 99.88 mole % D₂O, the density determinations indicated that

sample No. 1 (used in previous studies, 12) was 98.35 ± 0.01 mole % D₂O. The decrease in D₂O in sample No. 1 was apparently caused by the exchange with atmospheric water before use. Ion-exchanged (~8 MΩ) H₂O was used in all the calibration runs.

The magnetic float densitometer used to make the density measurements has been described in detail elsewhere (11). The densitometer was calibrated using the densities for H₂O tabulated by Kell (8). The H₂O and D₂O solutions were degassed before use to prevent the formation of bubbles on the magnetic float during an experiment. The precision obtained in duplicate runs was ±2 ppm. The mole % of the D₂O used in this study was checked from our density measurements using the linear equation, $d_{D_2O} = d_{H_2O} + AX_{D_2O}$ (where d is the density, A is a constant, and X is the mole % D₂O). The constant, $A = (d_{D_2O} - d_{H_2O})/100$, was determined from the density data for 100% D₂O and normal H₂O using the density data tabulated by Kell (8). This linear interpolation yielded 98.35 ± 0.01 mole % for sample No. 1 and 99.88 ± 0.01 mole % for sample No. 2 over the entire temperature range. Although the purity of the D₂O determined by this method is dependent

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on the densities selected for 100 mole % D₂O and H₂O (8), the fact that we obtain the same value for the mole % over a wide temperature range indicates the consistency of both our densities and those tabulated by Kell (8).

The temperature of the bath containing the magnetic float densitometer was set to $\pm 0.02^\circ\text{C}$ with Brooklyn calorimeter thermometers and regulated to better than $\pm 0.001^\circ\text{C}$ with a Hallikainen thermoregulator.

The apparatus used to make the viscosity measurements has been described in detail elsewhere (9). A Cannon-Ubbelohde (suspended level) viscometer with a flow time for H₂O at 25° of about 244 sec was used to measure the viscosity of D₂O. The flow times were measured to ± 0.002 sec with a Rehovoth viscometer reader and a TSI universal counter. The viscometer was calibrated with H₂O using the viscosities tabulated by Korson *et al.* (9). The temperature of the bath was set to $\pm 0.01^\circ$ with a Hewlett-Packard quartz crystal thermometer and regulated to $\pm 0.001^\circ$ with a Hallikainen thermoregulator.

RESULTS AND DISCUSSION

Flow times, τ , for D₂O were measured (to ± 0.002 sec) over the temperature range from 5 – 70° at 5° intervals. The absolute viscosity of D₂O, η , was determined from these flow times using the equation (9)

$$\eta = \tau K(d^0 - d^*) - Ld^0/\tau^2 \quad (1)$$

where d^0 is the density of D₂O (given in Table I), d^* is the density of 100% H₂O saturated air, K is the instrument constant and L is the kinetic energy correction constant. The constants K and L were determined from the flow times of H₂O (assuming that they are independent of temperature) using the values for the viscosity of water (9) at eight temperatures from 5 – 60° together with the densities of water tabulated by Kell (8). Since the constants were found to change slightly when the viscosity system was reassembled, the H₂O calibration runs were made after the D₂O run was completed (*i.e.*, without disassembling the system). These changes were caused by not placing the viscometer in exactly the same position in reference to the viscometer photocells. The constants, $K = 3.9318 \times 10^{-3}$ and $L = 91.83$ and $K = 3.9358 \times 10^{-3}$ and $L = 90.76$ were determined, respectively, for the first and second calibration runs. By use of these constants (the flow times for D₂O and the densities of D₂O), the viscosities of D₂O have been determined from 5 – 70° . The results are given in Table I along with the densities.

In Table II the viscosities of 100 mole % (obtained

Table II. Viscosity of Deuterium Oxide at Various Temperatures^a

Temp, °C	Run 1	Run 2	Literature Values
5.00	1.9822	1.9818	1.9825, ^b 1.9883 ^c
10.00	1.6737	1.6730	1.6742, ^b 1.6804 ^c
15.00	1.4356	1.4347	1.4357, ^b 1.4420, ^c 1.4319 ^d
20.00	1.2470	1.2471	1.2477, ^b 1.2515, ^c 1.2515 ^e
25.00	1.0961	1.0966	1.0964, ^b 1.0969, ^c 1.0969, ^f 1.0951 ^g
30.00	0.9730	0.9732	0.9728, ^b 0.9690, ^c 0.9793 ^d
35.00	0.8708	0.8710	0.8706, ^b 0.8619 ^c
40.00	0.7849	0.7854	0.7849 ^b
45.00	0.7125	0.7127	0.7123 ^b
50.00	0.6504	0.6504	0.6502, ^b 0.6560 ^d
55.00	0.5968	0.5966	0.5966 ^b
60.00	0.5501	0.5503	0.5500, ^b 0.5543 ^d
65.00	0.5093	0.5095	0.5092 ^b
70.00	0.4732	0.4732	0.4733, ^b 0.4762 ^d

^a Linearly extrapolated to 100% from 98.35% (run 1) and 99.88% (run 2). The literature values have been calculated from $\eta_{\text{rel}} = \eta_{\text{D}_2\text{O}}/\eta_{\text{H}_2\text{O}}$ using $\eta_{\text{H}_2\text{O}}$ from reference 9. ^b Reference 6. ^c Reference 10. ^d Reference 17. ^e Reference 15. ^f Reference 2. ^g Reference 7.

by linear extrapolation of the values given in Table I) are given along with the values obtained by other workers (2, 6, 7, 10, 15, 17). Our results for the viscosity of D₂O are in excellent agreement with the very careful work of Hardy and Cottingham (6).

The following equation can be used to obtain the viscosity of D₂O at temperatures between those listed in Table II.

$$\log \eta/\eta_{20} = A(20 - t) - B(t - 20)^2/(t - C) \quad (2)$$

where η is the viscosity of D₂O at any temperature (t , $^\circ\text{C}$) between 5° and 70° , η_{20} is the viscosity of D₂O at 20° (1.2471 cP), $A = 1.3580$, $B = 0.00067$, and $C = 96.71$ (with a standard deviation of ± 0.0003 cP).

In Figure 1 the viscosity of D₂O and H₂O (9) are given as a function of temperature. The viscosity of D₂O is larger

Table I. Density and Viscosity of Deuterium Oxide at Various Temperatures				
Temp, °C	Density, g/ml		Viscosity, cP	
	Run 1 ^a	Run 2 ^b	Run 1	Run 2
5	1.103909	1.105531	1.9745	1.9812
10	1.104218	1.105849	1.6675	1.6725
15	1.104113	1.105751	1.4306	1.4343
20	1.103580	1.105215	1.2431	1.2468
25	1.102714	1.104362	1.0928	1.0963
30	1.101491	1.103142	0.9700	0.9730
35	1.099978	1.101631	0.8683	0.8708
40	1.098213	1.099867	0.7828	0.7852
45	1.096210	1.097864	0.7106	0.7126
50	1.093966	1.095618	0.6487	0.6503
55	1.091500	1.093151	0.5953	0.5965
60	1.088852	1.090500	0.5488	0.5502
65	1.086042	1.087688	0.5080	0.5094
70	1.083177	1.084822	0.4720	0.4731

^a 98.35 mole % D₂O. ^b 99.88 mole % D₂O

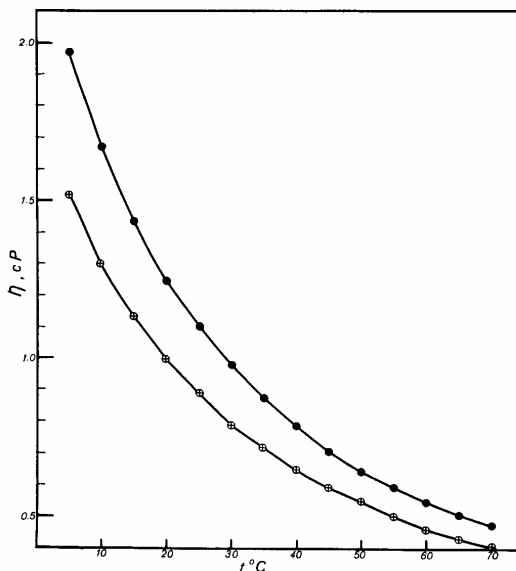


Figure 1. The viscosity of deuterium oxide, D₂O (closed circles) and normal water, H₂O (open circles), as a function of temperature

than H₂O over the entire temperature range; however, at the higher temperatures the viscosities of D₂O and H₂O appear to approach each other. For example, at 5° the difference between the viscosity of D₂O and H₂O is 0.4628 cP while at 70° the difference is only 0.0693 cP. One might attribute the decrease in the difference between the η of D₂O and H₂O to the formation of similar structure for D₂O and H₂O at high temperatures (*i.e.*, if the larger η of D₂O is due to greater structure). The effect of temperature on the differences between the compressibilities of D₂O and H₂O also agree with this suggestion (3, 4, 12).

In future work, we plan to investigate the temperature dependence of other pure solvents and hopefully use these results to obtain a better understanding of the structural properties of water by comparison.

LITERATURE CITED

- (1) Arnett, E., McKelvey, D., "Solute-Solvent Interactions," p 653, edited by Coetzee, J., and Ritchie, C., Marcel Dekker, New York, N. Y. (1969).
- (2) Baker, W. N., LaMer, V. K., *J. Chem. Phys.*, **3**, 406 (1935).
- (3) Davis, C. M., Jr., Bradley, D. L., *Ibid.*, **45**, 2461 (1966).
- (4) Feates, F. S., Ives, D. J. G., *J. Chem. Soc.*, (London) **1956**, p 2798.
- (5) Greyson, J., *J. Phys. Chem.*, **71**, 2210 (1967).
- (6) Hardy, R. C., Cottington, R. L., *J. Res. Natl. Bur. Stds.*, **42**, 573 (1949).
- (7) Jones, G., Fornwalt, H. J., *J. Chem. Phys.*, **4**, 30 (1936).
- (8) Kell, G. S., *J. Chem. Eng. Data*, **12**, 66 (1967).
- (9) Korson, L., Drost-Hansen, W., Millero, F. J., *J. Phys. Chem.*, **73**, 34 (1969).
- (10) Lewis, G. N., MacDonald, R. T., *J. Amer. Chem. Soc.*, **55**, 4730 (1933).
- (11) Millero, F. J., *Rev. Sci. Instrum.*, **38**, 1441 (1967).
- (12) Millero, F. J., Lepple, F. K., *J. Chem. Phys.*, in press (1971).
- (13) Nemethy, G., Scheraga, H. A., *J. Chem. Phys.*, **41**, 680 (1964).
- (14) Swain, C. G., Badar, R. F. W., *Tetrahedron*, **10**, 182 (1960).
- (15) Taylor, H. S., Selwood, P. W., *J. Amer. Chem. Soc.*, **56**, 998 (1934).
- (16) Thomas, M. R., Scheraga, H. A., Schrier, E. E., *J. Phys. Chem.*, **69**, 3722 (1965).
- (17) Timrot, D. L., Shiuskaya, K. P., *At. Energ.*, **7**, 459 (1959).
- (18) Whalley, E., "Proceedings of 1957 IUPAC Joint Conference on Thermodynamics and Transport Properties of Fluids," pub. by Inst. Mech. Eng., London, **1959**, p 15-25.

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