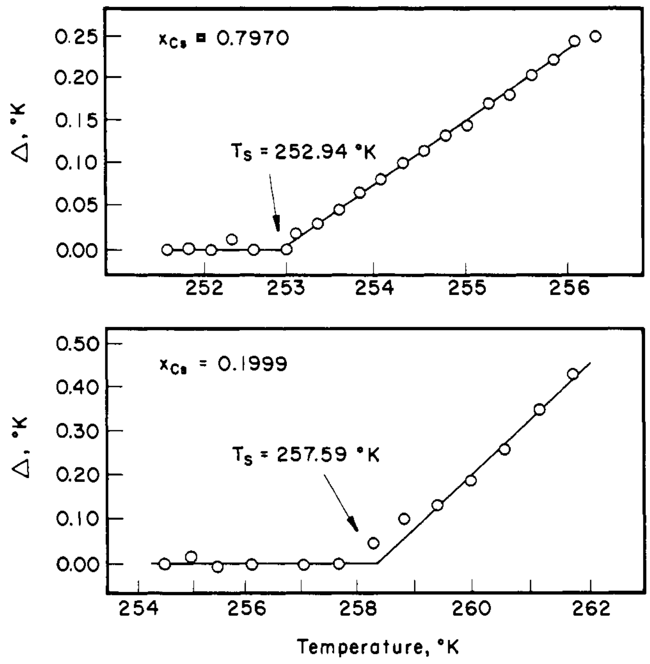

Figure 3. Representative plots of the curve-straightening technique that was used to locate solidus points

curves lack 0.15° K of merging at the freezing point minimum. This is about the difference that would be expected from the 0.1 mol % impurity in the samples.

The occurrence of the minimum (within experimental error) at a 1–1 stoichiometric composition suggests the possible formation of a 1–1 intermetallic compound. The thermal data alone, however, are not sufficient to confirm the existence of a compound.

Our results are in much better agreement with the earlier work of Rinck (*2*) than with that of Goria (*1*). Although Rinck's data show considerable scatter, the smoothed curve through his experimental points agrees with our results to within ±1° K. Agreement with the data of Goria (*1*) is much poorer, the differences being as large as ±8° K.

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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, D_2O, and normal water, H_2O. Many studies (*1, 5*) have also been made on the differences between electrolyte and nonelectrolyte solutions of D_2O and H_2O. The results of most studies (*1, 13, 16, 18*) indicate that D_2O solutions are more structured than H_2O solutions at the same temperature.

This study of the density and viscosity of D_2O solutions was made to provide precise thermodynamic and transport data that may prove useful in elucidating the causes of the structural differences between D_2O and H_2O as a function of temperature.

EXPERIMENTAL

The two samples of D_2O 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 % D_2O, the density determinations indicated that sample No. 1 (used in previous studies, *12*) was 98.35 ± 0.01 mole % D_2O. The decrease in D_2O in sample No. 1 was apparently caused by the exchange with atmospheric water before use. Ion-exchanged (~8 MΩ) H_2O 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 H_2O tabulated by Kell (*8*). The H_2O and D_2O 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 D_2O 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 % D_2O). The constant, $A = (d_{D_2O} - d_{H_2O})/100$, was determined from the density data for 100% D_2O and normal H_2O 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 D_2O determined by this method is dependent

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on the densities selected for 100 mole % D_2O and H_2O (*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 ±0.02° C with Brooklyn calorimeter thermometers and regulated to better than ±0.001° 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 H_2O at 25° of about 244 sec was used to measure the viscosity of D_2O. The flow times were measured to ±0.002 sec with a Rehovoth viscometer reader and a TSI universal counter. The viscometer was calibrated with H_2O using the viscosities tabulated by Korson *et al.* (*9*). The temperature of the bath was set to ±0.01° with a Hewlett-Packard quartz crystal thermometer and regulated to ±0.001° with a Hallikainen thermoregulator.

RESULTS AND DISCUSSION

Flow times, τ, for D_2O were measured (to ±0.002 sec) over the temperature range from 5–70° at 5° intervals. The absolute viscosity of D_2O, η, was determined from these flow times using the equation (*9*)

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

where d^0 is the density of D_2O (given in Table I), d^a is the density of 100% H_2O 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 H_2O (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 H_2O calibration runs were made after the D_2O 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 D_2O and the densities of D_2O), the viscosities of D_2O have been determined from 5–70°. The results are given in Table I along with the densities.

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 % D_2O. [b] 99.88 mole % D_2O

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 $\eta_{rel} = \eta_{D_2O}/\eta_{H_2O}$ using η_{H_2O} from reference *9*. [b] Reference *6*. [c] Reference *10*. [d] Reference *17*. [e] Reference *15*. [f] Reference *2*. [g] Reference 7.

In Table II the viscosities of 100 mole % (obtained 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 D_2O are in excellent agreement with the very careful work of Hardy and Cottington (*6*).

The following equation can be used to obtain the viscosity of D_2O at temperatures between those listed in Table II.

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

where η_t is the viscosity of D_2O at any temperature (t, °C) between 5° and 70°, η_{20} is the viscosity of D_2O 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 D_2O and H_2O (*9*) are given as a function of temperature. The viscosity of D_2O is larger

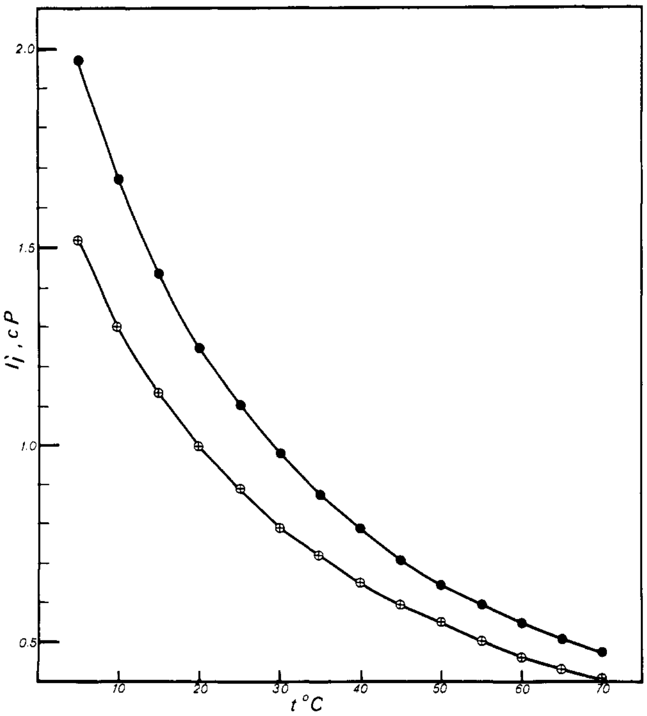

Figure 1. The viscosity of deuterium oxide, D_2O (closed circles) and normal water, H_2O (open circles), as a function of temperature

than H_2O over the entire temperature range; however, at the higher temperatures the viscosities of D_2O and H_2O appear to approach each other. For example, at 5° the difference between the viscosity of D_2O and H_2O 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 D_2O and H_2O to the formation of similar structure for D_2O and H_2O at high temperatures (*i.e.*, if the larger η of D_2O is due to greater structure). The effect of temperature on the differences between the compressibilities of D_2O and H_2O 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.

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Heats of Combustion, Heats of Formation and Vapor Pressures of Some Organic Carbonates

Estimation of Carbonate Group Contribution to Heat of Formation

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Heats of combustion were measured, using oxygen bomb calorimetry, for some organic carbonates—*i.e.*, ethylene carbonate, diethyl carbonate, propylene carbonate, vinylene carbonate, di-(*p*-phenylbenzyl)carbonate. Sublimation pressure of low vapor pressure compounds—*i.e.*, ethylene carbonate—were measured by the Knudsen effusion method. High vapor pressure compounds—*i.e.*, propylene carbonate, diethyl carbonate, and vinylene carbonate—were measured using a modified manometric apparatus. The gaseous phase heats of formation were used to estimate the carbonate group contribution to the heat of formation. A value of −133 ± 1 kcal/mole was obtained.

Simple methods of calculating thermodynamic properties of organic compounds readily and with a minimum of data have been developed by a number of workers, and have been reviewed critically by Reid and Sherwood (*11*), Janz (*6*) and Benson (*1*). From the various possibilities, the additive-atomic group method was selected to calculate the organic carbonate group contribution to the heat of formation in the gaseous state. An additive-atomic group contribution method for heats of formation (gas) has been developed by Franklin (*4*) for hydrocarbons and other organic compounds such as simple free radicals. The method of Franklin is based on the extension of the relations and principles developed by Pitzer (*10*) for the long-chain paraffins.

EXPERIMENTAL

Vapor Pressure Measurements. The Knudsen effusion method (*7, 12*) was employed to measure the sublimation pressure of low vapor pressure compounds, whereas a modified manometric method was employed for high vapor pressure compounds.

Knudsen Effusion Method. The measurement of weight loss in a known period of time at a known constant temperature allows the calculation of the vapor pressure, using the effusion formula, and assuming that the pressure in the vacuum above the effusion hole is negligibly small compared to the vapor pressure of compounds to be measured. A high vacuum system is required when using this method; details of this system are available elsewhere (*3*).

The following Knudsen effusion formula was used to calculate the sublimation pressure after insertion of proper values for the constants:

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