Table II. Derived Values for E_η

$LiNO_3$ investigation	Technique	E_η
This work	Capillary	4.58
Protsenko and Razumovskaya (*10*)	Capillary	4.77
Goodwin and Mailey (*5*)	Capillary	4.85
Dantuma (*3*)	Oscillational	4.34
Murgulescu and Zuca (*9*)	Oscillational	4.59
Zuca (*12*)	Oscillational	4.51

density values of Bloom et al. (*1*) for KNO_3 and those of Jaeger and Kapma (*6*) for $LiNO_3$.

The results are in Tables Ia and Ib, respectively, together with calculated values from previous measurements for $LiNO_3$. Calculated literature values at the experimental temperatures of the present investigation were generated from polynomial least-squares equations obtained using the P.D.P. Model 15 computer facility of this Laboratory. In Figure 1, the results of the various investigations (and techniques) are compared as the percent departure. This is defined as [(experimental value − recommended values)/recommended values × 100]. The results of Dantuma (*3*) 1928, oscillational) are off-scale (26% (540 K), increasing to 37.3% (610 K), decreasing to 26% (650 K)).

Discussion

The results for KNO_3 in this investigation cross-check the literature values well within the limits of experimental accuracy (±1.5%); indeed with the exception of one value (at 653 K), the agreement is within ±1% and better. One may confidently place the same reliance factor to the results for molten $LiNO_3$ since the measurements were in overlapping temperature ranges.

Examination of the temperature dependence of the viscosity data from these various studies of $LiNO_3$ shows an interesting result. A least-squares analysis was used to fit the data to an "Arrhenius" type exponential equation

$$\eta = A \exp(E_\eta/RT)$$

The derived values for E_η (kcal/mol) are given in Table II. Inspection shows that the results, collectively, are more or less in accord with the temperature variance of the viscosity of molten $LiNO_3$. The sample "quality" (i.e., chemical purity) thus seems uniformly satisfactory, and the suggestion that the variance in the actual viscosity values is probably due to technique thus receives additional support from this viewpoint.

From the results of our present study (Table I, column 2) the temperature dependence of the viscosity of $LiNO_3$ may be expressed by the following equations: (a) exponential equation, $\eta = (7.283 \times 10^{-2}) \exp(4578/RT)$ cP (% standard error of estimate, 1.31); (b) power series equation, $\eta = 70.567 - 0.20188T + (0.14976 \times 10^{-3})T^2$ (% standard error of estimate, 1.12); and from the latter, the values calculated at rounded temperatures are the following [η, cP (T, K)]: 5.222 (540), 4.835 (550), 4.479 (560), 4.152 (570), 3.856 (580), 3.589 (590), 3.352 (600), 3.146 (610), 2.969 (620), 2.822 (630), 2.705 (640), 2.619 (650). The NSRDS values which we advanced earlier were based on the results of Dantuma. The present reinvestigation shows that the NSRDS recommendation for $LiNO_3$ should be revised, using the data base of Goodwin and Mailey (*5*), Protsenko and Razumovskaya (*10*), and Murgulescu and Zuca (*9, 12*) together with the results of this study to develop the "best-value" recommendation.

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Viscosity of Heavy Water at High Pressures

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The viscosity of heavy water (D_2O) was measured in the liquid and dense-gas region of up to 500 °C (773.15 K) and 800 bar (80 MPa). A capillary-type viscometer was newly constructed and used. The experimental error is estimated to be 0.5% exclusive of uncertainty in density data. Experimental results quantitatively show pressure dependence of the viscosity of heavy water in a wide range of temperatures and pressures.

Although heavy water (D_2O) is one of the important substances especially in nuclear power engineering, its properties are not satisfactorily studied. Properties of heavy water under high pressure are often calculated from those of ordinary water with simple assumptions. Available knowledge, especially of transport properties, to approve this procedure is quite limited. At atmospheric pressure, several reports on the viscosity of heavy water are available, including one by Hardy and Cottington (*4*). Principal interest in these studies is in the ratio of viscosities of H_2O to D_2O. At high pressures, three investigations are available, all of them carried out in USSR. Their experimental ranges of temperature and pressure are shown in Figure 1. Timrot and Shuiskaya (*11*) used a capillary viscometer for the temperature range 15–288 °C and for the pressure range 44–319 bar in 1959, the quoted accuracy being 2%. In 1968 and 1971, Agayev and co-workers (*1, 2*) measured in the liquid region up to 275 °C and 1200 bar. The liquid and vapor region up to 500 °C and 500 bar was measured by Rivkin and co-workers (*6, 7*)

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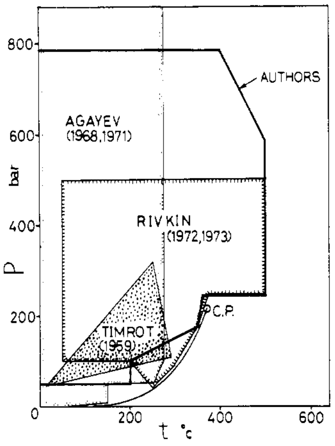

Figure 1. Measurements of viscosity of D_2O.

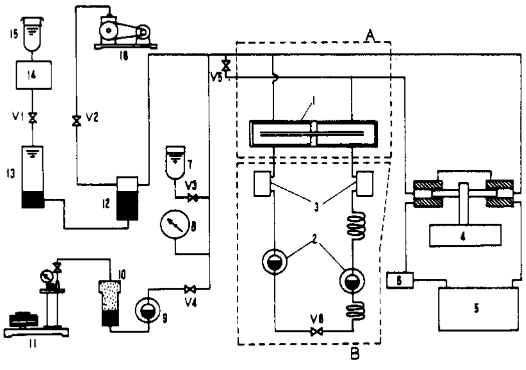

Figure 2. Experimental arrangement: 1, test section; 2, manometer; 3, mercury trap; 4, injector; 5, temperature controller; 6, counter system; 7, container (sample); 8, pressure gauge; 9, separator; 10, separator; 11, dead-weight gauge; 12, separator; 13, separator; 14, high-pressure pump; 15, container (water); 16, vacuum pump.

in 1972 and 1973. Apparatuses of Agayev and Rivkin were also of the capillary type. The viscosity of D_2O vapor at or below atmospheric pressure was measured by Bonilla and co-workers (*3*) and Timrot and co-workers (*12*). Viscosity measurement with a capillary viscometer requires reliable density data and this, especially in the critical region, limits the accuracy of the measurement, since the reliable equation of state for D_2O is not available in the critical and high-temperature regions.

The present paper describes the viscosity measurement of D_2O in the liquid and dense-gas region up to 500 °C and 800 bar with a capillary viscometer. (An outline of these results was presented at 8th International Conference on the Properties of Steam, Giens, 1974. The present paper gives more detailed data with a minor correction due to modification in pressure calculation and also some additional results.)

Experimental Method and Apparatus

The closed circuit capillary viscometer shown in Figure 2 was newly built for D_2O measurement, its principle being similar to one used for measurements of H_2O (*5*). The reproducibility of the new apparatus has been much improved. The pressure vessel, 1, was heated in a thermostatic bath with water (up to 80 °C), with oil (up to 150 °C), and with molten salt (up to 500 °C). The temperature was measured with a platinum resistance thermometer. Area A and area B in Figure 2 indicate thermostats of experimental temperature and of 20 °C. The manometer, 2, has two mercury containers connected with a coiled pipe. The mercury head in the mercury container was measured with a cathetometer through two high-pressure windows. The injector, 4, has two cylinders and a twin-head plunger with the driving mechanism. In order to attain sufficient preheating of the fluid, a coiled pipe 10 m long was sunk in the bath before entering the test section. Between the pressurizing system, 14, and the test section, and also between the dead-weight gauge, 11, and the

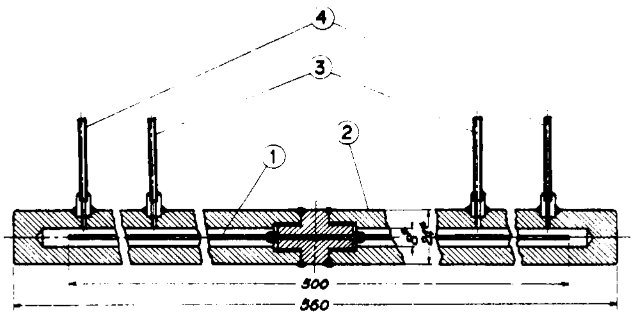

Figure 3. Test section: 1, capillary; 2, pressure vessel; 3, circulation pipe; 4, pressure pipe.

Table I. Viscosity of D_2O

Temp t, °C	Pressure P, bar	Density ρ, g/cm³	Viscosity η, 10^{-7}Pa s	Kinematic viscosity ν, 10^{-6}cm²/s
50.03	98.90	1.1006	6512	5916
50.06	294.86	1.1098	6568	5918
50.00	392.83	1.1143	6608	5930
50.03	588.78	1.1229	6640	5913
100.05	49.91	1.0647	3320	3118
100.02	147.88	1.0699	3360	3140
99.92	245.86	1.0750	3403	3166
99.93	343.83	1.0798	3445	3191
101.07	196.91	1.0716	3382	3156
101.11	392.85	1.0813	3441	3183
101.00	588.81	1.0906	3510	3218
101.05	784.77	1.0994	3571	3248
149.10	49.91	1.0195	2125	2085
149.16	147.88	1.0256	2154	2100
149.10	245.86	1.0317	2182	2115
149.10	343.84	1.0374	2216	2136
151.42	196.90	1.0264	2127	2070
151.39	392.85	1.0380	2180	2100
151.42	588.80	1.0487	2229	2126
151.42	784.76	1.0588	2276	2150
200.91	196.90	0.9711	1551	1597
200.89	392.84	0.9857	1610	1634
200.90	588.80	0.9989	1657	1659
200.89	784.76	1.0111	1703	1684
202.31	98.92	0.9613	1521	1583
203.06	196.89	0.9684	1543	1594
202.35	294.87	0.9769	1571	1608
202.18	392.84	0.9843	1590	1615
299.88	196.90	0.8107	992.5	1224
299.98	784.75	0.8912	1142	1281
300.06	196.90	0.8103	988.2	1220
300.08	392.84	0.8440	1065	1261
300.11	588.80	0.8698	1110	1275
350.03	177.29	0.6355	719.8	1133
350.01	196.90	0.6531	737.8	1130
349.97	294.88	0.7057	814.0	1154
350.04	490.82	0.7623	908.9	1192
375.02	245.87	0.5242	574.0	1095
375.02	294.85	0.5999	662.4	1104
375.04	392.82	0.6621	744.6	1125
375.04	588.73	0.7258	838.4	1156
374.99	784.66	0.7659	899.5	1175
399.96	392.81	0.5624	632.9	1131
399.95	588.73	0.6673	767.0	1149
399.94	784.66	0.7200	841.5	1169
400.71	245.88	0.1717	274.9	1618
400.79	294.86	0.3364	373.6	1145
499.94	245.88	0.0976	319.9	3364
499.93	392.81	0.1913	362.8	1928
499.95	588.72	0.3626	490.9	1358

test section, there are two sets of mercury separators, 9 and 10 and 12 and 13. The viscometer also contains an evacuating system, 16, temperature controller, 5, for the injector, and two mercury traps, 3. The capillary made of platinum was fixed in pressure vessel 2 with gold solder as shown in Figure 3. Capillary 1 has dimensions of 500 mm long and of about 0.3 mm in inner diameter. The vessel has entrance and exit chambers, each of them connecting two platinum pipes, circulation pipe 3 and pressure pipe 4.

Filling of the test section with D_2O was performed in such a manner as to prevent contamination by air. All measurements were conducted in the laminar flow condition, that is, with the Reynolds number of less than 700.

The viscosity η was calculated with the aid of the Hagen-Poiseuille equation:

$$\eta = \frac{C\pi\Delta P}{8QL}(1 + \alpha\Delta t)^3 - \frac{m\rho Q}{8\pi L(1 + \alpha\Delta t)} \qquad (1)$$

where C is the capillary constant, ΔP the pressure drop between capillary ends, m the kinetic energy correction factor, Q the volumetric flow rate, L the length of the capillary, ρ the density of the fluid, α the thermal expansion coefficient, and Δt the temperature difference from the reference temperature.

In the present study, the capillary constant C was determined using ordinary water as the calibration fluid at 50 °C and atmospheric pressure. After critical evaluation of the available data, the reference viscosity of ordinary water at 50 °C was selected as 5473.7×10^{-7} Pa s (5473.7 μP). The constant C was calculated from measured results on the 50 °C isotherm for pressures up to 500 bar, extrapolating to atmospheric pressure.

The density of D_2O was needed in order to know the flow rate Q in eq 1. In the present study, the density of D_2O was calculated with the aid of the principle of corresponding states applied to H_2O and D_2O. The relation including modification by Su (*10*) and a correction factor A is

$$v_D = A(z_{cD}/z_{cH})v_H \qquad (2)$$

where v and z_c are the specific volume and the critical compressibility factor. Suffixes D and H denote D_2O and H_2O, respectively. The correction factor A (1.0 above 350 °C and 0.9933 below 350 °C) has no theoretical background and was applied just for better fitting of the equation to measured PvT data of D_2O. The specific volume of H_2O was calculated with the aid of the 1967 ICPS equation of state (*9*). Deviations of calculated values of the specific volume of D_2O from experimental data by Rivkin (*8*) and Tsederberg (*13*) are less than 0.1% in liquid region and less than 0.5% in vapor region.

Results and Discussions

Measurements were performed along nine isotherms at pressures up to 800 bar. Results are shown in Table I. Density in Table I has been obtained using eq 2. Since the reliability of density data of D_2O is not so satisfactory as that of H_2O, we list here the kinematic viscosity ν also. The viscosity η can be corrected using the kinematic viscosity data as

$$\eta = \rho_D\nu \qquad (3)$$

when more reliable density data, ρ_D, are given.

Figures 4 and 5 show viscosity isotherms of present measurements as well as data by other authors. Agreements between present results and those by Agayev (*1*, *2*) and by Rivkin (*6*, *7*) are good when precision of these measurements and uncertainty in density data are considered. Deviations are less than 1% below 300 °C and less than 2% at higher temperatures.

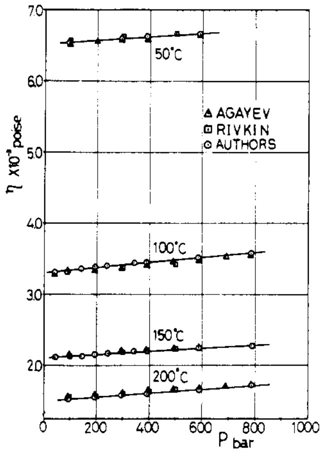

Figure 4. Viscosity of D_2O (I).

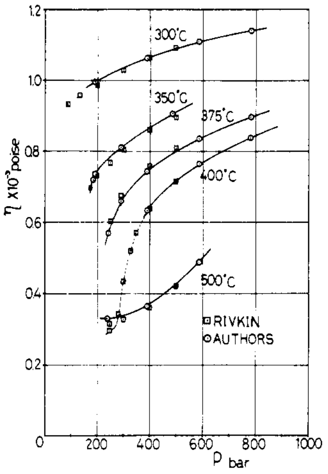

Figure 5. Viscosity of D_2O (II).

As explained earlier, the viscosity of H_2O at 50 °C and atmospheric pressure was selected as 5473.7×10^{-7} Pa s after averaging evaluated data and adjusting the viscosity at 20 °C and atmospheric pressure to 1.0020×10^{-3} Pa s. Calibration error of the capillary constant C, which is the sum of errors of calibration measurement and of the reference viscosity, is estimated to be 0.2%. Error in the capillary length L is less than 0.03%. Calculating the flow rate, the largest fraction of error came from the uncertainty in density of D_2O at the capillary, which was estimated to be 0.1% in liquid region and to be 0.5% in vapor region. Error in the flow rate Q is thus estimated to be 0.3% in the liquid region and 0.7% in the vapor region. The pressure drop, ΔP, along the capillary was calculated from the density of mercury and the density of D_2O, with errors less than 0.1%, and the height Δh of mercury column, error of about 0.1%. Error in ΔP is thus 0.2%. Error due to the uncertainty in the kinetic energy correction factor m in the liquid region does not exceed 0.04% (0.08% in vapor region), since the second term in eq 1 amounts to about 0.8% of the first term as the largest (in vapor region 1.5%). Uncertainty in temperature was 0.05 °C below 100 °C and about 0.1 °C above 100 °C. Pressure was measured to 0.1 bar. Thus the maximum error in the viscosity, exclusive of the uncertainty in density data, is estimated to be about 0.5%.

Purity of the D_2O sample was 99.87 mol %, the rest being H_2O.

Viscosity isotherms below 200 °C show linear dependence on pressure, although isotherms above 300 °C show significant nonlinearity. At supercritical temperature, the isotherm has "S" shape curvature and the steepest part shifts to higher pressure with increasing temperature. These trends are quantitatively very similar to those of H_2O throughout the whole region of present study.

Measurement of the viscosity of D_2O in the vapor region at moderate pressures and discussions on the ratio of viscosities of D_2O over those of H_2O will be reported in the succeeding report.

Glossary

A	constant in eq 2
C	capillary constant, cm^4
L	length of the capillary, cm
m	kinetic energy correction factor (inlet-length correction factor)
ΔP	pressure drop, Pa
Q	volumetric flow rate, cm^3/s
t	temperature difference, °C
v	specific volume, cm^3/g
z_c	compressibility factor at the critical point
α	thermal expansion coefficient, $^\circ C^{-1}$
ν	kinematic viscosity, cm^2/s
ρ	density, g/cm^3
η	viscosity, 10^{-7} Pa s, μP

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Properties of Potassium Sulfate Aqueous Solution and Crystals

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The properties of aqueous K_2SO_4 solutions and crystals had been measured. The saturation concentrations and the first and second supersaturation concentrations of K_2SO_4 solution were measured. Densities and viscosities of concentrated K_2SO_4 solutions were measured and diffusivity data for K_2SO_4 in solution were correlated by Wilke's diffusion factor. Specific surface area and shape factors for K_2SO_4 crystals were measured.

The properties of aqueous concentrated K_2SO_4 solution and crystals have been measured and correlated.

There are few studies on the growth of K_2SO_4 crystals from aqueous solution. Mullin and Gaska (*8*) and Rosen and Hulburt (*13*) reported that the overall K_2SO_4 crystal growth process is of second order with respect to the concentration difference, but Ishii and Fujita (*6*), Randolph and Rajagopal (*12*), and Ishii (*5*) stated that the crystal growth process consists of the two steps in series: diffusion of the solute from the bulk mother liquor to the crystal–liquid interface and interfacial crystallization in which the solute at the interface enters the crystal lattice. They reported that for K_2SO_4 both steps are first order with respect to the concentration difference, and thus the overall K_2SO_4 crystal growth process is first order. The overall crystal growth rate constant obtained by Rosen and Hulburt (*13*) includes the linear velocity of the mother liquor, but the linear velocity of the mother liquor ought not to affect the interfacial crystallization process but only the diffusion process, which is always of first order with respect to the concentration difference. According to Moyers and Randolph (*7*), for any kind of crystals the crystal growth rate can be always approximated by a first order in the case of low supersaturation concentration. Therefore, the difference of the reaction order for the K_2SO_4 crystal growth process among the different authors may be dependent on different supersaturation concentration ranges.

Of course, the reaction order of the crystal growth process must be dependent upon the type of crystal surface and its physical nature such as kinks and imperfect crystal lattices. To encourage more precise experimental measurements for K_2SO_4 crystal growth rate, the properties of aqueous K_2SO_4 solutions and crystals have been here reported.

Knowledge of the properties of the supersaturated solution is essential for studies on K_2SO_4 crystallization and can be obtained by extrapolation from the figures of this paper.

High-purity K_2SO_4 crystals were obtained from the Kokusan Chemical Works Ltd., and ion-exchanged water was used.

Experimental Sections and Correlations

(*1*) *Saturation Concentration.* The saturation concentration of aqueous K_2SO_4 solution had been measured in the previous study (*6*), in which the solution and growth rates of K_2SO_4 crystals in stirred tanks were measured.

Figure 1 shows a schematic diagram of the experimental apparatus. The stirred tank and the outer jacket were made of Pyrex glass to make visible the inside of the stirred tank. The dimensions of the stirred tank are shown in Table I. The diameter of the stirred tank, having four baffle plates, is 10 cm. For the depth of the solution to equal approximately the diameter of the stirred tank, 700 cm^3 of the aqueous K_2SO_4 solution was maintained unsaturated, but near the saturation concentration (about 5 °C higher than the saturation temperature), to prevent all crystals from precipitating from solution. The solution temperature was kept at a constant temperature of about 10, 15, 20, 25, 30, 35, 40, 45, or 50 °C for each run by flowing the thermostat water into the outer jacket of the stirred tank and measuring with a calibrated thermometer. Twenty grams of highest quality K_2SO_4 crystals of $-3.5+4$, $-6+7$, $-8+9$, $-10+12$, $-16+20$, $-28+32$, $-48+60$, $-60+65$, or

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