

Viscosity Measurements of Water in Region of Its Maximum Density

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The viscosity of water was precisely measured at closely spaced intervals over the temperature range 0–10°C. Fitting the data to a combination Arrhenius and Vogel-type equation revealed no thermal anomalies in the fluid behavior of water at the temperature of maximum density. The precision of the data was $\pm 0.014\%$.

There has been considerable controversy over the existence (2, 10, 12, 25) or nonexistence (11, 14, 16, 24) of thermal anomalies in the properties of water and aqueous solutions. When studies on the temperature dependence of ionic conductivities of aqueous solutions in the 0–10°C range were carried out in our laboratories (20), there were statistically significant variations between the fluidity of water and parameters derived from the transport properties. For example, when the ionic conductivities of some ions were plotted as a linear function of fluidity, deviations of -0.06% at 0°C to $+0.06\%$ at 5°C and then to -0.08% at 10°C were found. Since the precision of the viscosity values in the literature (1, 5, 9, 13, 18, 21, 23) was only 0.6% and recent readings were made only at 5°C intervals (13), it was decided to undertake a study of the precise variation of fluidity in this region.

In this paper, high-precision viscosity measurements are reported which are sufficiently closely spaced (0.5°C) to demonstrate the absence of any anomaly in the region studied. The observed viscosities and those interpolated from equations based on the reasonably sound theoretical concepts of glass transition temperatures and Arrhenius activation energies were compared, with special attention being given to the temperature range near the maximum density of water.

In addition, this paper provides a tabulation of viscosity values in a temperature range which is of considerable environmental importance and is thus coming under careful scrutiny by a wide variety of researchers.

Experimental

Cannon-Ubbelohde suspended meniscus viscometers were used in conjunction with a Hewlett-Packard 5901B auto viscometer and a Hewlett-Packard 5903A programmer. The viscometers were attached by means of epoxy cement to a plastic plate which was then cemented to the top of the insulated temperature bath. The effect of local heating from the light source of the meniscus detector was found negligible by comparison of duplicate runs using different types of light mountings on the viscometers. Once installed, the viscometers were left in position for all measurements of both standards and unknowns. Emptying, cleaning, and refilling operations were all carried out with the viscometers in situ. This technique ensured that there could be no change in the vertical alignment of the viscometer from one run to the next. Such precaution is essential if the most precise data are to be obtained because the pressure head must be maintained completely constant.

According to Caw and Wylie (4) in a study of capillary shape effects in viscometry measurements, the effect of surface tension differences between organic liquids (ca.

30 dynes cm^{-2}) and water (ca. 75 dynes cm^{-2}) largely balances out. In the temperature range 0–10°C, the surface tension varies from 75.6 to 74.2 dynes cm^{-2} . In view of the above, this small change indicates that surface tension effects can be neglected in the temperature range of our work. Emptying of the viscometers was accomplished by vacuum aspiration. A schematic diagram of the apparatus is shown in Figure 1.

The temperature bath was controlled to $\pm 0.002^\circ\text{C}$ by means of a Tronac PTC 1000A temperature controller. The bath included a cooling coil, a ballast heating element, and a control heating element. The bath temperature was measured to $\pm 0.001^\circ\text{C}$ by means of Beckmann thermometers which were calibrated against a platinum resistance thermometer (PRT). Both the PRT and Beckmann thermometers were calibrated in a mixture of crushed ice (frozen from distilled water) and water. The uncertainty of the absolute temperature was thus assumed to be $\pm 0.01^\circ$. The relative accuracy of the PRT was certified by the Division of Physics of the National Research Council of Canada according to the International Practical Temperature Scale of 1968.

It was possible to monitor the flow times directly by means of the digital display of the auto viscometer as well as obtain a hard copy of the data from the programmer printed tape output. Both means of display provided flow time to within 1 msec.

The water used in the experiments was doubly distilled in a Barnstead all-tin distillation system. It was then passed through mixed-bed and organic removal ion-exchange columns and filtered through a submicron filter. This water was then distilled from 0.01M potassium permanganate and sodium hydroxide in an all-glass, grease-free still. This redistilled water was then filtered through a 5- μ millipore filter directly into the viscometer.

The viscometers were thoroughly cleaned with KMnO_4 in concentrated H_2SO_4 and rinsed with the freshly distilled viscosity water several times before the final charging of the viscometer was carried out. After sufficient time had been allowed for thermal equilibrium to be established, the efflux bulb of the viscometer was filled to a constant level by the auto viscometer. This was achieved by pressurizing the filling tube of the viscometer with high-purity nitrogen until a definite number of seconds had elapsed after the meniscus had passed the upper

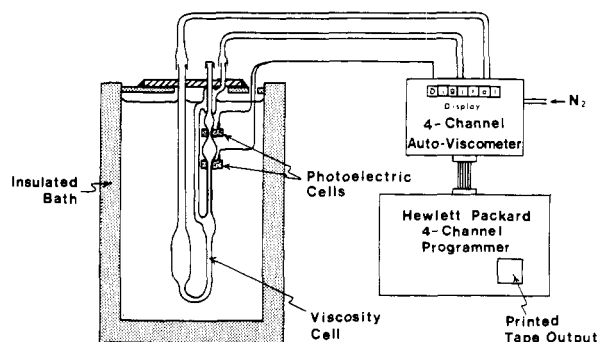


Figure 1. Schematic diagram of viscosity measuring apparatus showing arrangement of photoelectric cells and permanent attachment of viscometer to thermostated bath

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fiducial mark (the upper photoelectric cell). The nitrogen used was allowed to come to equilibrium with the water before pressurization of the cell.

The pressurizing N₂ and the back pressure in the viscometer bypass tube were then both automatically released, allowing the meniscus to fall past the upper photoelectric cell, starting the timer. An average of seven runs was performed at each temperature (0.5° intervals) on each viscometer, with the water being changed at the beginning of each temperature setting as well as between some runs at a given setting. To minimize systematic errors which may have occurred if the temperature was either continually raised or continually lowered, the temperature order was somewhat random. Readings of flow times were made at 10°, 5°, 2.5°, and 7.5°C and then in units of 0.5°C from 0.5° to 10.0°C, checking the earlier values en route.

Results and Calculations

To determine the absolute viscosity of water over the temperature range studied, it was first necessary to determine the cell constants for the viscometers used. This was done by fitting flow times and viscosities to the equation (3, 4, 26)

$$\nu = \frac{\eta}{d^0} = \tau K \left(1 - \frac{d^a}{d^0}\right) - \frac{L}{\tau^n} \quad (1)$$

in which ν is the kinematic viscosity, η is the absolute viscosity, K , L , and n are cell parameters, and d^0 and d^a are the density of water and air, respectively, at the temperatures corresponding to the flow time (τ). The density of water, d^0 , was calculated with the coefficients from Kell's (19) rational function at the appropriate temperatures. The density of air was calculated by use of an equation from the "Handbook of Chemistry and Physics" (17) inserting the appropriate air pressure, temperature, and vapor pressure of the moisture in the air (saturation assumed directly above water in cell). Daily variations in air pressure had no effect on the viscosity within the precision of the viscosity data.

The values of η used were the averages of reliable literature values which appear in Table I. Values of K and L were then obtained for each of $n = 1.90, 1.95, 2.0, 2.05,$ and 2.15 . For both viscometers the minimum deviation corresponded to $n = 2.0$ as proposed by Cannon et al. (3). For cell E384, $K = 0.0037410 \pm 0.0000041$ and $L = 42.88$ and for cell E386, $K = 0.0036838 \pm 0.0000038$ and $L = 52.79$. Whereas other workers (13, 21) have used only two calibration points in determining viscometer parameters, it was felt that using as many simultaneous sets of η and τ as possible would result in a more reliable extrapolation and interpolation in the 0–10°C range.

The viscosities obtained from Equation 1 with the above values of K and L and the observed flow times

Table I. "Standard" Viscosities for Cell Calibration

Temp, °C	τ , sec		η , cP, av	Lit values		
	E384 ^a	E386 ^a				
5	406.368	412.698	1.5181	1.5190 ^b	1.5170 ^c	1.5184 ^d
10	349.714	355.131	1.3064	1.3067 ^b	1.3061 ^c	
15	305.546	310.286	1.1381	1.1381 ^b	1.1381 ^c	
20	268.243	272.524	1.0020 ^e			
25	239.219	242.928	0.8903	0.8902 ^b	0.8903 ^c	0.8903 ^f

^a Refers to viscometer cell number. ^b Eicher and Zwolinski (13). ^c Cragoe in ref. 5. ^d Hardy and Cottingham (18). ^e Standard Reference value. ^f Coe and Godfrey (5).

were then fed into two types of equations. The first was a simple multiparameter fit of the type

$$\eta = A + BT + CT^2 + DT^3 + ET^4 \quad (2)$$

where T is in degrees Celcius. The second was the three-parameter fit of Eicher and Zwolinski:

$$\eta = \eta' \left(\frac{T}{T'}\right)^n \exp [B(T' - T)/(T' - T_0)(T - T_0)] \quad (3)$$

Table II. Viscosities Observed and Calculated from 0–10°C

Temp, °C	$\eta_{\text{obsd.}}$, cP	$\eta_{\text{calcd.}}^a$, cP	% dev
0.490	1.7608	1.7607	+0.008
0.987	1.7311	1.7310	+0.005
1.485	1.7018	1.7021	-0.012
1.984	1.6737	1.6739	-0.008
2.483	1.6465	1.6464	+0.008
2.982	1.6196	1.6196	+0.002
3.480	1.5936	1.5934	+0.008
3.979	1.5680	1.5681	-0.010
4.478	1.5433	1.5433	-0.002
4.977	1.5191	1.5191	-0.002
5.462	1.4964	1.4962	+0.011
5.962	1.4732	1.4732	+0.003
6.462	1.4509	1.4507	+0.014
6.962	1.4287	1.4287	-0.001
7.462	1.4070	1.4073	-0.017
7.962	1.3863	1.3863	-0.000
8.462	1.3660	1.3659	+0.007
8.962	1.3461	1.3460	+0.012
9.462	1.3265	1.3265	+0.003
9.962	1.3072	1.3074	-0.015

Standard deviation = 0.010

^a Equation 3 with $n = -1.864494$, $B = 191.4847$, and $T_0 = 190.2408$.

Table III. Comparison of Viscosities at Regular Intervals from 0–10°C

Temp, °C	$\eta_{\text{calcd.}}^a$, cP	$\eta_{\text{calcd.}}^b$, cP	$\eta_{\text{lit.}}^c$, cP	$\eta_{\text{lit.}}^d$, cP	$\eta_{\text{lit.}}^e$, cP	$\eta_{\text{lit.}}^f$, cP
0.0	1.7907	1.7907	1.7819	1.7867	1.7865	1.7919
0.5	1.7601	1.7601				
1.0	1.7303	1.7303	1.7205	1.7261		
1.5	1.7012	1.7012				
2.0	1.6730	1.6730	1.6629	1.6678		
2.5	1.6454	1.6455				
3.0	1.6186	1.6186	1.6085	1.6143		
3.5	1.5925	1.5925				
4.0	1.5671	1.5671	1.5572	1.5627		
4.5	1.5422	1.5422				
5.0	1.5180	1.5180	1.5087	1.5143	1.5170	1.5190
5.5	1.4944	1.4944				
6.0	1.4714	1.4714	1.4628	1.4684		
6.5	1.4490	1.4490				
7.0	1.4271	1.4271	1.4193	1.4241		
7.5	1.4057	1.4057				
8.0	1.3848	1.3848	1.3780	1.3819		
8.5	1.3644	1.3644				
9.0	1.3445	1.3445	1.3386	1.3422		
9.5	1.3250	1.3250				
10.0	1.3060	1.3060	1.3010	1.3038	1.3061	1.3067

^a Calculated from Equation 3 with $n = -1.864494$, $B = 191.4847$, and $T_0 = 190.2408$. ^b Calculated from Equation 2 with $A = 1.79082$, $B = -6.22487 \times 10^{-2}$, $C = 1.73711 \times 10^{-3}$, $D = -4.28856 \times 10^{-5}$, and $E = 6.74577 \times 10^{-7}$. ^c Dorsey (1929) (9) normalized to $\eta_{20} = 1.0020$. ^d Bingham and Jackson (1918) (1) normalized to $\eta_{20} = 1.0020$. ^e Cragoe in ref. 5. ^f Eicher and Zwolinski (1971) (13).

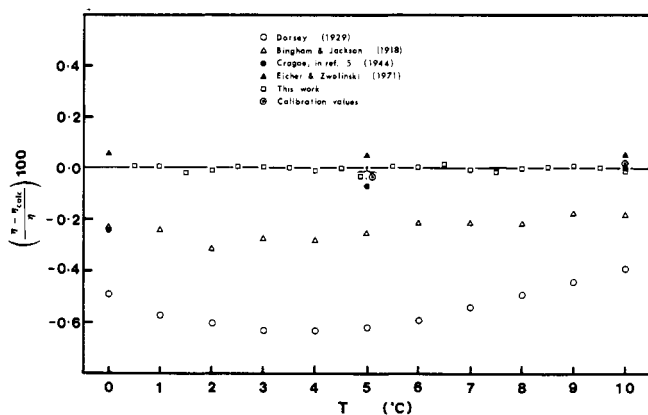


Figure 2. Percent deviation of various observations relative to viscosity computed from Equation 3 with $n = -1.864494$, $B = 191.4847$, and $T_0 = 190.2408$

where T' is the absolute temperature (293.15) at $\eta' = 1.0020$ cP, T is the absolute temperature, and n , B , and T_0 are the parameters obtained by a least-squares forced-fit of the data.

Table II shows the viscosities obtained from Equation 3 at the actual temperature used. There is a random distribution of error about the calculated values with a standard deviation of 0.010%. The fit to a five-parameter equation, 2, yielded coefficients $A = 1.79082$, $B = -6.22487 \times 10^{-2}$, $C = 1.73711 \times 10^{-3}$, $D = -4.28856 \times 10^{-5}$, and $E = 6.74577 \times 10^{-7}$. For this equation, temperatures were in $^{\circ}\text{C}$, and the standard deviation was 0.011%. Although this provides a fairly simple method of calculating η in the 0 – 10°C range, the Eicher and Zwolinski equation uses less parameters and has a slightly lower standard deviation.

The viscosities calculated at regular intervals from 0 – 10°C by both methods are shown in Table III along with the literature values.

Discussion

One of the objectives of this study was to determine whether or not there existed a significant difference between observed viscosities and those interpolated from Equation 3. This equation includes allowances for the free volume concept of water (6, 7, 8, 27) as well as the Arrhenius activation energy theory of rate processes (15, 22). Throughout the temperature range studied, the deviations are quite random, and there is none greater than twice the standard deviation. The absence of thermal anomalies in the fluid behavior of water in the temperature region of the molal volume minimum is shown in Figure 2. The relative experimental uncertainty was estimat-

ed as 0.014% which is about the same as the standard deviation.

Viscosity values in the 0 – 10°C range may be obtained to five significant digits from either Equation 2 or 3. Equation 2 is the simpler of the two in that it uses temperatures in Celsius degrees and may be quickly evaluated at any temperature between 0 and 10°C , by use of the simplest of calculating machines. Equation 3 has some theoretical basis and is slightly more precise, although somewhat more difficult to use. The percent difference from the present viscosities, of viscosities calculated from Equation 3 with the parameters of Eicher and Zwolinski (13), differ by a factor of three from the estimated precision of the present measurements (0.014%). Therefore, the new adjustable parameters are preferable in the range 0 – 10°C to those of Eicher and Zwolinski (13) which claim an accuracy of 0.2% over the range -10° to $+150^{\circ}\text{C}$.

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