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The relative viscosity of water has been measured with high precision in the range from 8 to 70° using a modified Cannon-Ubbelohde suspended-meniscus, dilution viscometer with a semiautomatic, optical viscometer reader. Measurements were made at 1° intervals with a relative precision of about 0.001%. The apparent energy of activation for viscous flow of water was calculated from these data. The result is given by an equation of the form $\Delta E^{\ddagger} = A + BT + CT^2 + DT^3 + ET^4$. The root-mean-square deviation from this expression was 3.7 cal/g-mol (*i.e.*, approximately 0.1% in $\Delta E^{\ddagger}$). The results obtained did not reveal any abrupt changes, at discrete temperatures, in the observed energy of activation values. The suggestion is offered that some of the thermal anomalies ("kinks") which have been reported in bulk properties of water may have arisen from structural transitions in ordered water structures near interfaces.

Introduction

Various workers[1-12] have reported the existence of thermal anomalies ("kinks") in the properties of bulk water and bulk aqueous systems. Other workers have specifically denied the existence of such anomalies.[13-16] Recent studies in our laboratory have been concerned with very careful measurements of various properties of water and aqueous solutions to determine if thermal anomalies do or do not exist. In this paper, we describe measurements that have been made on the viscosity of water from 8 to 70°, at 1° intervals. High-precision measurements were made by a semiautomatic method and the approach chosen was specifically designed to answer the question of whether or not evidence exists for thermal anomalies in the flow behavior of water.

A secondary objective of the present study was to provide accurate values for the viscosity of water without aspiring for the ultimate in accuracy, such as expected from a study in a standards laboratory. Numerous workers have carefully measured and compiled data for the viscosity of water at various temperatures.[17-29] The most reliable and thorough study comes from the National Bureau of Standards (from 0 to 60°);[25-27] the results of the present study compare favorably with those obtained at the National Bureau of Standards.

Experimental Method

Apparatus. Cannon-Ubbelohde suspended-meniscus, dilution viscometers were used for all the measurements. The viscometers were modified to allow connections to be made to them by means of ground-glass joints, rather than rubber tubing (to avoid contamination). The viscometer was positioned in a constant-temperature bath (of 5-gal. capacity, see Figure 1). The temperature bath was completely insulated with expanded polystyrene to minimize heat transfer. A small window was cut in the side of the temperature-bath insulation to allow the viscometer efflux bulb to be

observed. The temperature of the bath was controlled to better than ±0.001° using either a Hallikainen Thermotrol or a Bayley precision temperature controller. The bath was equipped with an auxiliary heater

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and a cooling coil; thus measurements could be made over an extended temperature range and the bath temperature could be changed rapidly. The temperature of the bath was measured to ±0.0001° with a Hewlett-Packard quartz crystal thermometer. As stated by the manufacturer, the accuracy is determined by "linearity" and "short-term stability" of the instrument. The absolute linearity, referred to a straight line through 0 and 100°, is better than ±0.02° in this temperature range. The instrument has a short-term stability of better than ±0.0002° (*i.e.*, "reading-to-reading variation at constant probe temperature") and a long-term (30 days) zero drift of less than ±0.01°. The thermometer probes were calibrated periodically in a mixture of shaved ice (frozen from distilled water) and water. It was presumed that the uncertainty of the absolute temperature was ±0.02°. The precision, however, approached 0.0002–0.0003° in consecutive measurements. The thermometer output was applied directly to a digital-to-analog converter (Hewlett-Packard) and was monitored on a strip-chart recorder. The temperature fluctuations in the thermostat during a run were less than ±0.0003° near ambient and were ±0.001° at the highest and lowest temperatures. We expected the fluctuations within the viscometer to be somewhat smaller.

The flow times were measured with a Rehovoth automatic viscometer reader. The reader consists essentially of a telescope with two photoelectric cells in the focal plane of the objective. The two photoelectric cells were placed so as to coincide approximately with the images of the upper and lower fiducial marks on the viscometer efflux bulb. Two light sources were placed in the bath, behind the viscometer. A Transistor Specialties, Inc. universal counter (Model 361) was connected to the external printer output of the viscometer reader. The counter provides a six-digit readout, allowing times to be recorded to within 1 msec.

The semiautomatic mode of operation of the instrument was simplified by the use of a specially designed clamping-and-positioning device shown in Figure 1. The viscometer was firmly clamped to a 0.5-in. stainless steel rod which was machined to sharp points at both ends. The bottom of the rod was set into a socket which was fixed with epoxy cement to the bottom of the constant-temperature bath. The top of the rod was secured with a clamp which made it easy to position the viscometer vertically. This clamping arrangement permitted the removal of the viscometer from the bath (for cleaning purposes) and its return to the original position. Because of the mode of operation of the automatic viscometer reader, it was imperative that the viscometer be returned to the original position at which the telescope of the viscometer reader was focused. The rigid positioning mechanism further served to eliminate vibrations due to vigorous stirring in the bath.
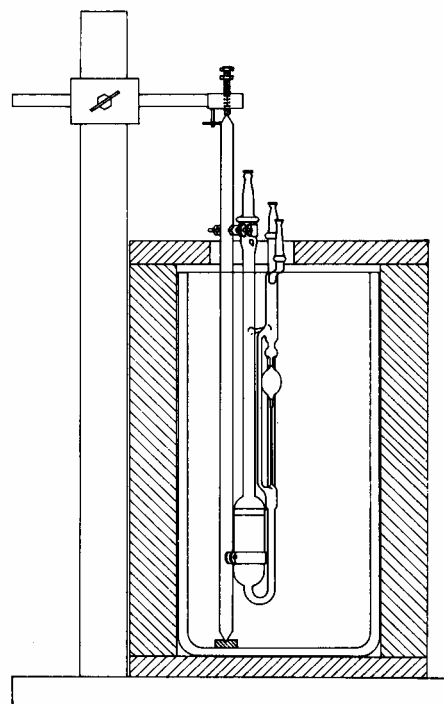

Figure 1. A schematic diagram of the clamping and positioning of the viscometer in an insulated constant-temperature bath.

Exploratory experiments indicated a difference of 0.7% in flow times when the viscometer was at a 5° deflection from the vertical. Since it is important that the effective pressure head be highly reproducible, a leveling device was used to provide vertical alignment of the viscometer at the beginning of each experiment. The leveling device consisted of a brass shaft with a leveling bubble mounted on one end, in a plane perpendicular to the shaft. The shaft was machined to fit into the large fill tube of the viscometer. With this device, it proved possible to ensure great precision in alignment.

Procedure of Operation. The water used in the experiments was prepared by the following two methods. Originally, the water was obtained from a Barnstead still and was redistilled in a single-stage, all-glass still. Water for the second group of runs was obtained from a three-stage glass still fed directly by a Barnstead still. The first stage contained a phosphoric acid–permanganate solution, the second stage contained an alkaline-permanganate solution, and the third stage contained only the distillate. As the steam left each boiling flask, it was passed through a superheater, consisting of a baffled glass cylinder, packed firmly with glass wool (first stage) or quartz wool (second and third stages). Each superheater was heated with electric heating tapes

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and was maintained between 140 and 200°. The final condenser was made of fused quartz. The resistance of the water was measured with a conductivity cell connected in parallel with the still output. The resistivity of the water was about 2.5×10^6 ohm cm. No differences in viscosity were observed between runs made with water produced by the two different methods. Subsequent to these measurements, improvements have been made in the operation of the still. Presently, argon is passed through the system during distillation. As a result of this modification, $(4-6) \times 10^6$-ohm cm water is now obtained routinely. The organic content (measured with a Beckman GC-5 gas chromatograph) is found to be less than 0.2 ppb.

Before use, the viscometers were thoroughly cleaned with cleaning solution (concentrated H_2SO_4 with $KMnO_4$) and were rinsed with distilled water. Any MnO_2 residue was subsequently removed with H_2O_2 in dilute HCl. The viscometer being used was charged with 10–30 ml of freshly distilled, filtered water and was positioned (as well as leveled) in the constant-temperature bath. The water was filtered immediately before use to remove lint or other particulate matter which might accidentally be introduced in the handling of the water. It was found that filtering was necessary in order to obtain the highest reproducibility in flow times. After thermal equilibrium was reached, the efflux bulb was filled by pressurizing the filling arm of the viscometer. This was accomplished by blowing air through a tube partially filled with Ascarite (to minimize the possible effects of CO_2 being added to the water). The tube was packed with quartz wool confined by a millipore filter and was connected to the inlet tube of the viscometer. After raising the level to the appropriate height, the liquid was permitted to fall (the pressure being the same on both sides of the liquid, namely, atmospheric). The "appropriate height" selected was the center of the upper viscometer bulb. This choice allowed the liquid to reach terminal velocity in the capillary before timing was started. Also, by raising the liquid to the same height for each run, it was possible to minimize uncertainty in drainage. When making a measurement, the meniscus passed the points at which the photoelectric cells were focused, and each cell, in turn, delivered start and stop pulses to the timer.

Flow times for pure water at constant temperature were reproducible to within ± 0.002–0.003 sec, out of approximately 380 sec at the lowest temperature (8°) and 115 sec at the highest temperature (70°). At room temperature, this corresponds to a relative precision of 0.001%.

Results and Calculations

Flow times for water were measured over a temperature range from 8 to 70° at 1° intervals. Table I shows a sample log of the data.[30] The temperature values presented in Table I for the individual runs are

the averages of values read every 10 sec during the given run. While any of these temperatures do not likely represent the absolute temperature, it is felt that the differences between consecutive, average temperatures (approximately 1° apart) are highly precise, probably within a few ten-thousandths of 1°.

Table I: Sample Viscosity Data Log

Run no.	Time of day	Temp, °C	Flow time, sec	Av time, sec	Av temp, °C
2a	13-43	40.0025	180.141		
2b	13-53	40.0024	180.139		
2c	13-58	40.0021	180.141		
2d	14-04	40.0021	180.142	180.141	40.0023
3a	14-24	41.0020	176.922		
3b	14-29	41.0016	176.925		
3c	14-53	41.0016	176.922	176.923	41.0017
4a	15-21	42.0024	173.799		
4b	15-26	42.0026	173.802		
4c	15-31	42.0027	173.802	173.801	42.0026

The flow times, at various temperatures, were used to calculate the apparent (Arrhenius) energy of activation, $\Delta E^{\ddagger}$, for the viscous flow of water defined by

$$\Delta E^{\ddagger} = R \frac{d \ln \tau}{d(1/T)} \simeq R \frac{d \ln \tau}{\Delta(1/T)} \tag{1}$$

where τ is the flow time in seconds, R is the gas constant, and T is the absolute temperature. It is assumed that since the measurements were made at 1° intervals that $\Delta \ln \tau / \Delta(1/T) \simeq d \ln \tau / d(1/T)$.

In order to facilitate the search for the existence or nonexistence of thermal anomalies, it was reasonable to use essentially a derivative method which promised the greatest precision in evaluating the data. It is for this reason that the data have been presented in terms of the apparent energies of activation.

The calculated, average vaues of $\Delta E^{\ddagger}$ as a function of temperature are shown in Figure 2. Each point represents the average $\Delta E^{\ddagger}$ of two or more (as many as five determinations) independent determinations at each temperature. Although the absolute flow times on occasion differed by as much as 0.04% from day to day, the values for the average apparent energy of activation, $\Delta E^{\ddagger}$, did not differ significantly. The average of the maximum spread of the individual values for the energy of activation, $\Delta E^{\ddagger}$, at any given temperature, obtained over a period of 2 years, is approximately 10 cal/mol, corresponding to 0.2% in $\Delta E^{\ddagger}$ at low temperatures and 0.3% at high temperatures.
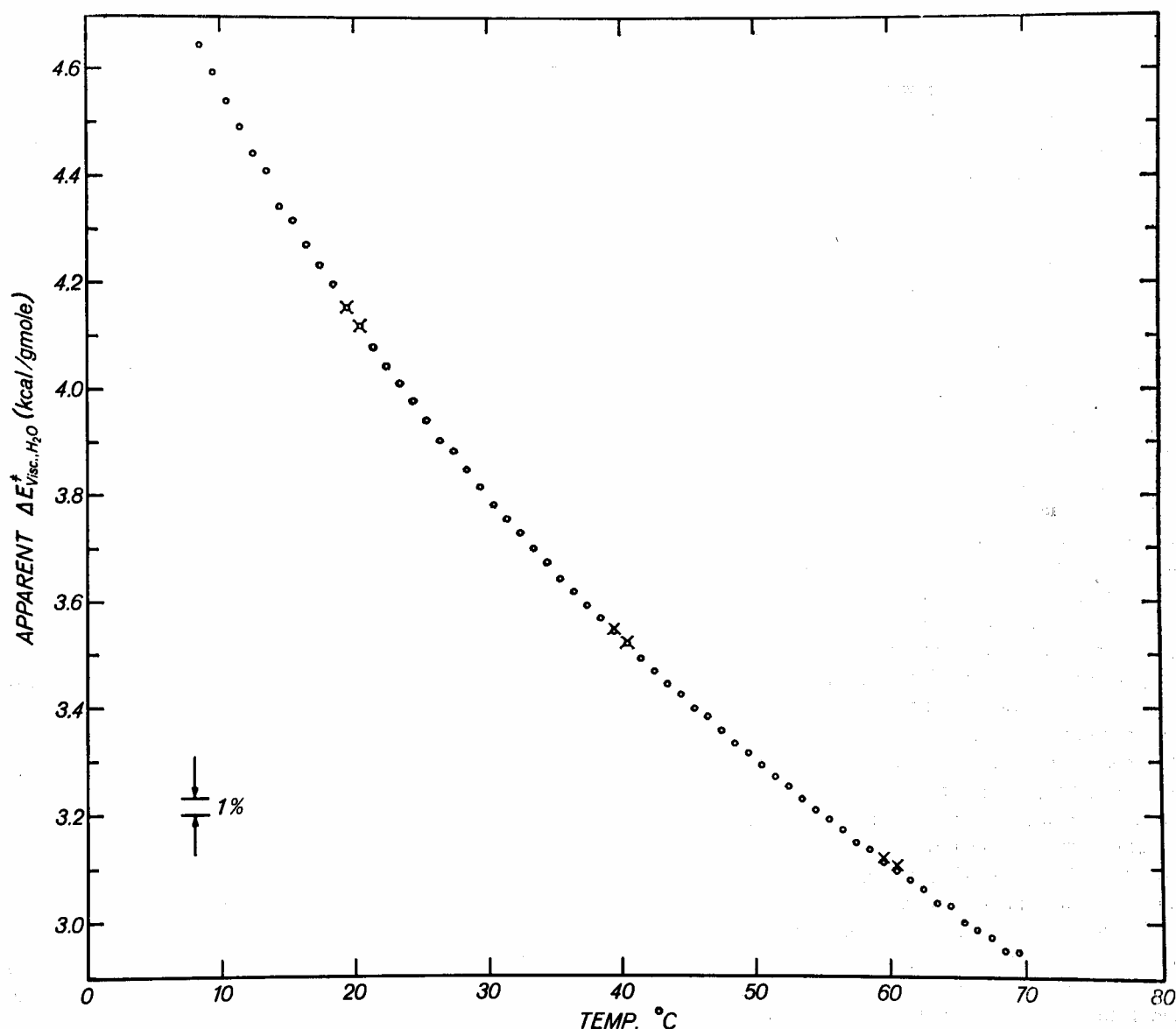
Figure 2. The apparent (Arrhenius) energy of activation, $\Delta E^{\ddagger}$, for the viscous flow of water as a function of the temperature: O, Cannon-Ubbelohde viscometer No. D619; X, Cannon-Ubbelohde viscometer No. D618. $\Delta E^{\ddagger} = A + BT + CT^2 + DT^3 + ET^4$ ($\sigma = \pm 0.1\%$).

The average $\Delta E^{\ddagger}$ values at various temperatures were fit to an equation of the form

$$\Delta E^{\ddagger} = A + BT + CT^2 + DT^3 + ET^4 \qquad (2)$$

where $A = 4.454967 \times 10^5$, $B = -5.1384039 \times 10^3$, $C = 2.2632508 \times 10^1$, $D = -4.4669185 \times 10^{-2}$, and $E = 3.321779 \times 10^{-5}$. The root-mean-square deviation between the experimental points and those calculated from this equation is 3.7 cal/mol or 0.1% at 30°. This deviation may be caused by an error in the temperature measurement of $\pm 0.001°$ or an error in flow time of ± 0.003 sec.

Most of the measurements were made with a single viscometer (Cannon-Ubbelohde dilution type, No. D619, size 50). As a check on these results, a number of measurements were made, at discrete temperatures,

using a second viscometer of the same type (No. D618, size 50). The values for the energies of activation, calculated from these measurements (also shown in Figure 2), agree within 0.15% with the least-squares best fit curve produced by the original data.

Having secured a reliable equation for the apparent energy of activation, $\Delta E^{\ddagger}$, for water as a function of temperature, one can, in principle, integrate this equation, solve for the constant of integration with an "accepted" flow time at one temperature, and calculate the flow times at any other temperature. From eq 1 and 2 one obtains upon integration

$$R \ln \tau = Q + \frac{A}{T} + B \ln T + CT + \frac{D}{2}T^2 + \frac{E}{3}T^3$$

$$(3)$$

The constant Q was evaluated by using the flow times of three independent determinations at 20° (τ = 274.363 ±0.002 sec and T = 293.1549 ± 0.0003°K). This calculation was made carrying 18 digits. The program was written in FORTRAN and was run on an IBM 1401 computer. The constant of integration Q was found to be equal to −25703.8837 cal/mol. Using this constant, flow times were then calculated at 5° intervals between 0 and 100° from eq 3.

The absolute viscosity of water, η, can be determined from the flow times, τ (obtained from eq 3), from the relationship

$$\nu = \frac{\eta}{d^0} = \tau K\left(1 - \frac{d^a}{d^0}\right) - \frac{L}{\tau^m} \qquad (4)$$

where ν is the kinematic viscosity, d^0 is the density of water, d^a is the density of air,[31] K is the instrument constant, L is the kinetic energy correction constant, and n is a constant that depends upon the shape of the capillary of the viscometer.[32,33] K, L, and n were determined (assuming they are independent of temperature) by using the values for the viscosity, η, of water at six temperatures. The values for the viscosity of water at 20, 25, 30, 40, 50, and 60° from the National Bureau of Standard[25-27] were used together with the flow times (calculated from eq 3) to determine optimal values for K, L, and n using a least-squares best fit. The optimal values were found to be K = 3.6678 × 10⁻³, L = 82.1, and n = 1.95. Using these constants and the flow times from eq 3, the viscosities of water at various temperatures have been calculated and are given in Table II. Also included in this table are selected literature values.

Although it has been customary to assume that n = 1 with capillary viscometers, it was proposed by Cannon, et al.,[34] that n = 2. The value of K and L have also been calculated by using only two literature values for the viscosity of H_2O^{24-26} at 20 and 60° and assuming that n = 2. This choice results in values of K = 3.6675 × 10⁻³ and L = 104.1. The viscosity values obtained by this method are essentially identical with those values secured in the first treatment. As an example, in the latter case, one obtains η_{45} = 0.59628 cP, while the other treatment yields η_{45} = 0.59631 cP.

The values for the viscosity of water shown in Table II agree very well with the literature values between 10 and 70°; however, at higher and lower temperatures the agreement is less satisfactory. Thus the equation for determining $\Delta E^{\neq}$ does not represent the viscous flow of water over the entire temperature range (0–100°) but only over the range in which measurements were made. The following equation can be used to obtain the viscosity of H_2O at temperatures between those listed in Table II

$$\log \frac{\eta_t}{\eta_{20}} = \frac{A(20 - t) - B(t - 20)^2}{t + C} \qquad (5)$$

where η_t represents the viscosity of water at any temperature (t) between 10 and 70°, η_{20} is the viscosity of water at 20°, A = 1.1709, B = 0.001827, and C = 89.93.

Discussion

The objectives of the present study were to obtain precise values for the viscosity of water as a function of temperature and, in particular, to determine if such data would or would not support the contention that thermal anomalies exist in the viscous flow of water at discrete temperatures. It is believed that the values for the viscosity of water obtained in this study compare favorably with those obtained by previous workers[25-27] and may, in fact, provide more precise data than have been available before (at least as far as the temperature dependence is concerned) in the interval from 10 to 70°.

Table II: The Viscosity of Water at Various Temperatures

Temp, °C	η_{H_2O}, cP — Present study	Lit. values[a]
0	1.7916	1.7865[b]
5	1.5192	1.5184,[c] 1.5170[b]
10	1.3069	1.3061[b]
15	1.1382	1.1381[b]
20	1.0020	(1.0020)[d]
25	0.8903	(0.8903)[b,e-g]
30	0.7975	0.7975,[b] (0.7976)[e]
35	0.7195	
40	0.6532	(0.6531),[b,c,e] 0.6526,[f] 0.6527[g]
45	0.5963	
50	0.5471	(0.5471),[b] 0.5467[f]
55	0.5042	
60	0.4666	0.4665,[c,g] 0.4668,[b] (0.4666)[f]
65	0.4334	
70	0.4039	0.4045[g]
75	0.3775	0.3784[g]
80	0.3538	0.3548,[c] 0.3546[e]
85	0.3323	
90	0.3128	0.3148,[c] 0.3143[g]
95	0.2949	0.2976[c]
100	0.2783	0.2822,[c] 0.2820[g]

[a] The numbers in parentheses are those used in the present treatment to evaluate the constants K, L, and n in eq 4. [b] C. S. Crague, unpublished work, quoted in ref 25. [c] From ref 26. [d] Reference value (1.0020 cP) used to calculate the viscosities at various temperatures from literature relative viscosities (relative to water at 20°). [e] From ref 25. [f] J. F. Swindells, unpublished work, quoted in ref 25. [g] From ref 29.

(31) The density of air was calculated ("Handbook of Chemistry and Physics," 35th ed, Chemical Rubber Publishing Co., Cleveland, Ohio, 1953) by assuming the air was 100% saturated with water vapor.

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One of the present authors (Drost-Hansen)[8-12] has reviewed much of the available data suggesting the existence of thermal anomalies ("kinks") in the properties of water and aqueous solutions. Based on the available evidence, it was proposed that thermal anomalies exist in the properties of water and aqueous solutions at a number of discrete temperatures. Several other investigators[3,35-37] have specifically claimed the existence of kinks in the energy of activation for viscous flow of water. The results of the present study suggest no evidence whatever for the reality of such anomalies.

A possible resolution to the conflicting evidence regarding the existence of anomalies in the bulk properties of water has been suggested in a recent note by Drost-Hansen.[38,38a] A review of all the available evidence for thermal anomalies in the properties of water and aqueous solutions suggests that the anomalies may, indeed, be real but possibly owe their existence to specific, interfacial effects. Elsewhere, Drost-Hansen[39] has presented a "three-layer model" of water near interfaces. It is suggested that the water near interfaces (for instance, the glass–water interface) may be structured and the interfacial structures possess definite, thermal stability limits. Thus the thermal anomalies sometimes seen in what has been presumed to be the viscosity of bulk water may be manifestations of spurious effects due to (more or less) abrupt changes in the properties of water near interfaces. However, the question of the existence of thermal anomalies in other *bulk* properties of water and aqueous solutions should not be dismissed lightly on this basis.

In summary, it is concluded that under conditions where surface interferences are minimized there is no evidence for the existence of thermal anomalies in the viscous flow of water between 8 and 70°. Earlier data[8-11] have frequently suggested the existence of such anomalies and it is proposed that the cause of these anomalies may be traced to structural transitions in ordered water structures near various interfaces (such as the glass–water as well as the air–water interface). Measurements are in progress in this laboratory to examine the hypothesis that the viscous flow of water near interfaces shows anomalies.

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(38a) NOTE ADDED IN PROOF. Since the writing of this paper, additional flow time measurements have been made at 1° intervals to obtain values in the temperature range of 0–25°, thus allowing us to extend the range of apparent energies of activation to include values from 0 to 8°. The data from the recent work have been combined with the data quoted in this paper, and a new set of values has been obtained for the coefficients in eq 2 for the apparent energy of activation. The new values are: $A = 5.912439 \times 10^5$, $B = -7.0249972 \times 10^3$, $C = 3.1775238 \times 10^1$, $D = -6.4329251 \times 10^{-2}$, and $E = 4.9045775 \times 10^{-5}$. The root-mean-square deviation ($\Delta E^{\ddagger}$ values from 0 to 70°) is 3.3 cal/mol or, again, approximately 0.1% at 30°. The new data do not suggest any anomalous behavior for the viscous flow of water in the lower temperature range and, in particular, no anomaly in the region of maximum density.

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