

# THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

## Part IV.—Observation of Energy-level Structure in the Intermolecular Potential Energy of Activation for Viscous Flow of Water

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The earlier measurements on the activation energy,  $\epsilon$ , of glycerol and ethylene glycol have now been followed up by similar accurate measurements in the case of water, based on the logarithmic derivative of the Andrade equation, viz.,

$$\epsilon/k = -T^2 \Delta \ln \eta / \Delta T$$

using a Beckmann thermometer for accurate measurement of the  $2^\circ\text{C}$ . interval,  $\Delta T$ . Preliminary experiments in the range of  $30^\circ\text{C}$ . to  $75^\circ\text{C}$ . have indicated the presence of a series of more or less sharp, regularly occurring steps in the energy,  $\epsilon$ . The temperature interval between successive steps is  $6^\circ\text{C}$ . on the average, as against  $12.1^\circ\text{C}$ . in the case of ethylene glycol. More refined and extensive measurements on water are in hand.

Preliminary viscosity experiments carried out on some mineral oils in this laboratory<sup>1</sup> had indicated a periodicity in the temperature variation of the activation energy,  $\epsilon$ , as determined from the equation

$$\eta = A \exp(\epsilon/kT), \quad (1)$$

where  $\epsilon$  measures the height of the intermolecular potential energy barrier<sup>2,3</sup> that has to be overcome for the relative movement of one layer of molecules with respect to the next (through a distance equal to the length of one molecular aggregate). More accurate measurements of  $\epsilon$  at intervals of  $5^\circ\text{C}$ . and  $2.5^\circ\text{C}$ . on redistilled glycerol<sup>4</sup> and ethylene glycol<sup>5</sup> showed that these liquids have constant  $\epsilon$  (and constant  $A$ ) over certain short, regularly recurring, ranges of temperature (Fig. 1), thus simulating an ideal non-associated liquid in these ranges.

Because of the importance of these previously unrecognized phenomena in the molecular theory of liquids, we have further extended these measurements to the important case of water (twice-distilled), taking readings at intervals of  $2^\circ\text{C}$ ., with temperature control to better than  $0.002^\circ\text{C}$ . The calculations, as in the earlier papers from this laboratory, are based on differentiation of the logarithmic form of equation (1), which yields

$$\epsilon/k = -T^2 \Delta \ln \eta / \Delta T, \quad (2)$$

the desired accuracy being attained by measuring the temperature interval,  $\Delta T$ , with a calibrated Beckmann differential thermometer, and taking viscosity measurements in a U-tube viscometer giving times of flow of the order of 1000 seconds. The results obtained in the range of  $30^\circ\text{C}$ . to  $75^\circ\text{C}$ . from two separate lots of twice-distilled conductivity water are shown in Table I and

Fig. 2 (Expt. I and Expt. II), together with the means of the two sets, the radii of the circles being equal to the experimentally estimated standard deviation of the plotted points, which is about  $\pm 0.009$  units of  $(\epsilon/k) \div 1000$ .

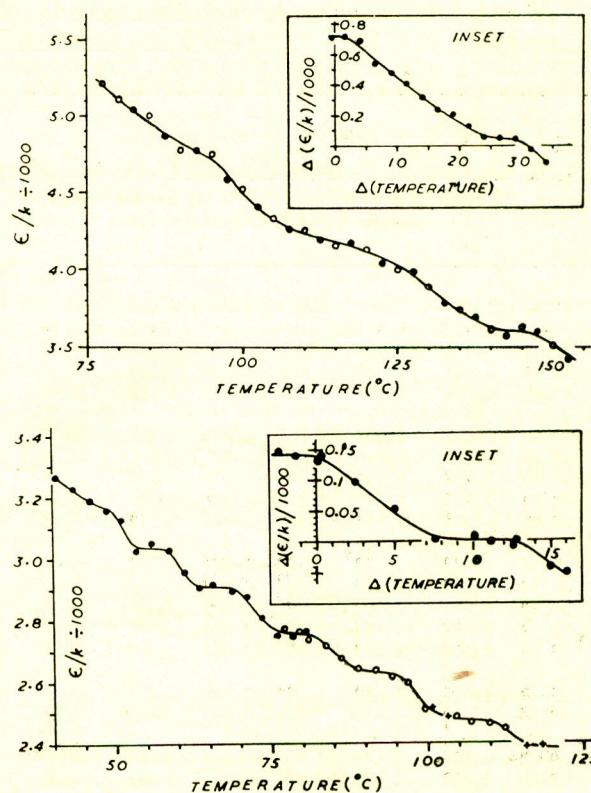


Fig. 1.—Plots showing the previously reported temperature dependence of the activation energy,  $\epsilon$ , of viscous flow for (top) glycerol and (bottom) ethylene glycol. The ordinates are  $(\epsilon/k)/1000$ , where  $k$  is Boltzmann's constant, and the insets show the averaged variation over one segment.

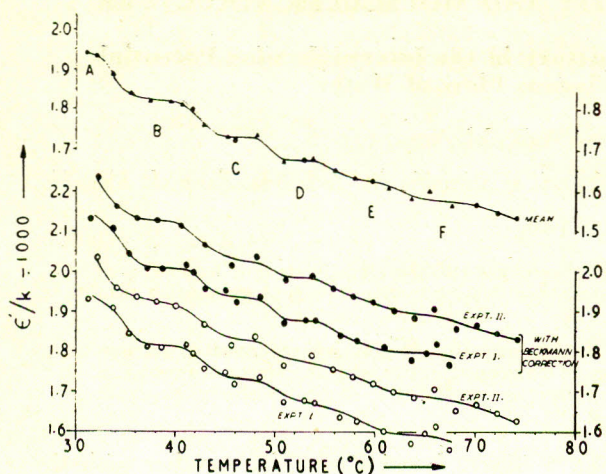


Fig. 2.—Graphs of  $(\epsilon/k)/1000$  obtained from preliminary measurements on water in the range of 30°C. to 75°C. Hollow circles, uncorrected values; solid circles, after application of Beckmann calibration corrections. Successive curves are displaced

The graphs of Fig. 2 demonstrate the reproducibility of the phenomena under investigation, and show the presence of several flat regions (A, B,.....F) of constant  $\epsilon$ , with definite steps between successive "flats". These steps decrease in height with increasing temperature, and are actually much sharper than those seen in Fig. 1, because the drop now extends over just 3°C. on the average, which is only 1°C. more than the experimental measuring interval of 2°C. The energy change,  $\Delta\epsilon$ , at each step, which varies from step to step, is of the order of  $0.1 \times (1000 k)$ , i.e. 0.009 electron volt, and is considerably lower than the thermal energy,  $kT$ . The repetition period of the steps for water is nearly 6°C., as against the corresponding figures of 12°C. and 25°C. in case of ethylene glycol and glycerol, respectively. These intervals are all closely mul-

upwards by 0.1 unit. The triangles (uppermost curve) represent the means of the corrected values from expts. I and II, and the successive steps observed are marked A,B,.....F.

TABLE I.—VALUES OF ACTIVATION ENERGY,  $\epsilon$ , OBTAINED WITH A MEASURING INTERVAL  $\Delta T=2^\circ\text{C}$ .

Experiment I					Experiment II					Overall Mean	
Temperature, °C.	$\frac{\epsilon}{k} / 1000 = -\frac{T^2}{1000} \frac{\Delta \ln \eta}{\Delta T}$		Mean	Corrected	Temperature, °C.	$\frac{\epsilon}{k} / 1000 = -\frac{T^2}{1000} \frac{\Delta \ln \eta}{\Delta T}$		Mean	Corrected	Temperature, °C.	$\frac{\epsilon}{k} / 1000$
	Temperature rising	Temperature falling				Temperature rising	Temperature falling				
31.20	1.928	1.932	1.930±0.002	1.930	—	—	—	—	—	31.20	1.930±0.002
33.65	1.914	1.912	1.913±0.001	1.904	32.19	1.930	1.933	1.932±0.001	1.936	32.19	1.936±0.001
35.25	1.848	1.840	1.844±0.004	1.844	34.07	1.864	1.859	1.862±0.003	1.858	33.86	1.881±0.023
37.06	1.806	1.801	1.804±0.002	1.808	36.10	1.835	1.843	1.839±0.004	1.839	35.67	1.841±0.002
38.63	1.803	1.807	1.805±0.002	1.805	38.08	1.818	1.818	1.818±0.000	1.816	37.57	1.812±0.006
41.10	1.816	1.818	1.817±0.001	1.807	40.48	1.800	1.809	1.804±0.004	1.806	39.55	1.806±0.001
41.80	1.794	1.799	1.796±0.002	1.778	40.48	1.800	1.809	1.804±0.004	1.806	40.79	1.806±0.000
42.89	1.756	1.751	1.754±0.002	1.758	—	—	—	—	—	41.80	1.778±0.002
45.01	1.741	1.744	1.742±0.002	1.742	42.87	1.768	1.769	1.768±0.001	1.760	42.88	1.759±0.001
46.04	1.732	1.732	1.732±0.000	1.732	45.56	1.720	1.716	1.718±0.002	1.721	45.28	1.732±0.011
48.54	1.732	1.735	1.734±0.002	1.725	—	—	—	—	—	46.04	1.732±0.001
50.90	1.672	1.682	1.677±0.005	1.679	48.14	1.733	1.729	1.731±0.002	1.726	48.34	1.726±0.000
52.97	1.677	1.684	1.680±0.004	1.672	50.99	1.671	1.671	1.671±0.000	1.672	50.94	1.676±0.003
53.95	1.670	1.674	1.672±0.002	1.673	—	—	—	—	—	52.97	1.672±0.003
56.50	1.645	1.640	1.642±0.002	1.635	53.70	1.687	1.684	1.686±0.002	1.678	53.82	1.676±0.002
58.20	1.647	1.648	1.648±0.000	1.652	55.79	1.667	1.657	1.662±0.005	1.662	56.14	1.648±0.013
60.92	1.605	1.612	1.608±0.004	1.603	57.80	1.631	1.640	1.636±0.004	1.635	58.00	1.644±0.008
63.60	1.582	1.573	1.578±0.004	1.578	59.79	1.616	1.618	1.617±0.001	1.616	59.79	1.616±0.001
65.05	1.592	1.599	1.596±0.004	1.596	61.87	1.604	1.606	1.605±0.001	1.598	61.40	1.600±0.002
67.42	1.565	1.574	1.570±0.002	1.566	63.88	1.587	1.588	1.588±0.001	1.588	63.74	1.583±0.005
—	—	—	—	—	65.92	1.601	1.603	1.602±0.001	1.595	65.48	1.596±0.004
—	—	—	—	—	68.05	1.546	1.547	1.546±0.001	1.550	67.74	1.588±0.008
—	—	—	—	—	70.06	1.573	1.574	1.574±0.001	1.566	70.06	1.566±0.001
—	—	—	—	—	72.24	1.546	1.547	1.546±0.001	1.546	72.24	1.546±0.001
—	—	—	—	—	74.20	1.533	1.534	1.534±0.001	1.526	74.20	1.526±0.001

tuples of 6.2°C., which thus appears to define a basic periodicity for the inter-molecular OH-group interactions common to these three liquids.

The above observations provide evidence for the existence of a well-defined periodic energy structure in the three liquids, probably associated with the molecular aggregation produced by the hydrogen bonds. Further experiments are presently being directed towards obtaining more accurate and extensive data for water, so as to elucidate the detailed structure of the steps, and towards investigating the factors causing the comparatively gradual drop between steps in the case of glycerol and ethylene glycol.

### References

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