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COMPARATIVE MEASUREMENTS OF THE TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX OF LIQUIDS AND SOLUTIONS

Part V.—Flow Activation Energy and Refractive Index Measurements on Amyl Alcohol, Isoamyl Alcohol and n-Butyl Alcohol

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The comparative measurements of $E\eta$, the activation energy of viscous flow and $-dn/dT$ the temperature derivative of refractive index are here extended to amyl alcohol, isoamyl alcohol and n-butyl alcohol. The $E\eta$ and $-dn/dT$ curves for these three alcohols exhibit a series of maxima and minima which tend to become more prominent at temperatures above 40°C. In each case, there are ten to eleven minima in the range between 20°C and 70°C, and the two sets of minima correspond with each other within less than 0.7°C on the average.

Introduction

Investigations on flow activation energy $E\eta$ carried out in a series of experiments by Qurashi and his co-workers have established two types of novel phenomena, namely (i) step-wise variations observed in water,[1] ethylene glycol[2] and solution of dilute aqueous ethanol,[3] and (ii) cyclic behaviour of $E\eta$ as seen from the measurements on benzene,[4] on ethanol solutions at the ethanol-rich end of the system,[5] and in mineral oils at high temperatures.[6] In an effort to throw further light on these phenomena, the measurements in the present series of papers include investigations of the derivatives of viscosity, density and refractive index of various liquids and solutions. These measurements have indicated a certain degree of correspondence between these three types of phenomena, and the comparison between the $E\eta$ jumps and the cyclic variations of $d\beta/dt$ made by Ali, Bhatti and Qurashi[7] points to possible structural changes occurring in liquids.

In order to further elucidate the correlation between these various quantities and their variation from system to system, it was considered desirable to examine some of the higher alcohols. The present communication deals with activation energy of viscous flow, $E\eta$, and the derivatives of refractive index ($-dn/dt$), both measured at one degree C intervals for (i) amyl alcohol (ii) isoamyl alcohol and (iii) n-butyl alcohol. An attempt is made to deduce some correlations between the two phenomena.

Experimental Technique

$E\eta$ is obtained by the differential method (as in the case of water, hydrocarbons and aqueous solutions), which is based on the differential of the Andrade equation, viz.

$$\begin{aligned} E\eta/R &= \Delta \ln\eta/\Delta\,(1/T) = -T^2\,\Delta \ln\eta/\Delta T \\ &= -T^2\,\Delta \ln \nu/\Delta\, T + T^2\,(\Delta\rho/\Delta T)/\rho \\ &= E\nu/R + T^2\beta \end{aligned} \qquad (1)$$

where ρ is the density, ν the kinematic viscosity, η the dynamic viscosity ($= \nu \times \rho$), and β is the coefficient of dilatation. (The term $T^2\beta$ forms a small slowly-varying correction factor which can be applied to the final E/R values.)

Flow measurements through a U-tube viscometer of B.S.S. pattern were recorded to an accuracy of ± 0.02 sec with a calibrated stop-watch, using a Townson and Mercer thermostat with temperature stability to ± 0.002°C or better. Corrections for the change of the equilibrium level of the liquid in the viscometer were applied, and the evaporation losses at higher temperatures were diminished by keeping a ballast-bottle device well-immersed in the thermostat.

TABLE 1.—BECKMANN READINGS, FLOW TIMES AND THE CALCULATED VALUES OF $(E/R) \div 1000 = -T^2 (\Delta \ln \nu) / \Delta T / 1000$ FOR AMYL ALCOHOL IN THE RANGE OF 24°C TO 75°C.

Heating sequence						Cooling sequence						
Temp. °C	Beckmann reading	Time of flow corrected for level	Mean temp. °C	$(E/R) \div 1000$ Uncorrected	$(E/R) \div 1000$ Corrected	Temp. °C	Beckmann reading	Time of flow corrected for level	Mean temp. °C	$(E/R) \div 1000$ Uncorrected	$(E/R) \div 1000$ Corrected	Mean $(E/R) \div 1000$
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
24.0	4.557±0.000	1190.36±0.02				24.0	4.552±0.001	1190.76±0.02				
			24.50	2.594	2.598±0.004				24.50	2.607	2.611±0.004	2.605±0.006
25.0	5.552±0.001	1156.16±0.03				25.0	5.555±0.000	1156.13±0.02				
25.0	1.820±0.001	1154.31±0.02				25.0	1.831±0.001	1154.08±0.03				
			25.50	2.603	2.605±0.005				25.50	2.594	2.596±0.005	2.601±0.005
26.0	2 815±0.000	1121.30±0.04				26.0	2.830±0.000	1121.03±0.02				
			26.50	2.571	2.574±0.005				26.50	2.589	2.591±0.005	2.583±0.008
27.0	3.814±0.001	1089.67±0.02				27.0	3.832±0.001	1089.11±0.02				
27.0	0.700±0.000	1089.00±0.01				27.0	0.688±0.000	1089.30±0.02				
			27.50	2.643	2.642±0.005				27.50	2.635	2.634±0.005	2.538±0.004
28.0	1.720±0.001	1057.00±0.02				28.0	1.680±0.001	1058.22±0.03				
			28.50	2.677	2.678±0.005				28.50	2.676	2.677±0.005	2.678±0.001
29.0	2.729±0.001	1026.08±0.03				29.0	2.683±0.002	1027.39±0.04				
			29.50	2.689	2.694±0.005				29.50	2.683	2.688±0.005	2.691±0.003
30.0	3.720±0.001	996.66±0.02				30.0	3.683±0.000	997.73±0.02				
			30.50	2.676	2.674±0.005				30.50	2.671	2.669±0.005	2.672±0.003
31.0	4.733±0.000	967.78±0.02				31.0	4.685±0.001	969.79±0.03				
31.0	3.314±0.001	970.75±0.03				31.0	3.300±0.000	971.33±0.02				
			31.50	2.551	2.556±0.005				31.50	2.554	2.559±0.005	2.558±0.002
32.0	4.310±0.000	944.55±0.02				32.0	2.304±0.000	944.86±0.02				
			32.50	2.544	2.540±0.005				32.50	2.562	2.559±0.005	2.550±0.010
33.0	5.309±0.001	919.20±0.03				33.0	5.297±0.001	919.48±0.02				
33.0	2.573±0.001	919.43±0.02				33.0	2.582±0.002	919.20±0.03				
			33.50	2.668	2.670±0.006				33.50	2.650	2.652±0.006	2.661±0.009
34.0	3.571±0.002	893.74±0.03				34.0	3.583±0.001	893.62±0.02				
			34.50	2.748	2.748±0.006				34.50	2.749	2.749±0.006	2.748±0.001
35.0	4.591±0.001	867.66±0.02				35.0	4.583±0.000	868.04±0.02				
35.0	3.219±0.000	859.59±0.02				35.0	3.105±0.001	858.80±0.02				
			35.50	2.678	2.680±0.004				35.50	2.681	2.683±0.004	2.682±0.001
36.0	4.233±0.001	834.59±0.02				36.0	4.105±0.000	834.97±0.02				
			36.50	2.526	2.523±0.004				36.50	2.535	2.533±0.004	2.528±0.005
37.0	5.200±0.002	813.46±0.03				37.0	5.105±0.003	813.19±0.04				
37.0	2.290±0.001	810.39±0.02				37.0	2.290±0.001	810.28±0.03				

(*Continued*)

(*Table 1 Continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
			37.50	2.579	2.581±0.005				37.50	2.558	2.560±0.005	2.570±0.011
38.0	3.275±0.000	789.41±0.02				38.0	3.270±0.001	789.49±0.02				
			38.50	2 624	2.626±0.005				38.50	2.638	2.640±0.005	2.633±0.007
39.0	4.275±0.002	768.37±0.03				39.0	4.250±0.000	768.75±0.02				
			39.50	2.697	2.695±0.005				39.50	2.712	2.710±0.005	2.703±0.008
40.0	5.250±0.001	747.98±0.02				40.0	5.238±0.002	747.96±0.03				
40.0	2.210±0.000	746.66±0.02				40.0	2.213±0.000	746.60±0.02				
			40.50	2.543	2.546±0.007				40.50	2.553	2.556±0.007	2.551±0.005
41.0	3.211±0.002	727.59±0.04				41.0	3.219±0.001	727.36±0.02				
			41.50	2.546	2.549±0.007				41.50	2.561	2.664±0.007	2.556±0.008
42.0	4.208±0.001	709.17±0.02				42.0	4.222±0.002	708.73±0.03				
			42.50	2.578	2.573±0.007				42.50	2.594	2.590±0.007	2.581±0 008
43.0	5.210±0.002	691.02±0.03				43.0	5.220±0.000	690.55±0.01				
43.0	0.862±0.001	689.62±0.01				43.0	0.881±0.001	689.30±0.02				
			43.50	2.734	2.734±0.006				43.50	2.736	2.736±0.006	2.735±0.001
44.0	1.880±0.000	670.92±0.02				44.0	1.874±0.000	670.87±0.02				
			44.50	2.637	2.636±0.006				44.50	2.551	2.550±0.006	2.543±0.007
45.0	2.912±0.001	653.07±0.03				45.0	2.866±0.001	654.25±0.03				
			45.50	2.716	2.721±0.006				45.50	2.722	2.727±0.006	2.724±0.004
46.0	3.947±0.000	635.24±0.02				46.0	3.857±0.001	637.10±0.01				
46.0	1.050±0.001	633.67±0.02				46.0	1.048±0.001	633.80±0.02				
			46.50	2.807	2.805±0.007				46.50	2.809	2.807±0.007	2.806±0.001
47.0	2.066±0.002	616.34±0.03				47.0	2.043±0.002	616.70±0.03				
			47.50	2.675	2.677±0.007				47.50	2.672	2.673±0.007	2.675±0.002
48.0	3.114±0.001	599.76±0.02				48.0	3.043±0.000	600.88±0.02				
			48.50	2.536	2.540±0.007				48.50	2.530	2.533±0.007	2.537±0.004
49.0	4.131±0.000	584.94±0.01				49.0	4.043±0.001	586.36±0.01				
			49.40	2.650	2.645±0.007				49.40	2.647	2.642±0.007	2.643±0.002
49.8	4.970±0.001	572.56±0.02				49.8	4.810±0.002	574.94±0.02				
49.8	1.562±0.000	573.96±0.01				49.8	1.562±0.001	574.06±0.01				
			50.40	2.706	2.705±0.008				50.40	2.708	2.707±0 008	2.706±0.001
51.0	2.863±0.001	555.01±0.02				51.0	2.762±0.002	556.50±0.03				
			51.50	2.673	2.675±0.008				51.50	2.660	2.662±0.008	2.668±0.007
52.0	3.923±0.001	540.29±0.02				52.0	3.762±0.001	542.63±0.02				
52.0	1.423±0.001	546.50±0.02				52.0	1.401±0.001	546.70±0.02				
			52.50	2.647	2.646±0.008				52.50	2.643	2.642±0.008	2.644±0.002
53.0	2.489±0.000	532.15±0.01				53.0	2.401±0.002	533.24±0.02				
			53.50	2.642	2.647±0.008				53.50	2.538	2.543±0.008	2.645±0.002
54.0	3.530±0.001	518.60±0.02				54.0	3.394±0.001	520.32±0.02				
			54.50	2.582	2.582±0.008				54.50	2.577	2.577±0.008	2.680±0.003
55.0	4.575±0.002	505.72±0.03				55.0	4.397±0.002	507.99±0.02				
55.0	2.517±0.000	512.13±0.01				55.0	2.412±0.001	512.67±0.03				
			55.50	2.569	2.573±0.008				55.50	2.586	2.590±0.008	2.582±0.009
56.0	3.495±0.001	501.33±0.02				56.0	3.482±0.001	499.70±0.02				
			56.50	2.644	2.644±0.008				56.50	2.637	2.637±0.008	2.641±0.004
57.0	4.700±0.902	486.83±0.03				57.0	4.470±0.002	487.86±0.02				

(*Table 1 Continued*)

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)	(11)	(12)	(13)
			57.50	2.635	2.633±0.008				57.50	2.642	2.640±0.008	2.637±0.004
58.0	5.631±0.000	476.00±0.01				58.0	5.477±0.000	476.13±0.02				
58.0	2.222±0.001	485.40±0.02				58.0	2.200±0.001	485.53±0.02				
			58.50	2.623	2.625±0.010				58.50	2.611	2.613±0.010	2.619±0.006
59.0	3.253±0.001	473.73±0.03				59.0	3.200±0.002	474.14±0.03				
			59.50	2.462	2.466±0.010				59.50	2.637	2.641±0.010	2.645±0.004
60.0	4.264±0.002	462.47±0.02				60.0	4.193±0.001	463.05±0.02				
60.0	2.490±0.001	462.40±0.02				60.0	2.487±0.002	461.42±0.03				
			60.50	2.559	2.561±0.011				60.50	2.563	2.565±0.011	2.563±0.002
61.0	3.473±0.000	451.09±0.02				61.0	3.564±0.001	450.12±0.02				
			61.50	2.529	2.529±0.011				61.50	2.534	2.534±0.011	2.532±0.003
62.0	4.504±0.002	440.71±0.03				62.0	4.556±0.002	440.13±0.02				
62.0	2.573±0.000	440.06±0.02				62.0	2.568±0.001	440.40±0.02				
			62.50	2.537	2.539±0.010				62.50	2.536	2.538±0.010	2.538±0.001
63.0	3.572±0.001	430.27±0.02				63.0	3.575±0.002	430.53±0.03				
			63.50	2.447	2.447±0.010				63.50	2.451	2.451±0.010	2.549±0.002
64.0	4.573±0.002	421.07±0.02				64.0	4.567±0.001	421.41±0.03				
64.0	2.516±0.001	420.07±0.02				46.0	2.519±0.000	499.99±0.02				
			64.50	2.401	2.403±0.011				64.50	2.141	2.146±0.011	2.410±0.007
65.0	3.530±0.002	411.17±0.03				65.0	3.535±0.001	411.05±0.02				
			65.50	2.535	2.535±0.011				65.50	2.531	2.531±0.011	2.533±0.002
66.0	4.503±0.000	402.42±0.02				66.0	4.494±0.001	402.44±0.03				
			66.50	2.529	2.526±0.011				66.50	2.531	2.527±0.011	2.527±0.001
67.0	5.471±0.011	393.97±0.02				67.0	5.465±0.002	393.98±0.02				
67.0	2 195±0.001	393.20±0.02				67.0	2.201±0.002	393.17±0.03				
			67.50	2.579	2.580±0.012				67.50	2.558	2.559±0.012	2.570±0.011
68.0	3.195±0.002	384.58±0.03				68.0	3.194±0.002	384.65±0.03				
			68.50	2.626	2.629±0.012				68.50	2.623	2.626±0.012	2.627±0.002
69.0	4.200±0.001	375.98±0.02				69.0	4.194±0.000	376.10±0.02				
			69.50	2.459	2.457±0.012				69.50	2.460	2.458±0.012	2.458±0.001
70.0	5.162±0.000	368.48±0.02				70.0	5.194±0.001	368.30±0.02				
70.0	0 102±0.001	370.65±0.02				70.0	0.100±0.001	370.66±0.02				
			70.50	2.535	2 536±0 013				70.50	2.536	9.537±0.013	2.537±0.001
71.0	1.103±0.000	362.77±0.02				71.0	1.093±0.002	362.84±0.03				
			71.50	2.522	2.520±0.013				71.50	2.527	2.525±0.013	2.523±0.003
72.0	2.100±0.001	355.17±0.03				72.0	2.061±0.002	355.37±0.02				
			72.50	2.550	2.552±0.013				72.50	2.545	2.457±0.013	2.555±0.003
73.0	3.100±0.002	347.75±0.02				73.0	3.053±0.000	347.94±0.01				
			73.50	2.577	2.577±0.013				73.50	2.568	2.568±0.013	2.573±0.005
74.0	4.096±0.001	340.40±0.02				74.0	4.059±0.001	340.54±0.02				
74.0	2.308±0.002	338.50±0.02				74.0	2.420±0.001	338.65±0.02				
			74.50	2.522	2.521±0.012				74.50	2.530	2.529±0.012	2.525±0.004
75.0	3.412±0.000	331.48±0.02				75.0	3.396±0.002	331.80±0.02				
			75.50	2.557	2.559±0.012				75.50	2.538	2.540±0.012	2.550±0.010
76.0	4.405±0.001	324.55±0.02				76.0	4.392±0.000	324.97±0.02				

The technique for the measurements of the derivative of refractive index (dn/dt) has been described in the previous papers dealing with the experiments on water,[8] benzene[9] and aqueous ethanol[10] solutions. It consists of measuring the change for every 2°C in θ, the angle of emergence (from the glass prism) of the beam of sodium light (λ=5893°A) passing through the cell of a Pulfrich critical-angle refractometer containing the test liquid, the temperature of which is stabilized to $\pm$0.02°C or better by circulating, through the chamber, water from an ordinary thermostat.

The change $\Delta\theta'$ measured in minutes of arc is proportional to dn/dT, the constant of proportionality being about 1.1×10^{-4}. The measurements are taken both during the heating and cooling sequences at intervals of 2°C and staggered as before by 1°C, so as to obtain finally an experimental point at every degree.

Results on Amyl Alcohol and Isoamyl Alcohol

The flow times, Beckmann readings and the calculated values of $(E/R)/1000$ for amyl alcohol (Analar grade) in the range of 24°C to 76°C, together with their estimated standard deviations for sets of successive readings, are given in Table 1. The mean values are plotted as solid circles in the top half of Fig. 1, and the graph exihibits a series of maxima and minima, the average period being 4.5° and mean amplitude of the order of 0.14 units, which is about 20 times the r.m.s. deviations ($\sim$0.008). The corresponding graph of dn/dt for one set of measurements by one of the authors is shown as triangles and crosses in Fig. 1, along with another set taken by another one of the authors (Mrs. Haider) in the range of 17°C to 60°C (inclined crosses). The mean graph of these two is plotted directly above these, through the hollow circles, and shows a clear series of maxima and minima. It is seen that the data for $E\eta$ and for $(-dn/dT)$ both exhibit eleven minima in the 50-degree interval between 20°C and 70°C. We may therefore presume a one-to-one correspondence between the two phenomena.

Next, isoamyl alcohol of BDH Analar grade was subjected to $E\eta$ measurements from 10°C to 71°C, at 1°C interval. The $E\eta$ values, both for heating and cooling sequences, together with their r.m.s. deviations, as estimated from those of Beckmann reading and flow times through the viscometer, are given in Table 2(a), and are plotted with solid circles in Fig. 2. Like amyl alcohol, this also shows a cyclic variation with period of 5°C, but the amplitude of oscillation is smaller, being only 0.07 units of $(E/R)/1000$. The dn/dt values obtained for two sets of refractometric measurements during heating and cooling are again shown in two lowest graphs. The mean curve, plotted (hollow circles) in the middle of Fig. 2, again has a period of 5°C, with average amplitude of 25 sec of arc, which is about 12 times the r.m.s. scatter.

In case of isoamyl alcohol, we find ten minima between 20°C and 50°C in the $E\eta$ curve as also in the mean curve for $(-dn/dt)$, thus confirming the existence of a one-to-one correspondence between the two sets of maxima and minima that was observed in case of amyl alcohol.

Results on n-Butyl Alcohol

The $(E/R)/1000$ values for both the heating and cooling sequences in the range of 15°C to 95°C are given in Table 3 and are shown by a smooth curve drawn through solid circles in Fig. 3. This exhibits roughly sinusoidal variations, with mean period of about 4.5°C, and average peak-to-peak amplitude of about 0.09 units of $(E/R)/1000$, which is 18 times the r.m.s. scatter. At the temperatures above 40°C, the amplitude of the oscillation appears to increase, the largest peak being of the order of 0.20 units of $(E/R)/1000$ at about 57°C. The corresponding (dn/dt) values were taken during heating and cooling sequences and in the bottom of Fig. 3, their overall means are plotted as hollow circles. This graph also shows eleven minima between 20°C and 70°C as for $E\eta$.

Discussion

It is seen that in case of the three higher alcohols studied in the above experiments, the clear maxima and minima found in the activation energy, E, have their counterpart in corresponding small maxima and minima in the plots of $-dn/dT$. The detailed comparison of the minima observed in these two quantities is shown for the three alcohols in Table 4a, b, and c.

An examination of this table shows that on the average the minima in $(-dn/dT)$ are 0.1$\pm$0.9°C behind those in E in case of amyl alcohol and 0.6°C$\pm$0.5°C, ahead in case of 1-isoamyl alcohol the mean scatter being $\pm$0.07°C. For butyl alcohol, the difference is again practically zero. Since the observations are taken at one degree intervals, one can hardly determine the individual minima to much closer than 0.7°C. As such, the valid conclusion from these experiments is that the minima in $-dn/dT$ agree with those in E within about $\pm$0.7°C.

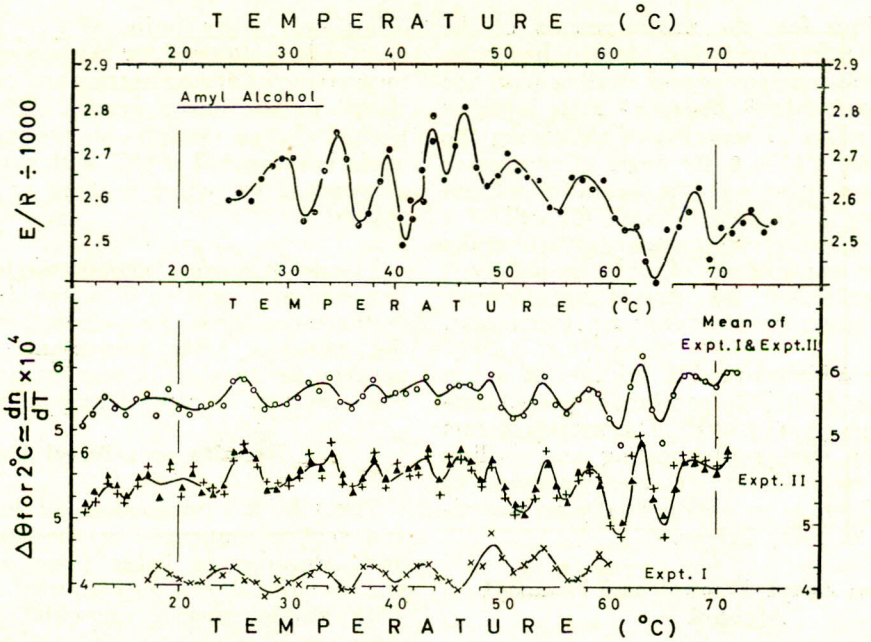

Fig. 1.—Top: Plot of flow activation energy $(E/R) \div 1000$ against temperature for amyl alcohol in the range of 24°C to 76°C, (solid circles), showing a series of maxima and minima with average period of 4.5°C.

Bottom: Graphs of $\Delta\theta$ for $2°C \simeq -(dn/dt) \times 10^4$ in the range of 10°C to 75°C; the means of the two experiment (I and II) by two different workers are shown by hollow circles in the upper graph of this figure. There is a general correspondence between the minima in the two properties.

TABLE 2(a).—MEASURED ACTIVATION ENERGIES $(E/R)/1000$ FOR ISOAMYL ALCOHOL IN THE TEMPERATURE RANGE OF 10°C to 71°C USING $\Delta T = 1°C$.

Mean temp. °C	$(E/R)/1000 = -T^2(\Delta \ln \nu/\Delta T)/1000$ Heating sequence	Cooling sequence	Mean	Mean temp. °C	$(E/R)/1000 = -T^2(\Delta \ln \nu/\Delta T)/1000$ Heating sequence	Cooling sequence	Mean
10.50	2.669±0.004	2.682±0.004	2.675±0.006	39.50	2.631±0.006	2.620±0.006	2.625±0.006
11.50	2.564±0.004	2.559±0.004	2.561±0.003	40.50	2.583±0.006	2.599±0.006	2.591±0.008
12.50	2.560±0.004	2.571±0.004	2.565±0.006	41.50	2.610±0.006	2.601±0.006	2.606±0.004
13.50	2.543±0.004	2.534±0.004	2.638±0.005	42.50	2.615±0.006	2.627±0.006	2.621±0.006
14.50	2.580±0.004	2.571±0.004	2.676±0.004	43.50	2.616±0.006	2.629±0.006	2.622±0.007
15.50	2.533±0.004	2.526±0.004	2.530±0.004	44.50	2.589±0.005	2.580±0.005	2.584±0.005
16.50	2.530±0.004	2.537±0.004	2.634±0.004	45.50	2.583±0.005	2.577±0.005	2.580±0.003
14.50	2.731±0.005	2.720±0.005	2.725±0.006	46.50	2.530±0.005	2.524±0.005	2.526±0.006
15.50	2.534±0.005	2.525±0.005	2.529±0.005	47.50	2.547±0.005	2.534±0.005	2.541±0.007
16.50	2.623±0.005	2.614±0.005	2.618±0.005	48.50	2.628±0.005	2.616±0.005	2.622±0.006
17.50	2.666±0.005	2.678±0.005	2.672±0.006	49.50	2.631±0.005	2.620±0.005	2.625±0.006
18.50	2.582±0.005	2.573±0.005	2.578±0.005	50.50	2.585±0.006	2.602±0.006	2.594±0.009
19.50	2.554±0.004	2.550±0.004	2.552±0.002	51.50	2.553±0.006	2.537±0.006	2.545±0.008
20.50	2.601±0.004	2.588±0.004	2.594±0.007	52.50	2.537±0.006	2.544±0.006	2.540±0.004
21.50	2.629±0.004	2.622±0.004	2.626±0.003	53.50	2.568±0.006	2.569±0.006	2.569±0.001
22.50	2.645±0.004	2.637±0.004	2.641±0.004	54.50	2.583±0.006	2.561±0.006	2.587±0.004
23.50	2.620±0.004	2.629±0.004	2.625±0.005	55.50	2.625±0.007	2.611±0.007	2.618±0.007
24.50	2.582±0.005	2.592±0.005	2.587±0.005	56.50	2.570±0.007	2.581±0.007	2.575±0.006
25.50	2.577±0.005	2.571±0.005	2.574±0.003	57.50	2.555±0.007	2.544±0.007	2.550±0.006
26.50	2.600±0.005	2.609±0.005	2.604±0.005	58.50	2.566±0.007	2.584±0.007	2.575±0.009
27.50	2.657±0.005	2.641±0.005	2.648±0.007	59.50	2.577±0.007	2.558±0.007	2.567±0.009
28.50	2.657±0.005	2.668±0.005	2.662±0.006	60.50	2.604±0.005	2.599±0.005	2.601±0.003
29.50	2.582±0.005	2.567±0.005	2.574±0.008	61.50	2.564±0.005	2.572±0.005	2.568±0.004
30.50	2.550±0.005	2.561±0.005	2.555±0.006	62.50	2.524±0.005	2.533±0.005	2.529±0.005
31.50	2.593±0.005	2.581±0.005	2.587±0.006	63.50	2.551±0.005	2.539±0.005	2.545±0.006
32.50	2.626±0.005	2.515±0.005	2.620±0.006	64.50	2.560±0.005	2.565±0.005	2.563±0.003
33.50	2.542±0.005	2.558±0.005	2.550±0.008	65.50	2.561±0.008	2.546±0.008	2.554±0.008
34.50	2.580±0.005	2.589±0.005	2.584±0.005	66.50	2.580±0.008	2.563±0.008	2.572±0.009
35.50	2.615±0.005	2.627±0.005	2.621±0.006	67.50	2.525±0.008	2.515±0.008	2.520±0.005
36.50	2.621±0.005	2.630±0.005	2.626±0.005	68.50	2.527±0.008	2.541±0.008	2.534±0.007
37.50	2.580±0.006	2.571±0.006	2.575±0.005	69.50	2.538±0.008	2.525±0.008	2.532±0.007
38.50	2.594±0.006	2.607±0.006	2.600±0.007	70.50	2.577±0.008	2.563±0.008	2.570±0.007

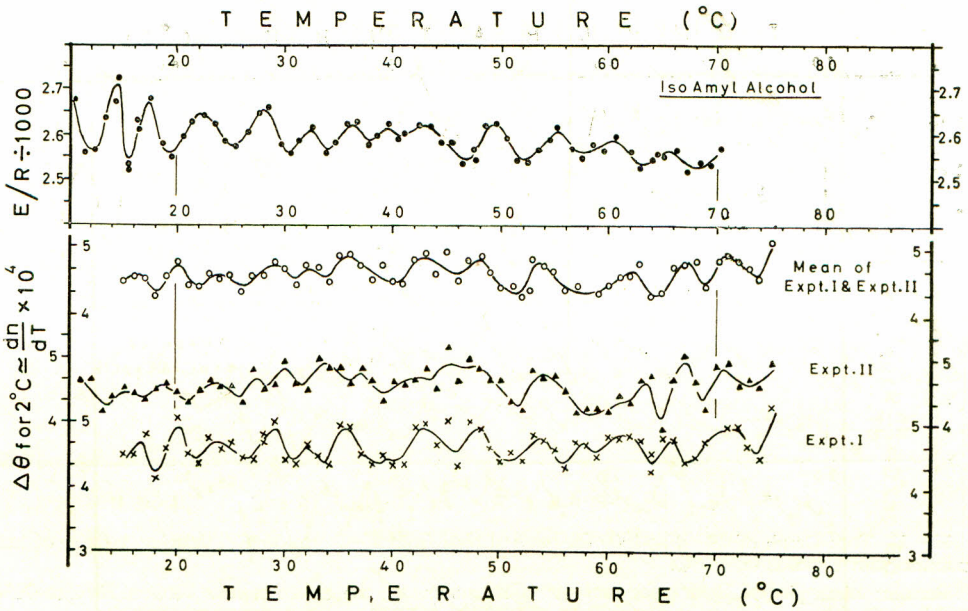

Fig. 2.—Top: Measured activation energy $(E/R) \div 1000$ for isoamyl alcohol from 10°C to 71°C, showing cyclic variations with average period of 5°C. Bottom: Corresponding $-(dn/dt)$ measurements for two sets of experiments (marked Expt. I and Expt. II), together with their means plotted above these as hollow circles. This also exhibits cyclic variation, which corresponds generally with that in E/R.

TABLE 2(b).—MEAN TEMPERATURE AND THE CALCULATED VALUES OF Δ θ (MINUTES) FOR 2°C CHANGE IN TEMPERATURE OF ISOAMYL ALCOHOL USING SODIUM YELLOW LIGHT IN THE RANGE 11°–75°C.

Mean temp. °C	Corrected value of Δθ From Expt. I	Corrected value of Δθ From Expt. II	Mean Δθ (minutes)	Mean temp. °C	Corrected value of Δθ From Expt. I	Corrected value of Δθ From Expt. II	Mean Δθ (minutes)
11.0	4′ 38″	—	4′ 38″	43.0	4′ 58″	4′ 51″	4′ 56″
12.0	4′ 40″	—	4′ 40″	44.0	4′ 40″	4′ 33″	4′ 38″
13.0	4′ 8″	—	4′ 8″	45.0	5′ 0″	5′ 2″	5′ 1″
14.0	4′ 22″	—	4′ 22″	46.0	4′ 21″	4′ 40″	4′ 30″
15.0	4′ 30″	4′ 30″	4′ 30″	47.0	5′ 0″	5′ 0″	5′ 0″
16.0	4′ 30″	4′ 24″	4′ 27″	48.0	4′ 56″	4′ 52″	4′ 54″
17.0	4′ 48″	4′ 20″	4′ 34″	49.0	4′ 36″	4′ 20″	4′ 38″
18.0	4′ 8″	4′ 30″	4′ 19″	50.0	4′ 20	4′ 38″	4′ 29″
91.0	4′ 38″	4′ 34″	4′ 36″	51.0	4′ 31″	4′ 20″	4′ 26″
20.0	4′ 4″	4′ 28″	4′ 46″	52.0	4′ 24″	4′ 11″	4′ 18″
21.0	4′ 30″	4′ 16″	4′ 23″	53.0	4′ 49″	4′ 50″	4′ 50″
22.0	4′ 20″	4′ 28″	4′ 24″	54.0	4′ 45″	4′ 44″	4′ 45″
23.0	4′ 42″	4′ 36″	4′ 39″	55.0	4′ 38″	4′ 44″	4′ 41″
24.0	4′ 34″	4′ 32″	4′ 33″	56.0	4′ 16″	4′ 30″	4′ 23″
25.0	4′ 40″	4′ 33″	4′ 37″	57.0	4′ 42″	4′ 9″	4′ 25″
26.0	4′ 26″	4′ 19″	4′ 22″	58.0	4′ 20″	4′ 16″	4′ 18″
27.0	4′ 25″	4′ 48″	4′ 37″	59.0	4′ 28″	4′ 12″	4′ 20″
28.0	4′ 42″	4′ 30″	4′ 36″	60.0	4′ 48″	4′ 10″	4′ 29″
29.0	4′ 0″	4′ 35″	4′ 48″	61.0	4′ 46″	4′ 27″	4′ 37″
30.0	4′ 24″	4′ 54″	4′ 39″	62.0	4′ 51″	4′ 21″	4′ 36″
31.0	4′ 20″	4′ 37″	4′ 28″	63.0	4′ 44″	4′ 40″	4′ 42″
32.0	4′ 38″	4′ 30″	4′ 34″	64.0	4′ 10″	4′ 38″	4′ 24″
33.0	4′ 28″	4′ 38″	4′ 33″	65.0	4′ 46″	3′ 54″	4′ 20″
34.0	4′ 20″	4′ 30″	4′ 25″	66.0	4′ 45″	4′ 42″	4′ 43″
35.0	4′ 56″	4′ 51″	4′ 55″	67.0	4′ 23″	5′ 4″	4′ 44″
36.0	4′ 57″	4′ 39″	4′ 48″	68.0	4′ 30″	4′ 38″	4′ 34″
37.0	4′ 31″	4′ 51″	4′ 41″	69.0	4′ 43″	4′ 14″	4′ 28″
38.0	4′ 22″	4′ 40″	4′ 31″	70.0	5′ 2″	4′ 44″	4′ 53″
39.0	4′ 30″	4′ 20″	4′ 25″	71.0	4′ 58″	4′ 54″	4′ 56″
40.0	4′ 20″	4′ 36″	4′ 28″	72.0	4′ 59″	4′ 35″	4′ 47″
41.0	4′ 21″	4′ 35″	4′ 28″	73.0	4′ 40″	4′ 42″	4′ 41″
42.0	4′ 55″	4′ 40″	4′ 40″	74.0	4′ 28″	4′ 34″	4′ 31″
				75.0	5′ 18″	4′ 54″	5′ 6″

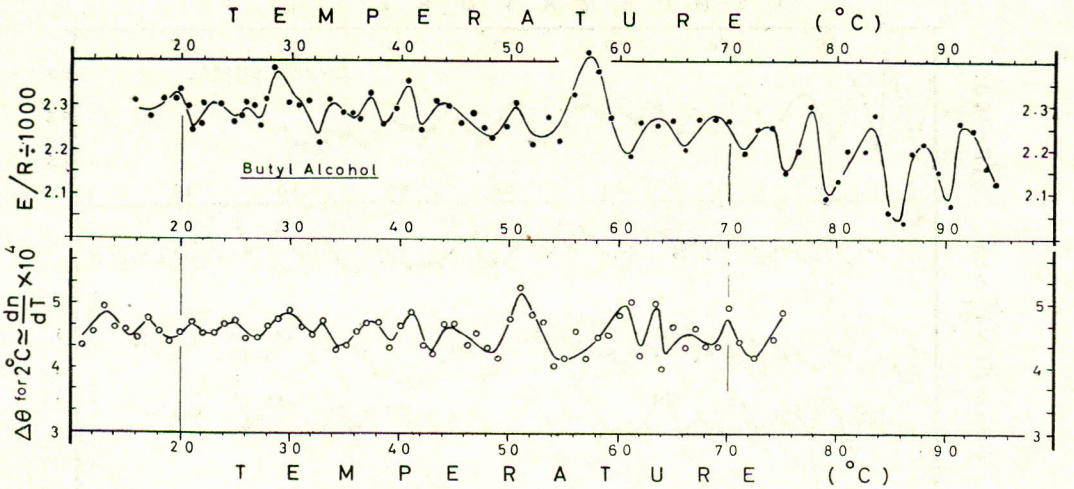

Fig. 3.—Top: Graph of $(E/R) \div 1000$ for butyl alcohol from 15°C to 95°C, showing a series of maxima and minima with a period of 4.5°C.

Bottom: Mean plot of (dn/dt) for two sets of measurements; the eleven minima between 20°C to 70°C for this graph again shows a definite correspondence with those in E/R.

TABLE 3.—MEASURED ACTIVATION ENERGIES $E/R/1000$ FOR n-BUTYL ALCOHOL IN THE RANGE 15°C TO 95°C.

Mean temperature °C	$(E/R) \div 1000 = -T^2(\triangle \ln\nu/\triangle T)/1000$			Mean temperature °C	$(E/R) \div 1000 = -T^2(\triangle \ln\nu/\triangle T)/1000$		
	Heating sequence	Cooling sequence	Mean		Heating sequence	Cooling sequence	Mean
15.50	2.311±0.003	2.300±0.003	2.306±0.006	50.50	2.312±0.006	2.301±0.006	2.306±0.006
17.20	2.281±0.003	2.270±0.003	2.276±0.006	52.00	2.204±0.006	2.219±0.006	2.212±0.008
18.50	2.309±0.003	2.315±0.003	2.312±0.003	53.50	2.271±0.006	2.280±0.006	2.275±0.005
19.50	2.310±0.004	2.321±0.004	2.316±0.005	54.50	2.220±0.006	2.231±0.006	2.226±0.006
19.80	2.340±0.004	2.329±0.004	2.335±0.006	56.00	2.321±0.007	2.330±0.007	2.325±0.005
20.50	2.300±0.004	2.292±0.004	2.296±0.004	57.00	2.430±0.007	2.420±0.007	2.425±0.005
21.00	2.344±0.004	2.231±0.004	2.237±0.007	58.00	2.382±0.006	2.367±0.006	2.375±0.008
21.65	2.257±0.004	2.262±0.004	2.260±0.003	59.50	2.270±0.006	2.279±0.006	2.275±0.005
22.20	2.292±0.004	2.307±0.004	2.300±0.008	61.00	2.183±0.006	2.198±0.006	2.190±0.008
23.50	2.306±0.004	2.297±0.004	2.302±0.005	62.00	2.270±0.006	2.263±0.006	2.266±0.004
24.80	2.269±0.004	2.260±0.004	2.265±0.005	63.50	2.266±0.007	2.255±0.007	2.261±0.006
25.50	2.271±0.004	2.281±0.004	2.276±0.005	64.80	2.263±0.007	2.274±0.007	2.268±0.006
25.80	2.308±0.006	2.315±0.006	2.312±0.004	66.00	2.200±0.007	2.209±0.007	2.205±0.005
26.50	2.292±0.006	2.299±0.006	2.296±0.003	67.50	2.277±0.007	2.263±0.007	2.270±0.007
27.20	2.258±0.006	2.246±0.006	2.252±0.006	68.80	2.262±0.007	2.277±0.007	2.270±0.008
27.80	2.314±0.006	2.307±0.006	2.310±0.004	70.00	2.263±0.007	2.272±0.007	2.268±0.005
28.50	2.380±0.005	2.372±0.005	2.376±0.004	71.50	2.200±0.007	2.191±0.007	2.196±0.005
29.80	2.309±0.005	2.294±0.005	2.302±0.008	72.80	2.243±0.007	2.256±0.007	2.250±0.007
30.50	2.290±0.006	2.301±0.006	2.296±0.006	74.00	2.258±0.006	2.252±0.006	2.255±0.003
31.50	2.312±0.006	2.300±0.006	2.306±0.006	75.25	2.142±0.008	2.159±0.008	2.151±0.009
32.50	2.209±0.006	2.222±0.006	2.216±0.007	76.50	2.197±0.008	2.207±0.008	2.202±0.005
33.50	2.317±0.006	2.308±0.006	2.312±0.005	77.50	2.308±0.008	2.295±0.008	2.302±0.007
34.50	2.280±0.006	2.291±0.006	2.286±0.006	79.00	2.087±0.008	2.102±0.008	2.095±0.008
35.50	2.275±0.006	2.285±0.006	2.280±0.005	80.00	2.133±0.008	2.126±0.008	2.130±0.004
36.50	2.262±0.006	2.267±0.006	2.265±0.003	81.00	2.193±0.008	2.206±0.008	2.200±0.007
37.50	2.320±0.006	2.331±0.006	2.326±0.006	82.50	2.204±0.008	2.197±0.008	2.200±0.004
38.50	2.264±0.007	2.247±0.007	2.256±0.009	83.50	2.280±0.008	2.270±0.008	2.275±0.005
39.50	2.299±0.007	2.288±0.007	2.294±0.006	84.50	2.068±0.007	2.053±0.007	2.060±0.008
40.50	2.356±0.007	2.373±0.007	2.365±0.009	86.00	2.030±0.007	2.044±0.007	2.037±0.007
41.80	2.252±0.007	2.240±0.007	2.246±0.006	86.50	2.186±0.009	2.201±0.009	2.194±0.008
43.50	2.306±0.007	2.317±0.007	2.312±0.005	88.00	2.214±0.009	2.221±0.009	2.218±0.004
44.50	2.309±0.007	2.292±0.007	2.300±0.009	89.25	2.159±0.009	2.244±0.009	2.152±0.008
45.50	2.266±0.007	2.259±0.007	2.262±0.004	90.50	2.069±0.009	2.082±0.009	2.075±0.007
46.50	2.286±0.006	2.279±0.006	2.282±0.004	91.50	2.275±0.010	2.056±0.010	2.265±0.010
47.50	2.246±0.006	2.259±0.006	2.252±0.007	92.50	2.238±0.010	2.252±0.010	2.245±0.007
48.50	2.227±0.006	2.336±0.006	2.232±0.005	93.50	2.169±0.010	2.152±0.010	2.160±0.009
49.50	2.260±0.006	2.252±0.006	2.256±0.004	94.50	2.119±0.010	2.131±0.010	2.125±0.006

TABLE 4.—COMPARISON OF TEMPERATURE AT MINIMA OF $-dn/dt$ AND $(E/R)\div 1000$.

(a) *Amyl alcohol*	..												
$(E/R)\div 1000$	..	23.0	31.5	36.6	40.8	(42.5)	45.0		49.0	55.8	62.0	54.5	70.0
$-dn/dt$	..	23.5	28.2	36.6	39.5		44.5	(48.5)	51.5	56.2	61.5	65.5	70.0
Difference	..	+.5	−3.3	+0.0	−1.3		−0.5		+2.5	+0.4	−0.5	+1.0	0.0
									Mean difference = − 0.1 ± 0.9°C				
(b) *Isoamyl alcohol*													
$(E/R)\div 1000$	..	19.5	25.0	30.2	33.5	(37.5)	40.2		46.5	52.0	57.5	63.0	67.8
$-dn/dt$	..	21.0	26.0	31.0	34.0		40.2		46.0	51.8	58.0	64.2	69.0
Difference	..	+1.5	+1.0	+0.8	+0.5		+0.0		−0.5	−0.2	+0.5	+1.2	+1.2
									Mean difference = + 0.6±0.5°C				
(c) *Butyl alcohol*	..												
$(E/R)\div 1000$	..	21.0	24.8	27.0	32.0	35.5	38.3		41.8	48.0	53.0	61.0	65.8
$-dn/dt$	..	19.0	22.8	27.0	32.0	34.5	39.0		43.0	48.3	54.5	62.0	64.2
Difference	..	−2.0	−2.0	0.0	0.0	−1.0	+0.7		+1.2	+0.3	+1.5	+1.0	1.6
									Mean difference = −0.2° ± 0.9°C				

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