PAKISTAN JOURNAL
OF
SCIENTIFIC AND INDUSTRIAL RESEARCH

Vol. 12, No. 3 April 1970

Pakistan J. Sci. Ind. Res., **12,** 175-180 (1970)

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

Part VI.—Dilatometric Measurements on n-Amyl Alcohol and Isoamyl Alcohol with 1°C Interval and in the Range of 20°C–70°C

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(Received April 30, 1969)

This communication presents refined measurements of coefficient of dilatation, $\beta(=dV/V_0dT)$, with 1°C interval in the range of 10°–70°C, on n-amyl alcohol and isoamyl alcohol. The variations in the value of β with temperature show a roughly sinusoidal component with an average cycle of 4.9°C and 5.3°C and an amplitude of 0 1 units of 3×10^4. Comparison of the previously reported mean temperatures of minima in E/R and $-dn/dt$ (cf. ref. 6) with temperatures at minima in the graphs of coefficient of dilatation show that there is reasonable one-to-one correspondence, the minima in β being ahead of those in E/R and $-dn/dt$ by 2 4°±0.4°C, i.e. almost exactly half a cycle. Thus, the minima in E and $-dn/dt$ correspond within the limits of present accuracy with the maxima in β.

Introduction

The measurements of coefficient of dilatation, β, on ethylene glycol[1] reported in Part I of this series showed a sinusoidal behaviour with an amplitude of 0.1×10^{-4} peak-to-peak, the minima agreeing within ±1°C with the temperatures of the known[2] jumps in flow activation energy, E/R. In Part II of this series, our measurements on pure benzene[3] revealed a one-to-one correspondence between the oscillatory changes in β and E/R, while the temperature derivative of refractive index, $-dn/dT$, appeared to be out of phase by $\pi/2$. In succeeding publications from this laboratory, measurements of coefficient of dilatation on a series of aqueous ethanol solutions[4,5] were reported, and graphs of $\Delta\beta/\Delta T$ were also plotted. It appears that here the jumps of E/R correspond with the minima of $\Delta\beta/\Delta T$ below 33°C, above which temperature the behaviour is not clear.

In the light of the above observations, it was considered worthwhile to look for such anomalies in other liquids as well, by undertaking measurements of refractive index and coefficient of dilatation. In Part V of this series,[6] the measurements of E/R and $-dn/dT$ on n-amyl alcohol, isoamyl alcohol and n-butyl alcohol revealed a probable interrelationship between the two quantities. The present paper reports refined measurements of coefficient of dilatation for n-amyl, and isoamyl alcohol in the range of 10°C 70°C, and a comparison of this data with that on E/R and $-dn/dT$ is made so as to elucidate the manner of their mutual correspondence.

Experimental Details

The method of obtaining the experimental values of coefficient of dilatation, β, was the same as adopted in previously reported work on ethylene glycol. The dilatometer capillary was connected to a compensating bottle placed in the thermostatic bath alongwith the dilatometer bulb. Meniscus height of liquid in the dilatometer capillary was measured, at each temperature, against a standard attached steel scale with an accuracy of ±0.1 mm, and with temperature accuracy of ±0.002°C up to 45°C and ±0.005°C above 45°C after allowing sufficient time (about 1/2 hr) to ensure an equilibrium state to be attained.

Measurements were taken in groups covering successive ranges of 10°C, in case of n-amyl alcohol, where a dilatometer with a conversion factor of 1.71 $(=\pi r^2/V)$ was used, and 5°C with isoamyl alcohol, where another dilatometer was used whose factor was 0.60, r and V being the mean radius of capillary and volume of dilatometer bulb, respectively. These groups were so arranged

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that meniscus level readings at one temperature in the two experiments did *not* correspond to the same position on the capillary length. This ensured smoothing of effects resulting from residual error, if any, remaining after the calibration correction of the capillary or from change of volume, V, with different settings of various groups (as a small portion of liquid was expelled for successive groups at higher temperature and was introduced for readings at lower temperature). The measurements were taken in sets of two experiments, the temperatures of measurements in one experiment being staggered by 0.5°C with respect to the other experiment.

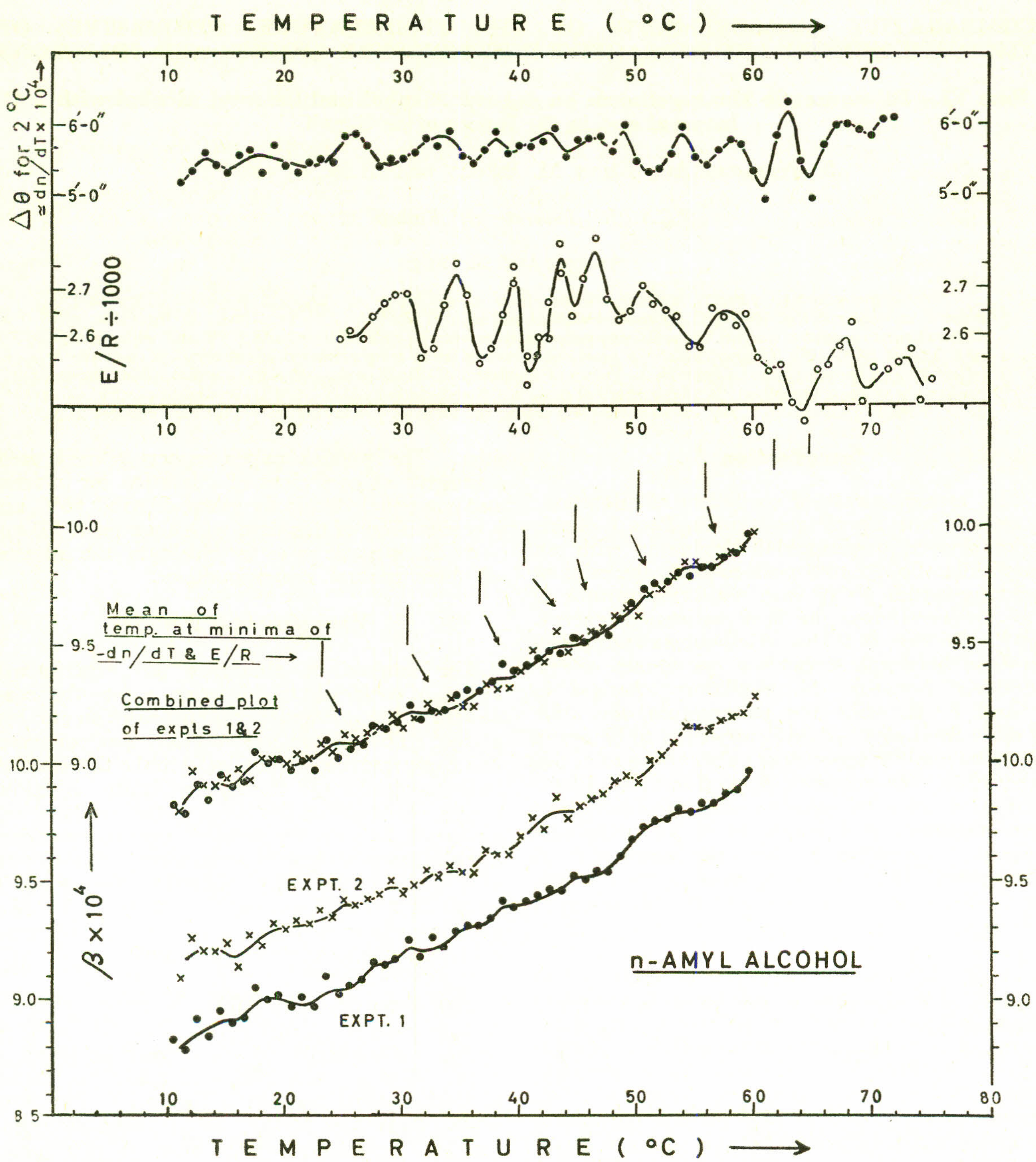

Fig. 1.

Measurements on n-Amyl Alcohol and Isoamyl Alcohol with $\Delta T = 1°C$

Measurements of coefficient of dilatation, β, for n-amyl alcohol (corrected for capillary non-uniformity) were carried out from 10°C to 60°C, in duplicate, at one-degree interval in groups covering 10°C in two sets. Each pair of experiments covered both heating and cooling sequences. The mean values of these duplicate experiments are plotted in Fig. 1 as expt. 1 (solid circles) and expt. 2 (inclined crosses), and tabulated in Table 1, with probable errors calculated giving due weight to uncertainty involved in the measured values of β for the respective pair.* The plots clearly bring forth the undulating character in the temperature variation of coefficient of dilatation. Positions of minima in β compare appreciably with the previously reported measurements on activation energy of viscous flow, E/R and refractive index $-dn/dT$,[6] reproduced in upper half of Fig. 1. The mean graph drawn through the combined plot of expts. 1 and 2 (uppermost graph in the lower part of Fig. 1) again shows a series of maxima and minima observed separately in expts. 1 and 2. The scatter of the measured points around the graph is ± 0.04 units of $\beta \times 10^4$, which compare with the r.m.s. deviations of expts. 1 and 2.

The short vertical lines shown above the combined plot represent the weighted mean of temperatures of the corresponding minima observed in the plots of E/R and $-dn/dT$. By comparing this temperature with the temperature of minima in dilatation, β, a one-to-one correspondence is observed, with the exception of two minima in E/R and $-dn/dT$ at 40.2°C and 44.8°C. These apparently correspond to only one minimum in the combined plot of β, although a one-to-one correspondence is shown in the separate graph of expt. 2. This may be due to smoothing of one minimum corresponding to 44.8°C in E/R and $-dn/dT$, because of the marginal accuracy of measured values of β.

Barring this minimum, a general one-to-one correspondence is evident. Differences in temperature at minima in β and those of weighted mean of E/R and $-dn/dT$ are given in Table 2, which shows that minima in β are on the average ahead of minima in E/R and $-dn/dT$ by $2.8° \pm 1.3°C$.

*The uncertainties quoted in Table 1 for the means of the two sets of experiments are based on the individual uncertainties as well as the differences between the values obtained in set I and set II.

Similar measurements were taken on isoamyl alcohol, using another dilatometer, where the meniscus height change for each degree is thrice that obtained in case of n-amyl alcohol, thus enabling the β values to be obtained with greater accuracy. With the accuracy thus increased, duplicate sets of measurements were not needed. Two experiments were carried out each in groups of 5°C, because liquid expansion in terms of meniscus height for each group corresponded to more or less full length (about 75 cm) of dilatometer capillary. The results are shown in Fig. 2, and compared with E/R and $-dn/dT$ data in Table 2.

Results and Discussion

A clear one-to-one correspondence between the temperatures at minima in E_η and $-dn/dT$ with those in β is evident from the general behaviour of both n-amyl alcohol and isoamyl alcohol. This is indicated in Figs. 1 and 2, by the arrow marks shown above the mean graphs of β, the short vertical lines being the mean temperatures at minima of E_η and $-dn/dT$, the curves for which are reproduced in the upper parts of Figs. 1 and 2.

A comparison of minima in β, E_η and $-dn/dT$ is made in Table 2, and a simple analysis of the differences that are shown in the third row is made in the last column. It is seen that, in case of n-amyl alcohol, the minima in β are ahead of those in E_η and $-dn/dT$ by $2.8°C \pm 1.3°C$ on the average, while two minima at 40.2°C and 44.8°C reported earlier,[6] correspond to only one minimum at 46.6°C in β. This is presumably a consequence of the accumulation of errors of measurements of β in this case. Considering the peak-to-peak amplitude of 0.15 units of $\beta \times 10^4$ as compared with 0.04 units for scatter of measured points around the graph, the oscillating variation of β with temperature appears meaningful. As the displacement of $2.8°C \pm 1.3°C$ is about half of 5.3°C, which is the average cycle of oscillations, the minima in β could be regarded as being out of phase with those of E_η and $-dn/dT$ by half cycle.

In isoamyl alcohol, the same type of correspondence is clearly shown in Fig. 2, and the scatter of measured points around the graph is one half because of greater sensitivity of dilatometer used. The only exceptions are two minima in β at 62.3°C and 66.4°C which correspond to only one minimum in E_η and $-dn/dT$ at 63.6°C. The minima in β are found to be ahead of those in E_η and $-dn/dT$ on the average by $2.0°C \pm 1.2°C$, i.e. again about half a cycle of the average period of $4.9°C \pm 0.5°C$. Summing up the behaviour of

Table 1.—Temperature and Measured Values of Coefficient of Dilatation, β, for n-Amyl Alcohol in the Range of 10°C–60°C for Experiments 1 and 2 Each with Two Sets Alongwith Probable Errors for Each Set and for Mean Values.

Temp. °C	Experiment I: $\beta\times10^4$ Set I	Experiment I: $\beta\times10^4$ Set II	Experiment I: $\beta\times10^4$ Mean	Temp °C	Experiment II: $\beta\times10^4$ Set I	Experiment II: $\beta\times10^4$ Set II	Experiment II: $\beta\times10^4$ Mean
10.5	8.838±0.041	8.817±0.005	8.828±0.025				
11.5	8.776±0.014	8.791±0.034	8.784±0.025	11.0	8.819±0.006	8.762±0.080	8.790±0.051
12.5	8.892±0.026	8.930±0.065	8.911±0.048	12.0	8.846±0.006	8.981±0.016	8.964±0.020
13.5	8.823±0.034	8.854±0.048	8.838±0.044	13.0	8.917±0.024	8.894±0.035	8.906±0.032
14.5	8.978±0.022	8.915±0.057	8.946±0.050	14.0	8.867±0.006	8.933±0.037	8.900±0.035
15.5	8.840±0.050	8.951±0.109	8.896±0.097	15.0	9.024±0.038	8.853±0.038	8.938±0.041
16.5	8.918±0.076	8.917±0.007	8.918±0.042	16.0	8.801±0.142	8.874±0.009	8.838±0.084
17.5	9.030±0.033	9.062±0.043	9.046±0.045	17.0	9.006±0.038	8.934±0.108	8.970±0.081
18.5	9.002±0.026	8.979±0.001	8.990±0.017	18.0	8.981±0.005	8.870±0.044	8.926±0.069
19.5	8.998±0.054	9.027±0.042	9.012±0.050	19.0	9.047±0.067	8.988±0.005	9.018±0.046
20.5	8.993±0.014	8.938±0.031	8.966±0.035	20.0	8.985±0.024	9.013±0.030	8.994±0.028
21.5	9.052±0.025	8.958±0.105	9.005±0.084	21.0	9.048±0.005	9.007±0.023	9.028±0.023
22.5	8.998±0.030	8.924±0.091	8.961±0.041	22.0	9.017±0.073	9.016±0.010	9.016±0.042
23.5	9.061±0.019	9.130±0.070	9.096±0.041	23.0	9.070±0.010	9.084±0.082	9.077±0.046
24.5	9.014±0.006	9.024±0.018	9.017±0.014	24.0	9.058±0.038	9.025±0.024	9.042±0.035
25.5	9.062±0.032	9.048±0.012	9.055±0.023	25.0	9.127±0.023	9.133±0.033	9.120±0.028
26.5	9.132±0.069	9.024±0.005	9.078±0.065	26.0	9.079±0.008	9.118±0.031	9.098±0.028
27.5	9.173±0.025	9.143±0.030	9.158±0 031	27.0	9.088±0.009	9.161±0.025	9.124±0.040
28.5	9.101±0.030	9.183±0.018	9.142±0.047	28.0	9.143±0.048	9.141±0.009	9.142±0.018
29.5	9.199±0.012	9.135±0.023	9.167±0.037	29.0	9.226±0.009	9.177±0.027	9.202±0.033
30.5	9.222±0.063	9.275±0.023	9.248±0.051	30.0	9.125±0.010	9.157±0.034	9.141±0.027
31.5	9.196±0.039	9.154±0 032	9.175±0.041	31.0	9.164±0.010	9.195±0.005	9.180±0.016
32.5	9.278±0.031	9.234±0 009	9.256±0.042	32.0	9.294±0.008	9.202±0.002	9.248±0.048
33.5	9.230±0.043	9.202±0.064	9.216±0.056	33.0	9.209±0.024	9.220±0.021	9.214±0.023
34.5	9.272±0.038	9.304±0.016	9.288±0.025	34.0	9.245±0.016	9.277±0.049	9.261±0.035
35.5	9.281±0.011	9.332±0 039	9.306±0.035	35.0	9.204±0.030	9.268±0.025	9.236±0.042
36.5	9.328±0.001	9.285±0.021	9.306±0.023	36.0	9.223±0.052	9.243±0.042	9.233±0.048
37.5	9.348±0.043	9.332±0.005	9.340±0.025	37.0	9.332±0.009	9.330±0.016	9.331±0.012
38.5	9.428±0.020	9.400±0.009	9.414±0.021	38.0	9.282±0.008	9.332±0.005	9.307±0.025
39.5	9.376±0.035	9.394±0.048	9.385±0.041	39.0	9.412±0.037	9.204±0.030	9.308±0.109
40.5	9.430±0.009	9.378±0.010	9.404±0.025	40.0	9.373±0.059	9.400±0.018	9.386±0.044
41.5	9.484±0.038	9.394±0.057	9.439±0 065	41.0	9.510±0.038	9.426±0.054	9.468±0.062
42.5	9.515±0.037	9.407±0.019	9.461±0.061	42.0	9.452±0.012	9.373±0.034	9.412±0 046
43.5	9.466±0.074	9.450±0.023	9.458±0.049	43.0	9.562±0.005	9.542±0.050	9.552±0.027
44.5	9.498±0.030	9.549±0.058	9.524±0.051	44.0	9.496±0.032	9.428±0.057	9.462±0.045
45.5	9.516±0.008	9.489±0.023	9.502±0.021	45.0	9.510±0.009	9.521±0.072	9.516±0.040
46.5	9.520±0.008	9.552±0.010	9.536±0.018	46.0	9.555±0.009	9.533±0.016	9.544±0.016
47.5	9.518±0.016	9.544±0.005	9.531±0.016	47.0	9.552±0.030	9.579±0.055	9.566±0.044
48.5	9.549±0.021	9.656±0.030	9.602±0.050	48.0	9.656±0.036	9.576±0.005	9.616±0.044
49.5	9.672±0.018	9.675±0.030	9.674±0.024	49.0	9.649±0.014	9.537±0.005	9.643±0.010
50.5	9.724±0.048	9.733±0.056	9.728±0.052	50.0	9.733±0.030	9.586±0.024	9.610±0.059
51.5	9.746±0.009	9.754±0.007	9.750±0.009	51.0	9.708±0.015	9.692±0.068	9.700±0.042
52.5	9.710±0.040	9.804±0.006	9.757±0.052	52.0	9.736±0.052	9.711±0.038	9.724±0.047
53.5	9.846±0.023	9.761±0.030	9.804±0.049	53.0	9.783±0.018	9.772±0.001	9.778±0.010
54.5	9.746±0.038	9.827±0.037	9.786±0.052	54.0	9.858±0.017	9.836±0.043	9.847±0.032
55.5	9.879±0.033	9.770±0.021	9.824±0.060	55.0	9.822±0.009	9.870±0.005	9.846±0.025
56.5	9.826±0.052	9.824±0.008	9.825±0.030	56.0	9.788±0.037	9.862±0.012	9.825±0.044
57.5	9.830±0.030	9.932±0.066	9.866±0.060	57.0	9.859±0.072	9.879±0.071	9.869±0.070
58.5	9.868±0.045	9.900±0.012	9.880±0.034	58.0	9.941±0.001	9.822±0.007	9.886±0.064
59.5	9.892±0.180	10.039±0.018	9.966±0.123	59.0	9.929±0.010	9.870±0.024	9.900±0.034
				60.0	9.923±0.006	10.016±0.021	9.974±0.052

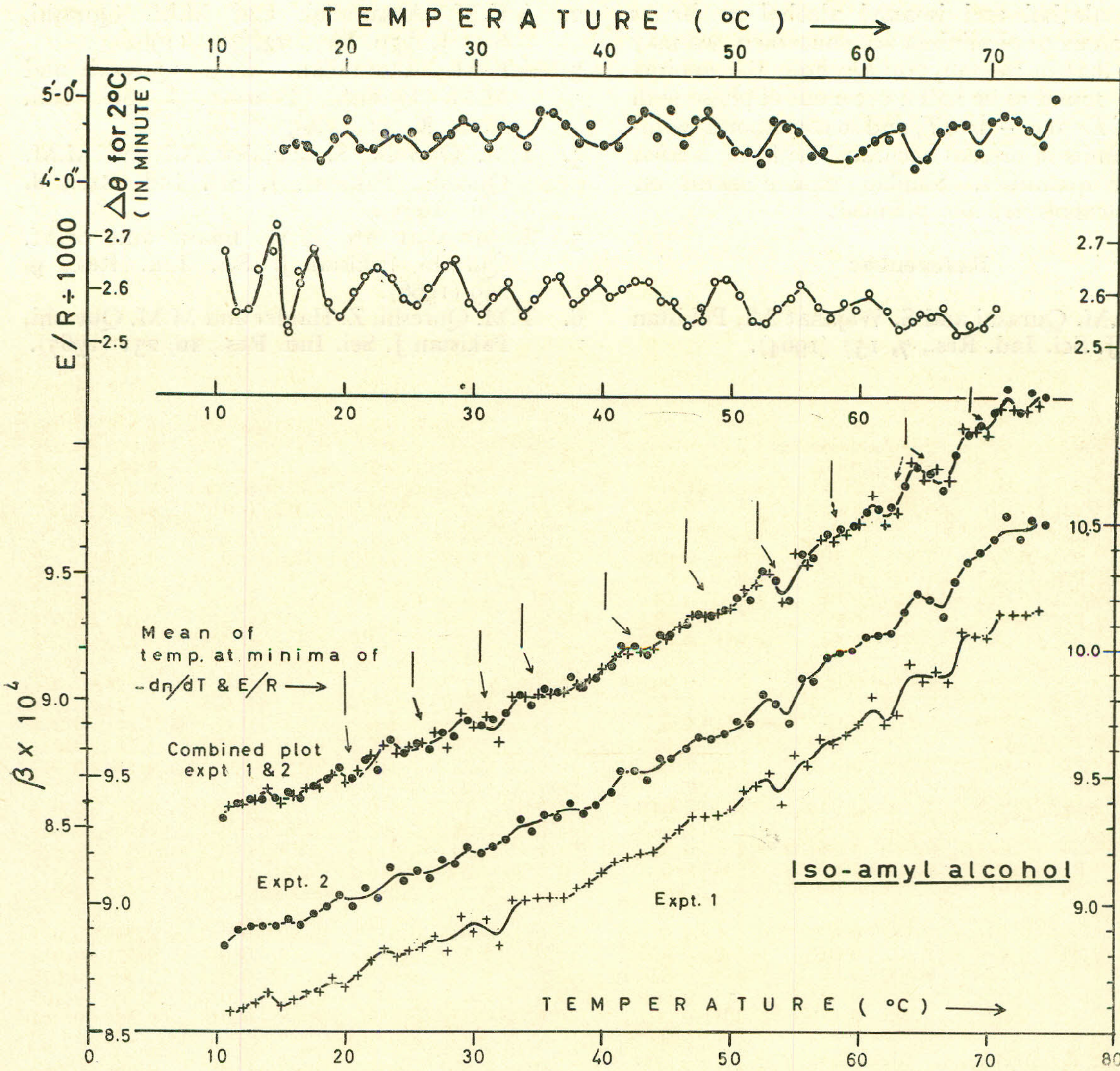

Fig. 2.

TABLE 2.—COMPARISON OF TEMPERATURES AT THE MINIMA OF COEFFICIENT OF DILATATION, β, WITH THOSE AT MINIMA IN E / R AND $-dn/dT$ IN n-AMYL ALCOHOL AND ISOAMYL ALCOHOL IN THE TEMPERATURE RANGE OF 20°C–70C°, RESPECTIVELY.

					n-Amyl alcohol								
Coefficient of dilatation, (a)	25.6	34.0	38.4		46.6		—	52.0	57.0	—	—	—	average cycle: 5.3°C±0.5°C
Mean temperature at minima in E/R and $-dn/dT$ (b)	23.2	29.8	36.6	40.2	(42.5)*	44.8	(48.5)*	50.2	56.0	—	—	—	
Difference (c)	+2.4	+4.2	+3.8		+3.7±1.0		—	+1.8	+1.0	—	—	—	Mean difference: +2.8°C±1.3°C
					Isoamyl alcohol								
(a)	21.2	26.6	31.6	37.5	—	44.0	49.8	54.2	59.0	62.3	66.4	70.0	average cycle: 4.9°C±0.5°C
(b)	20.2	25.5	30.6	33.8	(37.5)*	40.2	46.2	51.9	57.8	63.6		68.4	
(c)	+1.0	+1.0	+1.0	+3.7	—	+3.8	+3.6	+2.3	+1.2	+0.7±2.0		+1.6	Mean difference: +2.0°C±1.2°C

n-amyl alcohol and isoamyl alcohol as far as correspondence of minima are concerned, we may deduce that in monohydric alcohols, the minima of β are found to be half a cycle out of phase with those of $E\eta$ and $-dn/dT$, and so correspond (within the limits of present accuracy) with the *maxima* in these quantities. Similar measurements on other alcohols are also planned.

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