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

Part IV.—The Coefficient of Dilatation and its First Derivative for 9% and 14% Aqueous Ethyl Alcohol Solution

Tayeb M. Qureshi and S. Wajahat Ali

Physics Division, Central, Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

AND

M. M. Qurashi

Defence Science Organization, Ministry of Defence, Government of Pakistan, Karachi

Some accurate dilatometric measurements are reported on two dilute aqueous ethanol solutions, containing 8.7 percent and 13.5 percent (by weight) of ethanol in the temperature range of 20°C. to 50°C. The measurements have been made at intervals of 1°C., using a dilatometer with a very long capillary, with which a reproducibility of the order of 1 percent of β, the coefficient of dilatation, is obtained. Measurements on jumps in activation energy of flow, Eη, are also presented for 13.8 percent aqueous ethanol.

Four separate graphs of β, each based on a separate set of measurements show a series of marked undulations, with regions of nearly constant β, separated by sharp rises in β,. The mean plots of β confirm these features, and the plots of $\Delta\beta/\Delta T \times 10^5$ bring these out even more markedly. The values of $\Delta\beta/\Delta T \times 10^5$ oscillate over a range of about 0.5 for each solution. An examination of the temperatures at the minima of $\Delta\beta/\Delta T$ shows a certain correspondence with the positions of the jumps in E/R observed in the corresponding solutions. This correspondence is exact below 35°C., while above this temparature, the jumps in E/R are 1.2 °C. $\pm$ 0.2°C. ahead of the minima in $\Delta\beta/\Delta T$, and therefore agree with the minima in the cyclic component of β itself, as in the case of ethylene glycol. Further experiments on other solutions are in progress.

Introduction

In part I of this series, some dilatometric measurements on ethylene glycol were reported,[1] and it was shown how the coefficient of dilatation could be measured at intervals of 1°C. to 2°C. and to an accuracy of $\pm 0.1 \times 10^{-5}$. This accuracy readily enabled us to investigate the periodic variations in β of the order of $\pm 1 \times 10^{-5}$, and it was found that most of the minima in β correspond with the jumps in flow activation energy Eη. Since it was previously noticed[2] that aqueous solutions of ethyl alcohol containing 8 to 20 percent alcohol exhibit these energy jumps very markedly and there exists a regular progression for the temperature of these jumps against concentration, [2,3] it was considered of interest to examine some alcohol solutions in this range for possible variations in the coefficient of dilatation. The apparatus used was the same as described in Part I of this series, with the auxiliary Beckmann thermometers for measuring ΔT. The dilatometer capillaries were recalibrated and the mean calibration curve plotted, so as to reduce the outstanding errors till further.

Experiments with 9% Ethyl Alcohol in Water

The solution was prepared by adding a known volume of redistilled rectified spirits to redistilled water, and the alcohol concentration was checked by measuring the viscosity and density of the solution. The dilatometer was filled by evacuating it and then connecting the capillary end to a vessel containing the solution. The small bubble of air remaining in the dilatometer bulb was then expelled by slightly warming the bulb with the capillary dipping in the solution. When the filled dilatometer was placed in position vertically inside the thermostat, the open end of the capillary was protected from the atmosphere by connecting it to a small bottle containing a quantity of the same alcohol solution.

The measurements were made at intervals of $\Delta T = 1°C$. in groups covering successive ranges of 10°C. The thermostat was maintained at each temperature for a period of 30 to 40 minutes to allow a steady state to be reached before taking readings of the level in the dilatometer capillary.

This period was found in previous work[1] on ethylene glycol to be sufficient for ensuring stability to within 0.1 mm. Five to ten observations of the meniscus were then taken to 0.1 mm. against the standard steel scale, spread over a period of ten minutes, so as to cover several "on-off" cycles of the thermostat control. Readings at successive temperatures were taken in this way, until 3/4 length of the capillary had been utilized. For the stronger alcohol solution, it was necessary to remove some of the solution, and then go on to higher temperatures. The values of $\Delta l/\Delta T$ in successive intervals were calculated and corrected for capillary calibration.

This procedure was repeated during cooling at the same temperatures, and the means of the value of $\Delta l/\Delta T$ during heating and cooling were obtained. The experimental data, as well as the overall mean values of $1.39 \times \Delta l/\Delta T = \beta \times 10^4$, for the first experiment on 8.7 percent ethanol solution are given in Table 1(a). The results re plotted

Table 1 (a).—Temperature, Beckmann Reading, Meniscus Level Reading, Change in Meniscus Leval (Δl corrected), Coefficient of Dilatation (β) alongwith its Mean Value of Heating and Cooling Sequence for 8.7% w/w. Ethanol in Water with Measuring Interval of Temperature $\Delta T = 1°C.$, in the Range 20–45°C. (Experiment 1.).

Temperature °C.	Cooling sequence				Heating sequence				Mean $\beta \times 10^4$
	Backmann reading	Meniscus height c.m.	Δl corrected c.m.	$1.39 \times \Delta l/\Delta T \rightleftharpoons \beta \times 10^4$	Beckmann reading	Meniscus height c.m.	Δl corrected	$1.39 \times \Delta l/\Delta T \rightleftharpoons \beta \times 10^4$	
1	2	3	4	5	6	7	8	9	10
20.5	1.187 ± 0.004	18.15	1.67 ± 0.02	2.321	3.019 ± 0.002	18.12	1.66 ± 0.02	2.317	2.319 ± 0.002
	2.187 ± 0.003	19.82			4.015 ± 0.004	19.78			
21.5	2.178 ± 2.003	19.82	1.78 ± 0.02	2.471	4.017 ± 0.003	19.75	1.79 ± 0.02	2.500	2.485 ± 00.14
	3.188 ± 0.003	21.60			5.012 ± 0.005	21.54			
22.5	3.188 ± 0.003	21.60	1.83 ± 0.02	2.540	0.173 ± 0.002	21.47	1.81 ± 0.02	2.513	2.526 ± 0.014
23.5	4.189 ± 0.33	23.44	1.94 ± 0.02	2.699	1.174 ± 0.005	23.29	1.90 ± 0.02	2.628	2.664 ± 0.036
	5.188 ± 0.004	25.39			2.179 ± 0.004	25.20			
24.5	0.064 ± 0.005	25.52	1.98 ± 0.02	2.749	2.179 ± 0.004	25.20	2.01 ± 0.02	2.807	2.778 ± 0.029
25.5	1.065 ± 0.004	27.52	2.06 ± 0.02	2.877	3.174 ± 0.003	27.23	2.05 ± 0.02	2.849	2.863 ± 0.014
26.5	2.060 ± 0.004	29.61	2.21 ± 0.02	3.059	4.174 ± 0.005	29.31	2.16 ± 0.02	2.989	3.024 ± 0.035
	3.064 ± 0.004	31.86			5.178 ± 0.004	31.51			
27.5	3.064 ± 0.004	31.86	2.18 ± 0.02	3.032	0.698 ± 0.002	31.54	2.21 ± 0.02	3.059	3.046 ± 0.014
28.5	4.063 ± 0.002	34.09	2.33 ± 0.02	3.231	1.702 ± 0.002	33.80	2.33 ± 0.02	3.226	3.228 ± 0.003
	5.065 ± 0.002	36.48			2.706 ± 0.005	36.18			
29.5	0.926 ± 0.004	36.52	2.35 ± 0.02	3.276	2.706 ± 0.005	36.18	2.35 ± 0.02	3.263	3.270 ± 0.006
30.5	1.923 ± 0.003	38.93	2.47 ± 0.02	3.436	3.707 ± 0.004	38.59	2.43 ± 0.02	3.363	3.400 ± 0.036
31.5	2.922 ± 0.004	41.46	2.41 ± 0.02	3.363	4.711 ± 0.001	41.08	2.46 ± 0.02	3.422	3.392 ± 0.030
	3.918 ± 0.003	43.92			5.710 ± 0.002	43.59			
32.5	3.918 ± 0.003	43.92	2.60 ± 0.02	3.627	0.782 ± 0.001	0.68	2.55 ± 0.02	3.541	3.584 ± 0.044
	4.914 ± 0.004	45.57			1.783 ± 0.001	3.18			

(*Table 1 (a) Continued*)

1	2	3	4	5	6	7	8	9	10
	0.320±0.000	3.10			1.783±0.001	3.18	2.61±0.02	3.641	3.634±0.007
33.5			2.61±0.02	3.627					
	1.320±0.002	5.66			2.779±0.002	5.74	2.65±0.02	3.683	3.697±0.014
34.5			2.67±0.02	3.711					
	2.320±0.002	8.28			3.779±0.001	8.43	2.77±0.02	3.841	3.838±0.003
35.5			2.76±0.02	3.836					
	3.320±0.002	11.00			4.781±0.001	11.07	2.80±0.02	3.887	3.899±0.012
36.5			2.82±0.02	3.911					
	4.322±0.004	13.78			5.782±0.002	13.84			
	4.322±0.004	13.78			0.774±0.003	13.90			
37.5			2.85±0.02	3.965			2.81±0.02	3.875	3.920±0.045
	5.321±0.003	16.60			1.782±0.002	16.69			
	0.232±0.002	16.74			1.782±0.002	16.69			
38.5			2.79±0.02	3.886			2.88±0.02	4.019	3.952±0.068
	1.230±0.000	19.52			2.778±0.002	19.56			
39.5			2.92±0.02	4.054			2.88±0.02	4.022	4.038±0.016
	2.231±0.001	22.44			3.773±0.003	22.44			
40.5			3.03±0.02	4.228			3.02±0.02	4.168	4.198±0.030
	3.227±0.003	25.49			4.780±0.001	25.48			
41.5			3.03±0.02	4.182			3.06±0.02	4.336	4.259±0.077
	4.234±0.003	28.55			5.780±0.002	28.57			
	4.234±0.003	28.55			0.479±0.002	28.66			
42.5			3.18±0.02	4.416			3.07±0.02	4.322	4.369±0.047
	5.235±0.002	31.78			1.466±0.004	31.78			
	0.367±0.002	31.84			1.466±0.004	31.78			
43.5			3.17±0.02	4.410			3.24±0.02	4.481	4.445±0.036
	1.366±0.004	35.08			2.471±0.002	35.09			
44.5			3.29±0.02	4.550			3.30±0.02	4.568	4.559±0.009
	2.371±0.004	38.45			3.475±0.002	38.47			
45.5			3.32±0.02	4.618			3.27±0.02	4.527	4.572±0.045
	3.370±0.006	41.85			4.479±0.002	41.82			

Standard deviation. $= \pm 0.03$

as Expt. I for heating (triangles) and cooling (crosses) separately in Fig. 1 (top), together with the mean (hollow circles), the three graphs being successively displaced upwards by 0.3 units of $\beta \times 10^4$, and the vertical scale marked for the mean graph. The reproducibility of the measurements is seen to be of the order of ± 0.02 unit of $\beta \times 10^4$ (which compares with the estimated standard deviations of 0.02 in Table 1(a), and the mean graph particularly shows a number of regions of practically constant β, separated by relatively sharp increases in β. This is brought out more explicitly in the corresponding graph of $\Delta\beta/\Delta T \times 10^5$, (cf. Table 1(b)) marked Expt. I (hollow circles) in the lower half of Fig. 1.

In order to confirm these striking features, the whole series of measurements was repeated with the temperatures staggered by 1/2 degree throughout; also the position of the liquid meniscus was shifted by 20 cm. so as to use a different portion of the dilatometer capillary for any particular tem-

perature range. A synopsis of the results is given in Table 1(b), and the mean values of $\beta \times 10^4$ for this set are plotted as solid circles in the uppermost graph of Fig. 1, along with the values from the previous set (hollow circles). The two sets of data are seen to be consistent within the previously estimated limits of error, and the combined graph clearly brings out the features of successive regions of nearly constant β.

The values of $\Delta\beta/\Delta T \times 10^5$ calculated from the second set of measurements are plotted as solid circles in the lowermost graph in Fig. 1, while the combined plot of $\Delta\beta/\Delta T \times 10^5$ for Expt. I and II is shown above this. This combined plot exhibits a series of maxima and minima with a period of nearly 4.0°C., and the short vertical arrows inserted above this plot indicate the temperatures at which jumps in activation energy E/R (and minima of $-dn/dT$) are observed in this ethanol solution, as estimated from previously reported experiments by Qureshi, Haider and
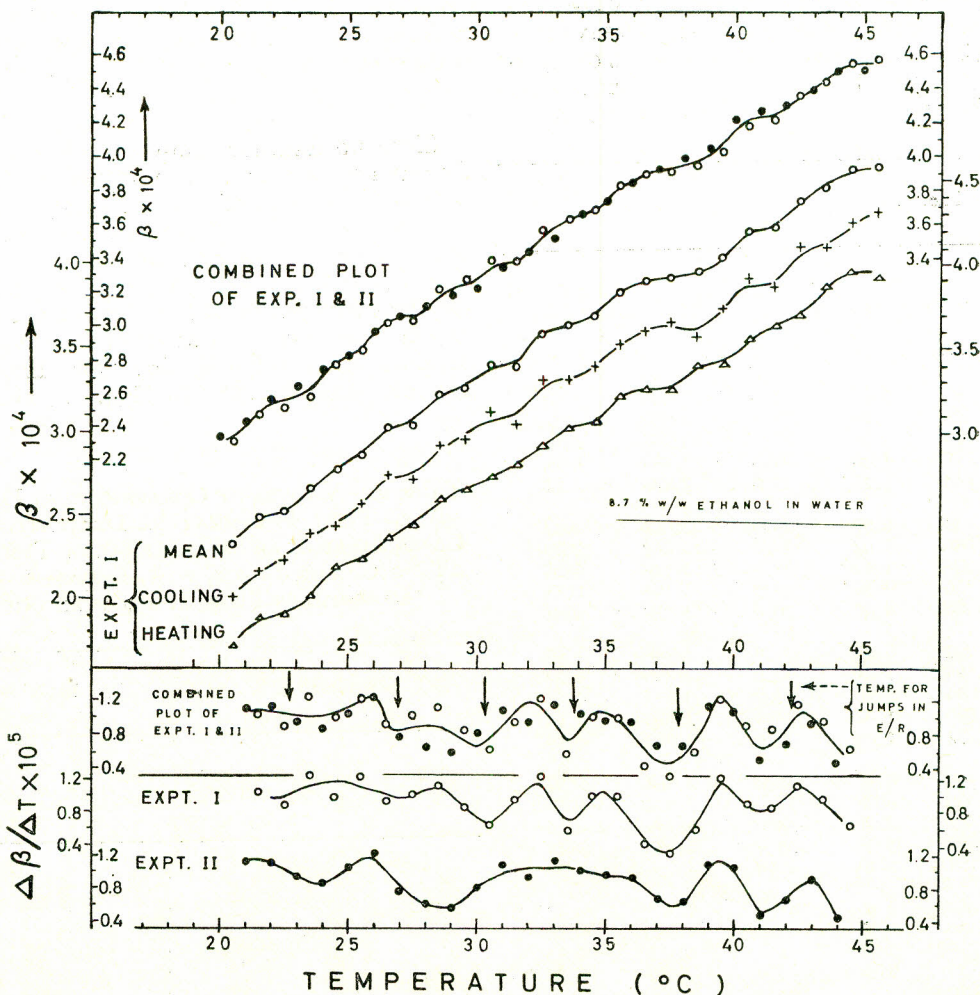
Fig. 1.—Graphs of the coefficient of dilatation, β, and of Δβ/ΔT against temperature for 8.7% aqueous ethanol solution.

The upper part of the figure shows the first plots of $\beta \times 10^4$ during the heating and cooling sequences (triangles and hollow circles, respectively), together with the mean for Expt. I (hollow circles) displaced upward successively by 0.3 units of $\beta \times 10^4$, while the topmost graph (for which the vertical scale is marked) is a combined plot of the mean data for Expt. II (solid circles) and Expt. I (hollow circles).   The features of successive regions of nearly   constant β separated by sharp rise in β are observed.

The lower part of the figure shows the corresponding graphs of $\Delta\beta/\Delta T \times 10^5$ for Expt. I (hollow circles), Expt. II (solid circles) and the combined plot with solid and hollow circles.   The short vertical arrows above this combined plot indicate the temperatures at which the sharp jumps in $E\eta$, occur in this particular solution, and are seen to agree with the minima of Δβ/ΔT below 35°C.

Qurashi.[3],[4] It is seen that below 35°C. these arrows agree within ±0.6°C. with the minima of Δβ/ΔT, while above this temperature the arrows are apparently about 1°C. *ahead* of the minima. These findings differ considerably from those in case of ethylene glycol, where all the jumps in E/R were found to coincide with the minima in β itself.

Measurements with 13.5% Aqueous Ethanol

It was therefore considered worthwhile to examine another concentration of ethanol. Accordingly, a 13.5 percent (w/w) aqueous solution of ethanol was prepared, and after the usual verification of its concentration, the dilatometer was filled with this

Table 1 (b).—Values of Coefficient of Dilatation (β), its First Temperature Derivative ($\Delta\beta/\Delta T$) Calculated over an Interval of Temperature $\Delta T = 2°C$. for 8.7% w/w. Ethanol in Water (Experiment I and II Plotted in Fig. 1.)

Experiment I			Experiment II		
Temp. °C.	$\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ with $\Delta T = 2°C$.	Temp. °C.	$\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ with $\Delta T = 2°C$.
20.5	2.319		20.0	2.345	
21.5	2.485	1.04	21.0	2.449	1.13
22.5	2.526	0.90	22.0	2.571	1.10
23.5	2.664	1.26	23.0	2.668	0.94
24.5	2.778	1.00	24.0	2.758	0.84
25.5	2.863	1.23	25.0	2.836	1.05
26.5	3.024	0.92	26.0	2.968	1.13
27.5	3.046	1.02	27.0	3.062	0.74
28.5	3.228	1.12	28.0	3.116	0.57
29.5	3.270	0.86	29.0	3.176	0.65
30.5	3.400	0.61	30.0	3.228	0.86
31.5	3.392	0.92	31.0	3.348	1.09
32.5	3.584	1.21	32.0	3.446	0.94
33.5	3.634	0.56	33.0	3.537	1.14
34.5	3.697	1.02	34.0	3.674	1.04
35.5	3.838	1.01	35.0	3.744	0.95
36.5	3.899	0.41	36.0	3.864	0.94
37.5	3.920	0.26	37.0	3.932	0.68
38.5	3.952	0.59	38.0	3.999	0.65
39.5	4.038	1.23	39.0	4.062	1.14
40.5	4.198	1.10	40.0	4.228	1.06
41.5	4.259	0.86	41.0	4.274	0.42
42.5	4.369	0.93	42.0	4.321	0.68
43.5	4.445	0.95	43.0	4.411	0.92
44.5	4.559	0.64	44.0	4.504	0.50
45.5	4.572		45.0	4.500	

solution and the two series of measurements carried out essentially as for the previous solution. The results are summarised in Table 2, and the plots are shown in Fig. 2, the solid circles being the mean of heating and cooling for Expt. II and hollow circles for Expt. I.

These graphs show the same essential characteristics of regions of almost constant β separated by sharp rise in β, with the difference that these rises are now somewhat less steep than with the previous more dilute solution. The graphs of $\Delta\beta/\Delta T \times 10^5$ are also remarkable for the good reproducibility and small scatter, particularly in the combined plot for the two experiments on this

solution. The mean period between successive minima is 4.4°C. which is to be compared with the value of 4.0°C. for the 8.7 percent ethanol solution.

Since no data for jumps in E/R was available between 11 percent and 20 percent ethanol, therefore measurements of activation energy were also carried out on a 13.8 percent ethanol solution, and the results obtained are given in Table 3. Fig. 3 is a plot of this data, and the temperatures for the sharp jumps of E/R estimated from this graph are indicated as short vertical arrows against the combined plot (for Expt. I and II) of $\Delta\beta/\Delta T \times 10^5$ in Fig. 2. Here again

Table 2.—Values of Coefficient of Dilatation (β), its First Temperature Derivative ($\Delta\beta/\Delta T$) Calculated over an Interval of Temperature $\Delta T = 2°C$. for 13.5% w/w. Ethanol in Water (Experiment I and II Plotted in Fig. 2).

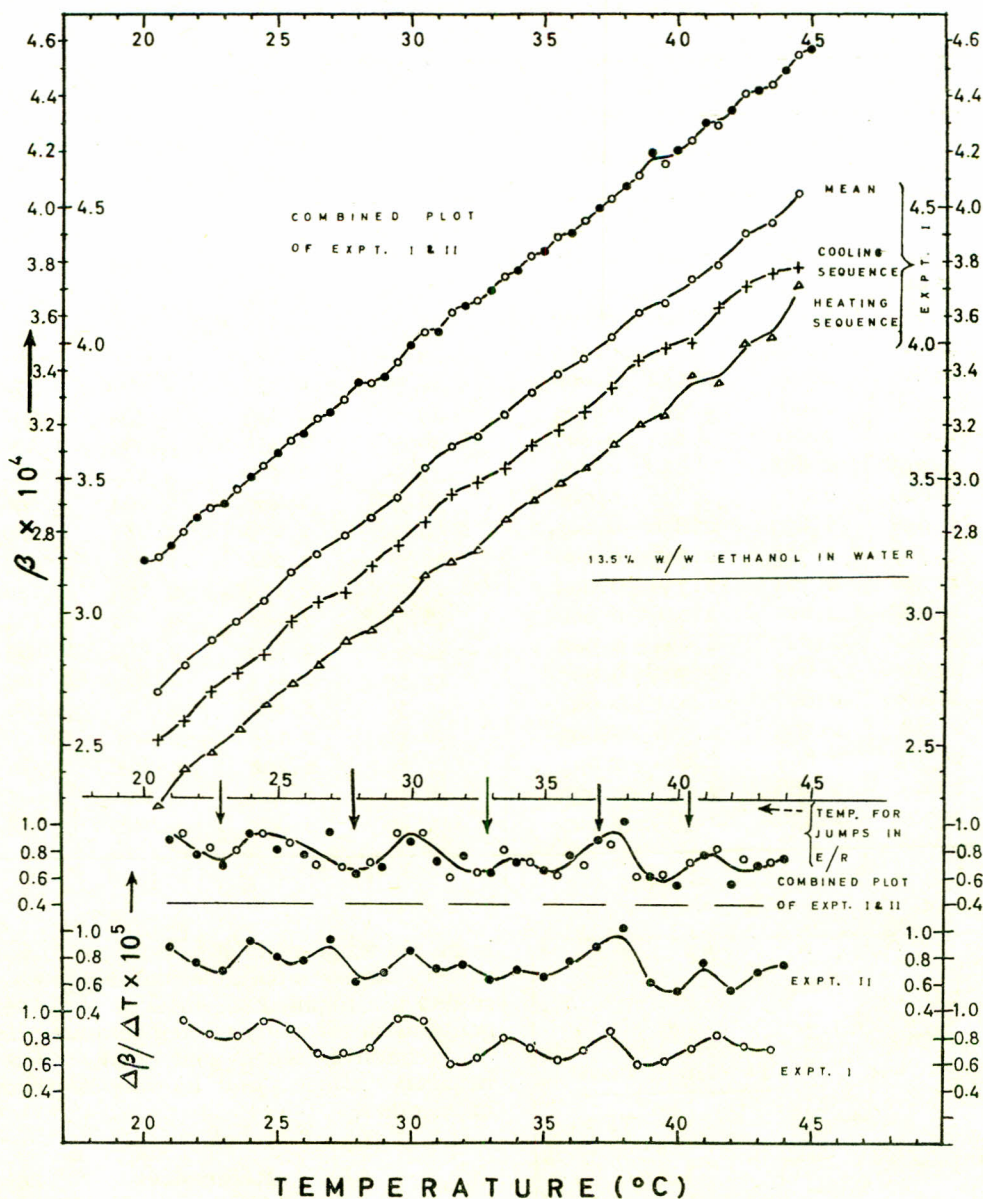| Experiment I			Experiment II		
Temp. °C.	$\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ with $\Delta T = 2°C$.	Temp. °C.	$\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ with $\Delta T = 2°C$.
20.5	2.700		20.0	2.690	
21.5	2.800	0.93	21.0	2.752	0.88
22.5	2.886	0.82	22.0	2.867	0.77
23.5	2.965	0.80	23.0	2.906	0.70
24.5	3.046	0.92	24.0	3.006	0.93
25.5	3.148	0.86	25.0	3.092	0.82
26.5	3.219	0.69	26.0	3.171	0.78
27.5	3.286	0.68	27.0	3.248	0.94
28.5	3.355	0.72	28.0	3.358	0.62
29.5	3.430	0.94	29.0	3.371	0.69
30.5	3.543	0.93	30.0	3.496	0.86
31.5	3.616	0.60	31.0	3.542	0.72
32.5	3.662	0.64	32.0	3.640	0.76
33.5	3.744	0.80	33.0	3.694	0.64
34.5	3.822	0.72	34.0	3.769	0.72
35.5	3.888	0.62	35.0	3.839	0.66
36.5	3.946	0.70	36.0	3.900	0.78
37.5	4.028	0.85	37.0	3.994	0.89
38.5	4.116	0.60	38.0	4.078	1.03
39.5	4.148	0.63	39.0	4.200	0.61
40.5	4.242	0.72	40.0	4.200	0.54
41.5	4.292	0.82	41.0	4.308	0.77
42.5	4.406	0.74	42.0	4.354	0.55
43.5	4.439	0.72	43.0	4.418	0.69
44.5	4.549		44.0	4.492	0.74
			45.0	4.566	

Fig. 2.—Graphs of the coefficient of dilatation, β and of Δβ/ΔT against temperature for 13.5% aqueous ethanol solution. The symbols used are as in Fig. 1 for the more dilute solution; the upper part of the figure shows the plots for $\beta \times 10^4$, while the lower part is for $\Delta\beta \times \Delta T \times 10^5$, and the short vertical arrows indicate the temperatures for the jumps in Eη found from Fig. 3.

these arrows coincide with the (three) minima below 35°C., but are about 1.5°C. ahead of the corresponding minima at temperatures above 35°C.

Discussion

Thus, it may be concluded that below 35°C., the minima in Δβ/ΔT coincide with the jumps in E/R for the same ethanol solution. Above this temperature, the jumps in E/R are 1.2°±0.2°C. ahead of the minima. Since this difference corresponds to 1/4 of a full period of 4.2°±0.2°C., therefore we may deduce that, above 35°C., the jumps in E/R agree with the minima in the cyclic component of β itself, rather than Δβ/ΔT; this state of affairs *agrees with* that previously found[1] in the

Table 3.—Measured Activation Energies (E/R ÷ 1000) for 13.8% w/w Dilute Aqueous Ethanol in the Range of 8-50° C., Using Temperature Interval $\Delta T = 1°C$.

| Mean temperature (°C.)	$E/R \div 1000 = -(T^2 \Delta \ln \nu / \Delta T)/1000$			Temperature (°C.)	$E/R \div 1000 = -(T^2 \Delta \ln \nu / \Delta T)/1000$		
	Heating sequence	Cooling sequence	Overall mean		Heating sequence	Cooling sequence	Overall mean
8.50	3.030	3.041	3.036 ± 0.006	29.50	2.487	2.502	2.494 ± 0.007
9.50	3.014	3.000	3.007 ± 0.007	30.50	2.492	2.498	2.495 ± 0.003
10.50	3.021	3.030	3.026 ± 0.005	31.50	2.472	2.477	2.474 ± 0.003
11.50	3.003	3.017	3.010 ± 0.007	32.50	2.471	2.479	2.475 ± 0.004
12.50	3.029	3.020	3.024 ± 0.005	33.50	2.365	2.357	2.361 ± 0.004
13.50	2.906	2.917	2.912 ± 0.006	34.50	2.375	2.369	2.372 ± 0.003
14.50	2.910	2.901	2.906 ± 0.004	35.50	2.346	2.355	2.350 ± 0.005
15.50	2.832	2.818	2.825 ± 0.007	36.50	2.377	2.364	2.370 ± 0.007
16.50	2.833	2.828	2.830 ± 0.003	37.50	2.300	2.282	2.291 ± 0.009
17.50	2.828	2.813	2.820 ± 0.008	38.50	2.297	2.294	2.296 ± 0.002
18.50	2.838	2.833	2.836 ± 0.003	39.50	2.276	2.285	2.280 ± 0.005
19.50	2.717	2.729	2.723 ± 0.006	40.50	2.288	2.301	2.294 ± 0.006
20.50	2.738	2.721	2.730 ± 0.009	41.50	2.175	2.166	2.170 ± 0.005
21.50	2.010	2.021	2.016 ± 0.006	42.50	2.182	2.168	2.175 ± 0.007
22.50	2.042	2.027	2.034 ± 0.008	43.50	2.163	2.175	2.169 ± 0.006
23.50	2.588	2.602	2.595 ± 0.007	44.50	2.173	2.163	2.168 ± 0.005
24.50	2.615	2.607	2.611 ± 0.004	45.50	2.178	2.182	2.180 ± 04002
25.50	2.592	2.599	2.596 ± 0.003	46.50	2.115	2.104	2.110 ± 0.006
26.50	2.597	2.604	2.600 ± 0.004	47.50	2.109	2.122	2.116 ± 0.007
27.50	2.601	2.588	2.594 ± 0.006	48.50	2.108	2.100	2.104 ± 0.004
28.50	2.500	2.490	2.495 ± 0.005	49.50	2.095	2.102	2.098 ± 0.004
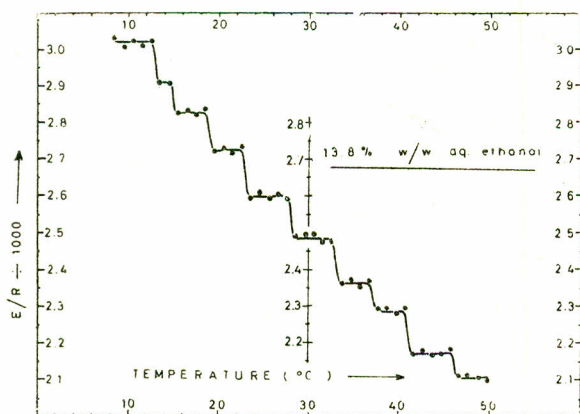
Fig. 3.—Graph of activation energy of viscous flow $E\eta$ measured for 13.8% aqueous ethanol solution with a measuring interval $\Delta T = 1°C$. The short vertical lines connecting successive regions of constant $E\eta$ show the sharp jumps.

case of *ethylene glycol*. We may therefore conjecture that aqueous ethanol solutions behave in an abnormal manner below 35°C., possibly due to very strong inter-molecular binding. Further studies are planned to elucidate these points, together with the study of temperature derivative of refractive index and with reference to benzene,[5] where β and $E\eta$ vary in phase with each other.

References

1. M. M. Qurashi and S. Wajahat Ali, Pakistan J. Sci. Ind. Res., **7,** 157 (1964).
2. M.M. Qurashi and A.K.M. Ahsanullah, Proc. Roy. Soc., **285, A,** 480 (1965).
3. Z. Haider and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **8,** 103 (1965).
4. T.M. Qureshi, Z. Haider and M.M. Qurashi, Pakistan J. Sci. Ind. Res. (in press).
5. A.K.M. Ahsanullah, T.M. Qureshi and M.M. Qurashi, Pakistan J. Sci. Ind. Res., **8,** 11 (1965).