TEMPERATURE DERIVATIVES OF VISCOSITY, DENSITY AND REFRACTIVE INDEX FOR THE WATER-ETHANOL SYSTEM

Part III.—Measurement of Coefficient Dilatation and its Temperature Derivative for 6% to 14% Aqueous Ethanol and their Correlation with Jumps in Flow Activation Energy

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The present communication presents measurements of coefficient of dilatations, β, at temperature interval of $\Delta T = 1°C$. and temperature derivative, $\Delta\beta/\Delta T$ on 5.8% and 10.4% (by weight) aqueous ethanol in the range of 20°C to 45°C Mean graphs of measured values of $\beta \times 10^4$ show good reproducibility of the order of ± 0.015 units of $\beta \times 10^4$

Periodic features in the graphs of β and $\Delta\beta/\Delta T$ are observed with average period of $4°C \pm 0.5°C$ (5.8%) and $5°C \pm 0.9°C$ (10.4%), which is compared with the previous results on 8.7% and 13.5% aqueous ethanol. The amplitude of the oscillations in $\Delta\beta/\Delta T$ apparently decrease progressively with the increase of ethanol concentrations. Below 33°C, the minima of $\Delta\beta/\Delta T$ roughly correspond with $E\eta$ jumps, and apparently show a shift of 0.12°C with respect to $E\eta$ jumps for every 1% change in ethanol concentration. This would fit in the analysis of standard data on density of water (Qurashi, 1963).

Above 33°C the behaviour is complex, but at a lower ethanol concentration it seems to follow the behaviour below 33°C.

Introduction

In an earlier paper, some dilatometric measurements on ethylene glycol[1] using a long calibrated dilatometer were reported, and an accuracy of $\pm 0.1 \times 10^{-5}$ in the value of coefficient of dilatation, β, was attained. This enabled the authors to investigate the periodic variations in β, and it was found that generally the minima in β correspond with the jumps previously found in flow activation energy $E\eta$. Certain similar correlations were obtained between activation energy of viscous flow, refractive index (n) and coefficient of dilatation of water, [4,3] and in benzene [5] the maxima of $d\eta/dT$ appeared to be one-quarter of a period out of phase. Accurate measurements on the activation energy on several solutions in the range of 0%—11% w/w aqueous ethanol first indicated the presence of a regular progression for the temperatures of the jumps against ethanol concentration.[6,7] Subsequent measurements on dilatation of aqueous ethanol solution[8] of 8.7% and 13.5% and activation energy measurements at concentration intervals of 0.9% ethanol have suggested that these ethanol solutions show a number of interesting anomalies.[9] Thus, a one-to-one correspondence between the energy jumps and minima of $d\beta/dT$ is valid up to about 35°C, and there is a shift of about a quarter period above this temperature. The present communication presents dilatation measurements on two more concentrations, namely 5.8% and 10.4% of aqueous ethanol in the range 20° to 45°C, and the values for four solutions from 5.8% to 13.5% ethanol are compared with the energy jumps observed in the corresponding solutions.

Experiments with 5.8% w/w Aqueous Ethanol

The solution was prepared by adding a known volume of absolute alcohol to thrice distilled water, and then verifying its concentration (in terms of weight by weight) by two different methods, i.e., density and viscosity measurement. The solution was then filled in the dilatometer with the usual precautions, as described for the previously re-

ported experiments:[8] the dilatometer was first cleaned, evacuated and then the solution was allowed to fill in, the few ml. of air that remained being subsequently expelled by alternate heating and cooling with the whole system kept enclosed. The dilatometer was fixed vertically in the thermostat with temperature controlled to $\pm 0.005°$C. on the average. A compensating bottle containing the same solution was also placed in the thermostat and connected to the dilatometer capillary to avoid change in ethanol concentration. Readings of the height of the solution meniscus level in the capillary were taken after equilibrium to 0.1 mm. with the help of a standard meter scale attached with the capillary. A period of 30 to 40 minutes, as found in the previous work, was allowed before every reading so that the liquid level in the capillary attains a steady state, and 5 to 10 repeated readings were taken for each temperature. The measurements were taken at intervals of $\Delta T = 1°$C in two successive groups, less than 3/4 of the total capillary length being used for each group. Each group was repeated with heating and cooling sequences. A quantity of solution equivalent to the expansion for about 12°C was expelled from the dilatometer for measurements at successively higher temperatures.

The values of coefficient of dilatation, β, for both cooling and heating sequences obtained after applying capillary correction were calculated using the equation $\beta = 1.39 \, \Delta l / \Delta T$, where 1.39 is the constant factor equal to $\pi r^2/V$ for the dilatometer used, r being the radius of the capillary and V the volume of the bulb of the dilatometer. The means for the heating and cooling sequences are given in Table 1(a), and plotted in Fig. 1 as solid

TABLE 1.—Experimental Values of Coefficient of Dilatation, β, and of $\Delta\beta/\Delta T$ for 5.8% w/w and 10.4% w/w Aqueous Ethanol Solution in the Range 20°C to 45°C.

	Experiment I			Experiment II	
Temperature °C	Mean value of $\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ (with $\Delta T = 2°$C)	Temperature °C	Mean values of $\beta \times 10^4$	$\Delta\beta/\Delta T \times 10^5$ (with $\Delta T = 2°$C)
1	2	3	4	5	6

(a) 5.8% w/w Aqueous Ethanol

20.0	2.090±0.005		20.5	2.093±0.003	
21.0	2.195±0.005	1.00	21.5	2.170±0.001	1.17
22.0	2.292±0.005	0.90	22.5	2.327±0.011	1.04
23.0	2.378±0.002	0.66	23.5	2.378±0.003	0.89
24.0	2.427±0.002	0.93	24.5	2.505±0.012	1.10
25.0	2.566±0.009	1.11	25.5	2.597±0.007	1.18

Continued

Table 1 continued

1	2	3	4	5	6
26.0	2.649±0.000	0.73	26.5	2.740±0.002	1.16
27.0	2.712±0.002	1.04	27.5	2.829±0.005	1.03
28.0	2.856±0.007	0.96	28.5	2.946±0.022	0.94
29.0	2.904±0.008	1.06	29.5	3.017±0.029	0.53
30.0	3.068±0.020	1.36	30.5	3.052±0.050	1.29
31.0	3.176±0.011	0.92	31.5	3.265±0.066	1.16
32.0	3.252±0.014	0.98	32.5	3.283±0.000	0.52
33.0	3.372±0.002	0.88	33.5	3.368±0.002	1.02
34.0	3.428±0.005	0.75	34.5	3.488±0.013	1.05
35.0	3.522±0.007	0.74	35.5	3.578±0.010	0.59
36.0	3.577±0.016	0.72	36.5	3.606±0.005	0.28
37.0	3.666±0.018	0.98	37.5	3.633±0.019	0.60
38.0	3.774±0.009	0.94	38.5	3.727±0.002	0.96
39.0	3.854±0.014	0.64	39.5	3.826±0.042	0.99
40.0	3.903±0.011	0.30	40.5	3.925±0.008	0.88
41.0	3.914±0.014	0.54	41.5	4.002±0.002	1.04
42.0	4.010±0.002	0.99	42.5	4.134±0.020	1.14
43.0	4.112±0.005	0.68	43.5	4.229±0.001	0.65
44.0	4.146±0.004	0.92	44.5	4.264±0.004	
45.0	4.296±0.013				

Standard deviation $= \pm 0.010$ Standard deviation $= \pm 0.015$

(b) 10.4% w/w Aqueous Ethanol.

19.5	2.564±0.008				
20.5	2.675±0.018	0.96	20.0	2.606±0.002	
21.5	2.770±0.006	1.16	21.0	2.727±0.005	1.16
22.5	2.906±0.020	0.98	22.0	2.838±0.003	0.98
23.5	2.966±0.010	0.91	23.0	2.923±0.006	0.90
24.5	3.088±0.010	0.81	24.0	3.018±0.005	1.07
25.5	3.128±0.004	1.12	25.0	3.137±0.005	0.98
26.5	3.312±0.010	1.11	26.0	3.214±0.006	0.88
27.5	3.350±0.001	0.72	27.0	3.314±0.004	0.93
28.5	3.457±0.002	0.84	28.0	3.400±0.004	1.00
29.5	3.518±0.010	1.03	29.0	3.514±0.003	0.93
30.5	3.663±0.004	1.10	30.0	3.586±0.007	0.79
31.5	3.739±0.000	0.99	31.0	3.672±0.004	0.76
32.5	3.811±0.002	0.84	32.0	3.738±0.003	1.08
33.5	3.906±0.003	0.94	33.0	3.887±0.005	1.01
34.5	3.998±0.006	0.90	34.0	3.940±0.003	0.90
35.5	4.086±0.008	0.68	35.0	4.068±0.020	0.82
36.5	4.134±0.004	0.79	36.0	4.104±0.013	0.52
37.5	4.244±0.004	0.98	37.0	4.172±0.017	0.81
38.5	4.330±0.008	0.88	38.0	4.266±0.020	0.78
39.5	4.420±0.000	0.76	39.0	4.329±0.000	0.97
40.5	4.582±0.020	0.88	40.0	4.460±0.003	1.02
41.5	4.595±0.004	0.80	41.0	4.533±0.012	0.69
42.5	4.642±0.004	0.70	42.0	4.598±0.011	0.70
43.5	4.736±0.012	0.62	43.0	4.673±0.007	0.77
44.5	4.766±0.010		44.0	4.752±0.021	0.86
			45.0	4.844±0.002	

Standard deviation $= \pm 0.010$ Standard deviation $= \pm 0.010$

circles (lowest curve in the upper part of graph). The limits of error indicated for β in Table 1(a) are obtained as half the difference between the values from the heating and cooling sequences.

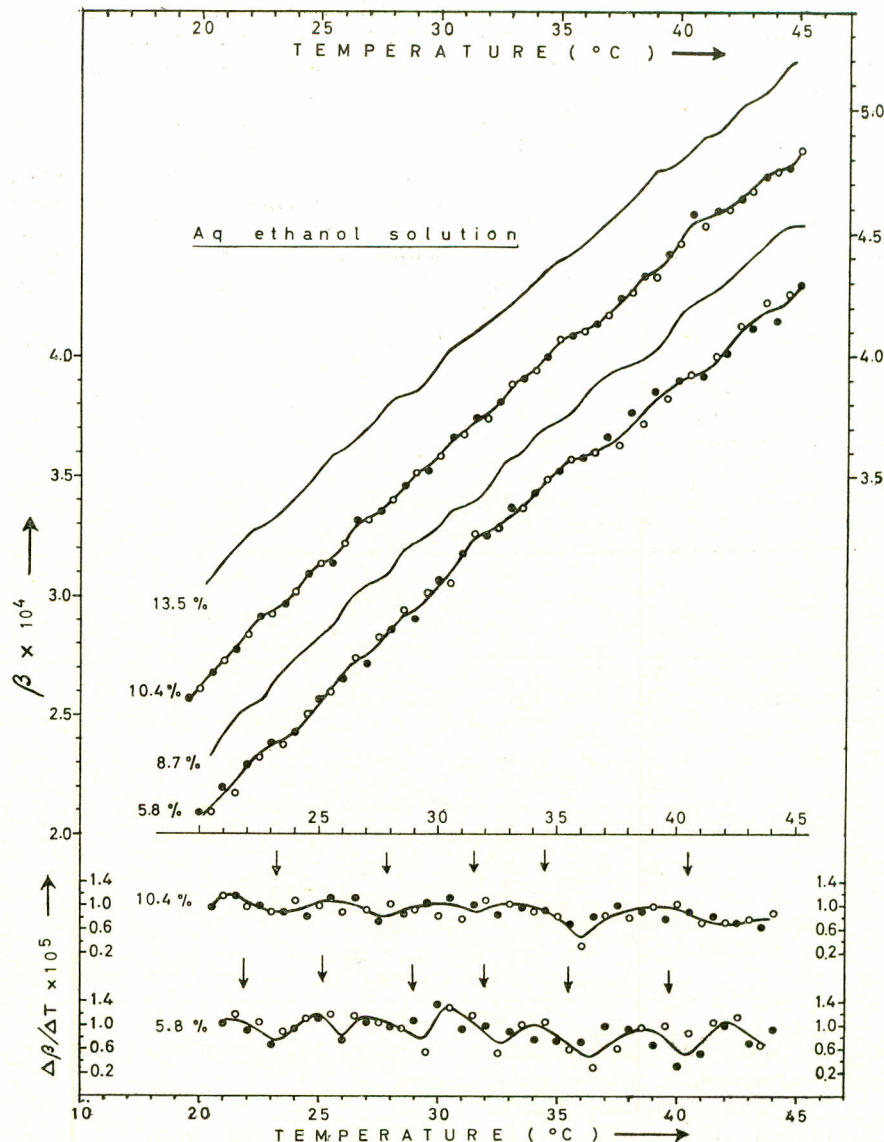Fig. 1.—Plots of measured coefficient of dilatation, β, (top of figure) and its first temperature derivative, $\triangle\beta/\triangle T$, (bottom of figure) against temperature for 5.8% and 10.4% aqueous ethanol solutions. (Solid circles are for Experiment I and hollow circles for Experiment II). Solid lines without measured points in the upper part of the graph represent the curves reproduced from previous measurements of β for 13.5% and 8.7% aqueous ethanol. The short vertical arrows inserted above the graphs for $\triangle\beta/\triangle T$ mark the temperatures for jumps in flow activation energy, $E\eta$ for the corresponding solutions.

A second set of measurements was taken with the same temperature interval of $\Delta T = 1°C$, but with the individual temperatures staggered by 0.5°C with respect to those in the first set for both cooling and heating sequences. The quantity of liquid in the capillary was also altered in such a way that if in the first set a particular meniscus measurement corresponds to the lowest part of the capillary, the readings are obtained in the second set near the middle portion of the capillary, thus tending to smooth out any residual errors remaining after applying the capillary calibration corrections.

The mean graph of $1.39 \Delta\beta/\Delta T$ for both experiments indicates a reproducibility of ± 0.015 units of $\beta \times 10^4$, and shows definite regions of nearly constant β. This is brought out more

clearly in the corresponding graph of $\Delta\beta/\Delta T \times 10^5$, plotted in the lower part of Fig. 1 as solid circles for Experiment I and hollow circles for Experiment II, and tabulated in Table 1(a) alongside the values of β with standard deviations. This combined graph shows a series of maxima and minima of $\Delta\beta/\Delta T$, with an average period of $4°C \pm 0.5°C$, and good concordance between the hollow and solid circles. The short vertical arrows inserted above this plot indicate the temperatures at which jumps in activation energy E_η are observed.[7] It is seen that, contrary to the previous findings, none of the minima quite agree with the jumps in E_η, but are ahead of the jumps on the average by $0.8° \pm 0.3°C$, which is almost a quarter period for this solution (cf. Table 2.). In previous work on 8.7% and 13.5% aqueous ethanol solutions, the minima of $\Delta\beta/\Delta T$ seemed

constant* (1.71). Two series of measurements were carried out, and the mean values are plotted as solid circles for one set and hollow circles for the other set in the upper part of Fig. 1, while Table 1 (b) gives the two sets of values as Experiments I and II. The graphs based on measurements of coefficient of dilatation, β, on 13.5% and 8.7% aqueous ethanol from the previous work are drawn as solid lines on the same scale for comparison. The two sets of measurements on the 10.4% ethanol solution show good reproducibility, and the combined plot for this solution exhibits a little less scatter of measured points than the measurements on 5.8% solution. The graph again exhibits a series of regions of almost constant β connected by sharp rise in β. (It may be noted that the values of β obtained from our experiments run parallel to the values obtained from International

TABLE 2.—TEMPERATURE FOR JUMPS IN E_η/R AND MINIMA IN $\Delta\beta/\Delta T$, ALONGWITH THE TEMPERATURE SHIFT OF $\Delta\beta/\Delta T$ MINIMA FROM E_η/R JUMPS, IN THE RANGE 20°C. TO 45°C.

Percentage composition	Ordinal number of jump/minimum	1	2	3	4	5	6	Mean Difference		Average period of cycle
								Below 33 C.	Above 33°C.	
13.5% w/w ethanol	(1) Jump in E	22.9	27.9	32.9	37.0	—	40.5			
	(2) Minimum of $\Delta\beta/\Delta T$	22.9	27.8	32.5	35.5	—	39.9			
	(3) Difference (°C.)	+0.0	−0.1	−0.4	−1.5	—	−0.6	−0.2°C.	−1.0°C.±0.4°C.	4.4°C.±0.7°C.
10.4% w/w ethanol	(1)	23.3	27.4	31.7	34.5	—	40.7			
	(2)	23.5	27.7	31.2	35.9	—	42.3			
	(3)	+0.3	+0.3	−0.5	+1.4	—	+1.6	0.0°C.	+1.5°C.±0.1°C.	5.0°C.±0.9°C.
8.7% w/w ethanol	(1)	22.8	27.0	30.4	33.8	37.9	42.3			
	(2)	23.7	27.2	29.9	33.6	37.5	41.6			
	(3)	+0.9	+0.2	−0.5	−0.2	−0.4	−0.7	+0.2°C.	−0.4°C.±0.2°C.	4.0°C.±0.6°C.
5.8% w/w ethanol	(1)	22.0	25.2	29.0	32.0	35.5	39.7			
	(2)	23.2	26.0	29.3	32.7	36.3	40.2			
	(3)	+1.2	+0.8	+0.3	+0.7	+0.8	+0.5	+0.8°C.	+0.7°C.±0.1°C.	4.0°C.±0.5°C.

to agree with jumps in E_η with one-to-one correspondance upto $35°C$, above which the minima of $\Delta\beta/\Delta T$ in case of 13.5% w/w aqueous ethanol were $1.0° \pm 0.6°C$ behind the jumps in E_η and $0.6° \pm 0.2°C$ behind for 8.7% w/w aqueous ethanol.

Experiments with 10.4% w/w Aqueous Ethanol

To help trace this peculiar behaviour in the full range of concentrations, it was considered desirable to make β and $\Delta\beta/\Delta T$ measurements on more solutions. Therefore, measurements on another aqueous ethanol solutions of intermediate concentrations, i.e., 10.4% w/w was undertaken, with the usual care and verification of its concentration. The (calibrated) dilatometer used for this solution had a slightly different

Critical Table (1929), but are 0.1 unit of $\beta \times 10^4$ lower).

The plot of $\Delta\beta/\Delta T \times 10^5$ for 10.4% ethanol solution is plotted in lower part of Fig. 1, and brings out the periodic features of β more explicitly in the form of the succession of maxima and minima with average period of $5° \pm 0.9°C$. The peak-to-peak amplitude of 0.3 units of $\Delta\beta/\Delta T \times 10^5$ on the average, is about the same as for 13.5% (w/w) aqueous ethanol. The short vertical arrows inserted above this graph again indicate the temperatures at the jumps in E_η for this solution, obtained by interpolation from the plots of jumps in E_η (for various aqueous ethanol solutions previously reported) against percentage com-

*This value replaces the previously quoted constant of 1.5 used for the 13.5% ethanol solution in an earlier communication, which was due to an error of calculation.

position. The three jumps in $E\eta$ at 23.3°C, 27.4°C and 31.7°C agree with the minima of $\Delta\beta/\Delta T$, but the other two jumps at 34.5°C and 40.7°C are behind the minima of $\Delta\beta/\Delta T$ by 1.5°C±0.1°C, which is a little more than a quarter of a full cycle of periodic oscillations for this solution.

Discussion

A comparison of the present measurements on derivative of coefficient of dilatation, i.e. $\Delta\beta/\Delta T$, on 5.8% and 10.4% aqueous ethanol with the previous measurements on 8.7% and 13.5% aqueous ethanol is made in Fig. 2, and it is interesting to see that the amplitude of the oscillations in $\Delta\beta/\Delta T$ *decreases* progressively with the increase of ethanol concentration. The short
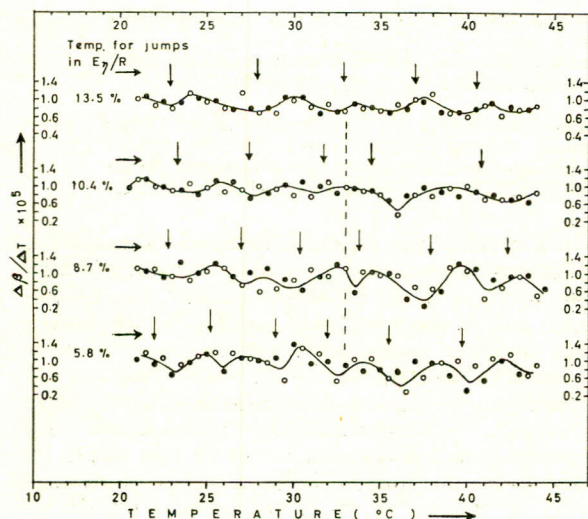

Fig. 2.—Plots of measured values of $\Delta\beta/\Delta T$, calculated with temperature interval $\Delta T=2$°C for 13.5%, 10.4%, 8.7% and 5.8% aqueous ethanol. (Solid circles for Experiment I and hollow circles for Experiment II.) The short vertical arrows inserted above each graph show temperatures for jumps in flow activation energy, $E\eta$, for the respective solutions. The breakdown of one-to-one correspondence is apparent to the right of the vertical broken line at 33°C.

vertical arrows drawn above each graph indicate the various jumps in $E\eta$. It is apparent that one-to-one correspondence of jumps in $E\eta$ and minima of $\Delta\beta/\Delta T$ is approximately true in the temperature region below 33°C (indicated by the vertical broken line in Fig. 2) in case of all the four solutions, but above this temperature the behaviour is rather erratic. A detailed comparison of the

temperatures at the minima of $\Delta\beta/\Delta T$ with the temperatures at the corresponding jumps of $E\eta$ is attempted in Table 2.

Confining our attention first to the region below 33°C., we find from Table 2 that while the minima of $\Delta\beta/\Delta T$ are on the average 0.8°C *ahead* of the jumps in $E\eta$ for 5.8% ethanol solution, these minima are 0.2°C *behind* the jumps in case of 13.5% ethanol. This corresponds to a uniform relative shift of 0.12°C. for each 1% change in ethanol concentration, which is confirmed by the data for 7.8% and 10.4% ethanol solutions. If this shift can be extrapolated to 0% ethanol, then the minima of $\Delta\beta/\Delta T$ for pure water would be nearly 1.5°C i.e.a a quarter cycle ahead of the $E\eta$ jumps, which should accordingly be in step with the *downward* slopes of the $\Delta\beta/\Delta T$ graph, and therefore with the minima of $\Delta^2\beta/\Delta T^2$. This is in agreement with the analysis[3] of the standard data on density of water made by one of the authors of the present communication.

The behaviour of the $\Delta\beta/\Delta T$ graphs of Fig. 2 above 33°C. is rather complex, and all that can be safely said at this stage is that, at the *lower* ethanol concentrations, it approaches the behaviour below 33°C. Measurements at closer concentration intervals are in hand to elucidate these aspects further.

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