TEMPERATURE DEPENDENCE OF THE INTERMOLECULAR ACTIVATION ENERGY FOR FLOW IN LIQUIDS AND SOLUTIONS

Part I.—Investigation of the Influence of Alcohol Concentration on the Activation Energy Jumps in Dilute (0 to 11%) Aqueous Ethyl Alcohol

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Following the discovery of discontinuities in the activation energy of flow in several hydroxylic liquids, the investigations are here extended to the simple binary series of ethyl alcohol and water. The experiments have been carried out using a very small measuring interval $\Delta T = 1$ deg. C. in the equation

$$\varepsilon/k = \Delta \ln\eta/\Delta(1/T) = -T^2 \Delta \ln\eta/\Delta T$$

and preliminary results in the range of 10°C. to 50°C. on 5% and 11% aqueous alcohol and on pure water for comparison are reported here. The measured values of $(\varepsilon/k)/1000$ are reproducible to ± 0.012, i.e. to about 0.5% for aqueous alcohol and to about half this figure in the case of pure water.

Graphical comparison provides indications for a systematic shift of corresponding energy jumps towards higher temperatures, amounting to 3–5°C. for 10% alcohol concentration, accompanied by an average increase of about 16% in the activation energy. The depths of two of the jumps in the case of 11% alcohol are such (nearly 6% of the total ε/k) that they are readily discernible in the earlier standard data on 10% alcohol as well. Further work on higher alcohol concentrations is in progress.

1. Introduction

The intermolecular activation energy for the viscous flow of a liquid is clearly a function of the intermolecular structure within the liquid. Accurate measurements of this energy at close temperature intervals carried out recently in this laboratory on several pure hydroxylic liquids, namely glycerol,[1] ethylene glycol,[2] and water,[3] have shown the presence of sharp recurring segments, over each of which the energy is constant but undergoes a rapid change from one segment to the next. Since these investigations have a bearing on the development of a consistent theory of the liquid state, it was natural to extend the measurements to the case of binary solutions, and some preliminary results reported on ethyl alcohol containing 5 to 12% of water showed a periodic nearly sinusoidal variation of the activation energy.[4] The present communication describes similar experiments carried out at the other end of the water-alcohol system, namely, on dilute alcohol of concentration upto 11%, with a view to correlating the energy step structure with that observed in pure water. Because of the significance of small scale variations, a measuring interval of 1 deg. C. has been used throughout these measurements, and this has necessitated some repetition of the earlier work on water, which had been carried out with a measuring interval of 2 deg. C. in the range 5° to 40°C.

2. Experimental Procedure

The basis of all the measurements[1-4] is the differential of the logarithm of the Andrade[5] equation, viz.,

$$\varepsilon/k = -\Delta \ln \eta / \Delta(1/T) = -T^2 (\Delta \ln \eta/\Delta T), \quad (1)$$

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which is the analytical analogue of the established procedure of taking the mean slope of the curve for $\ln\eta$ against $1/T$ in the range T, $T + \Delta T$. For use with kinematic viscometry, this equation can be recast into the form

$$\varepsilon/k = -T^2(\Delta\ln\nu/\Delta T) - T^2(\Delta\ln\rho/\Delta T)$$
$$= \varepsilon'/k + T^2\beta. \tag{2}$$

where $T^2\beta = T^2(\Delta\rho/\Delta T)/\rho$ is a small correction term, β being the coefficient of dilatation of the experimental sample.

The apparatus used in these experiments was the same as that for the previously reported measurements on water,[3] including the vapour-equilibrium bottle containing a large surface of the particular solution under test. Measurements of the flow times were made to about one part in 10,000 at intervals of nearly 1 deg. C., which were measured with a Beckmann differential thermometer; the means of several observations at each temperature were used in the calculations, and measurements were made with both rising and falling temperature sequences. The equilibrium level of the liquid in the large bulb of the U-tube No. 1 (B.S.S.) viscometer used was repeatedly measured at each temperature with a cathetometer to an accuracy of nearly 0.002 cm., and this level was adjusted every 10 degrees C. so as to keep the level correction small. The temperature during each flow measurement was maintained to within 0.002 deg. C., and Beckmann readings were taken every minute or half-minute during flow.

The pure water was prepared by repeated distillations as for conductivity work, and the alcohol solutions were made by pipetting a calculated volume of redistilled ethyl alcohol into 50 ml. of double distilled water and shaking. The concentrations were checked by the viscosity measurements at 20°C. and 25°C. during the main experiment itself.

3. Experiments with 5% Ethyl Alcohol in Water

The first set of experiments was carried out with the 5% (by weight) ethyl alcohol solution, which has a viscosity nearly 15% higher than water at corresponding temperatures, and was therefore expected to show significant departures in the activation energy also. The actual temperatures, Beckmann readings and times of flow recorded in the range of 11°C. to 53°C. are given in Table 1(a) for the rising and falling temperature sequences, together with the calculated values of $(\varepsilon'/k)/1000$. The standard deviations as estimated from those of the temperature and flow-time in each group corresponding to one setting of the Beckmann thermometer are about 0.015. Table 1(b) gives the overall means
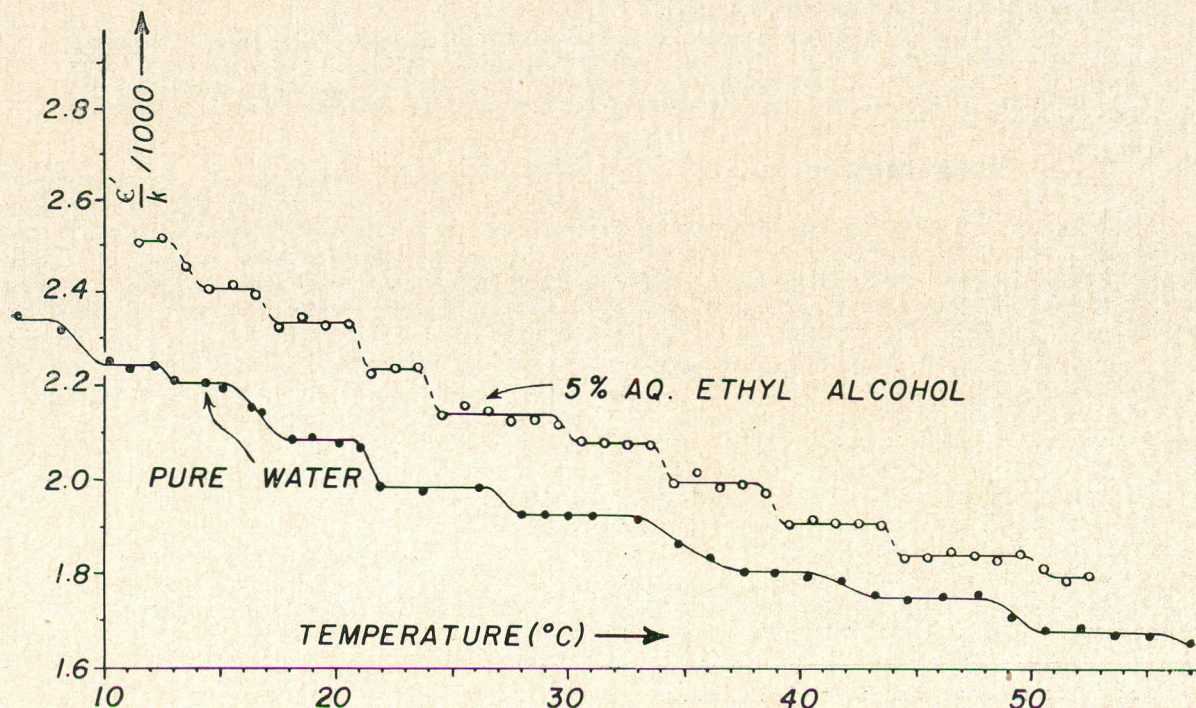

Fig 1.—Comparison of the values of $(\varepsilon'/k)/1000$ for 5% aqueous ethyl alcohol (upper curve) with the earlier data for pure water (bottom curve), showing a general similarity, except in the region of 32° to 40°C.

TABLE 1(a).—BECKMANN READING, FLOW TIMES AND THE CALCULATED VALUES OF $(\varepsilon'/k) \div 1000$ $= -T^2 (\Delta\ln\nu/\Delta T) \div 1000$ FOR 5% AQUEOUS SOLUTION OF ETHYL ALCOHOL FROM 10 °C. TO 53 °C. WITH $\Delta T = 1°C$.

| | Heating sequence | | | | | Cooling sequence | | | |
Temperature °C.	Beckmann reading uncorrected	Time of flow corrected for level	Mean temp. °C.	$(\varepsilon'/k) \div 1000$ uncorrected for Beckmann calibration	Temperature °C.	Beckmann reading uncorrected	Time of flow corrected for level	Mean temp. °C.	$(\varepsilon'/k) \div 1000$ uncorrected for Beckmann calibration
11.00	5.873±0.001	399.33±0.03			11.00	5.245±0.001	399.08±0.04		
12.00	4.842±0.001	386.88±0.03	11.50	2.486	12.00	4.230±0.001	386.64±0.04	11.50	2.526
13.00	3.833±0.001	374.95±0.04	12.50	2.530	13.00	3.223±0.001	374.87±0.02	12.50	2.502
13.00	4.868±0.001	374.92±0.07			13.00	3.833±0.001	374.95±0.03		
14.00	3.853±0.001	363.65±0.01	13.50	2.468	14.00	2.810±0.000	363.68±0.03	13.50	2.448
15.00	2.839±0.001	353.11±0.04	14.50	2.397	15.00	1.776±0.000	352.87±0.02	14.50	2.412
15.00	2.607±0.001	353.30±0.06	15.50	2.412	15.00	2.592±0.001	353.18±0.04		
16.00	1.597±0.001	343.11±0.04			16.00	1.599±0.001	343.14±0.04	15.50	2.417
16.00	5.192±0.001	343.58±0.02			16.00	5.170±0.001	343.31±0.02		
17.00	4.168±0.001	333.71±0.06	16.50	2.386	17.00	4.164±0.001	333.54±0.05	16.50	2.405
18.00	3.132±0.001	324.32±0.05	17.50	2.325	18.00	3.127±0.001	324.15±0.03	17.50	2.324
18.00	3.145±0.001	324.72±0.05			18.00	3.137±0.001	324.60±0.02		
19.00	2.104±0.001	315.57±0.05	18.50	2.333	19.00	2.099±0.001	315.36±0.05	18.50	2.364
20.00	1.130±0.001	307.23±0.04	19.50	2.352	20.00	1.131±0.001	307.24±0.06	19.50	2.305
20.00	5.166±0.001	307.21±0.05			20.00	5.166±0.001	307.20±0.04		
21.00	4.155±0.001	298.93±0.05	20.50	2.328	21.00	4.164±0.001	298.95±0.03	20.50	2.337
22.00	3.122±0.001	291.10±0.04	21.50	2.228	22.00	3.123±0.001	291.11±0.03	21.50	2.221
23.00	2.112±0.001	283.68±0.02	22.50	2.232	23.00	2.120±0.000	283.71±0.02	22.50	2.242
23.00	4.773±0.000	283.77±0.01			23.00	4.776±0.001	283.95±0.03		
24.00	3.780±0.001	276.74±0.05	23.50	2.220	24.00	3.782±0.000	276.79±0.04	23.50	2.256
25.00	2.748±0.001	269.88±0.02	24.50	2.152	25.00	2.761±0.001	270.09±0.07	24.50	2.126
25.00	2.744±0.000	269.88±0.05			25.00	2.748±0.001	269.93±0.02		
26.00	1.752±0.001	263.54±0.03	25.50	2.135	26.00	1.753±0.001	263.44±0.04	25.50	2.179
27.00	0.756±0.001	257.30±0.05	26.50	2.158	27.00	0.740±0.001	257.16±0.07	26.50	2.136
27.00	4.594±0.001	257.24±0.04			27.00	4.602±0.001	257.18±0.06		
28.00	3.590±0.000	251.19±0.03	27.50	2.140	28.00	3.590±0.001	251.16±0.04	27.50	2.113
29.00	2.579±0.000	245.30±0.02	28.50	2.133	29.00	2.548±0.001	245.12±0.04	28.50	2.123
30.00	1.548±0.001	239.55±0.03	29.50	2.105	30.00	1.549±0.001	239.49±0.03	29.50	2.128
30.00	5.282±0.00	240.02±0.04			30.00	5.274±0.000	239.99±0.03		
31.00	4.285±0.000	234.66±0.03	30.50	2.086	31.00	4.275±0.000	234.64±0.04	30.50	2.079
32.00	3.272±0.000	229.39±0.03	31.50	2.079	32.00	3.270±0.000	229.41±0.01	31.50	2.080
33.00	2.270±0.000	224.32±0.04	32.50	2.081	33.00	2.270±0.000	224.37±0.03	32.50	2.073
33.00	5.198±0.000	225.81±0.03			33.00	5.197±0.000	225.94±0.04		
34.00	4.204±0.001	220.91±0.06	33.50	2.072	34.00	4.205±0.001	221.04±0.06	33.50	2.076
35.00	3.199±0.001	216.27±0.04	34.50	1.997	35.00	3.202±0.001	216.41±0.04	34.50	1.996
36.00	2.164±0.001	211.60±0.06	35.50	2.007	36.00	2.161±0.001	211.66±0.06	35.50	2.028
36.00	4.180±0.000	211.58±0.03			36.00	4.180±0.001	211.61±0.03		
37.00	3.176±0.001	207.25±0.03	36.50	1.973	37.00	3.149±0.001	207.11±0.03	36.50	1.997
38.00	2.152±0.001	202.90±0.04	37.50	1.998	38.00	2.152±0.001	202.91±0.06	37.50	1.983
38.00	4.298±0.000	202.26±0.03			38.00	4.298±0.001	202.25±0.02		
39.00	3.299±0.000	198.21±0.04	38.50	1.964	39.00	3.284±0.001	198.10±0.02	38.50	1.984
40.00	2.278±0.000	194.28±0.04	39.50	1.936	40.00	2.281±0.000	194.27±0.05	39.50	1.901
40.00	5.284±0.000	194.14±0.05			40.00	5.278±0.000	193.98±0.02		
41.00	4.274±0.000	190.32±0.02	40.50	1.933	41.00	4.273±0.001	190.24±0.04	40.50	1.904
42.00	3.277±0.001	186.66±0.04	41.50	1.926	42.00	3.275±0.001	186.63±0.03	41.50	1.899
42.00	4.804±0.000	185.83±0.05			42.00	4.799±0.001	185.68±0.04		
43.00	3.796±0.000	182.29±0.04	42.50	1.900	43.00	3.793±0.000	182.11±0.04	42.50	1.920
44.00	2.802±0.000	178.85±0.04	43.50	1.920	44.00	2.798±0.000	178.72±0.03	43.50	1.892

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Table 1(a). *Contd.*

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	Heating sequence					Cooling sequence			
Temperature °C.	Beckmann reading uncorrected	Time of flow corrected for level	Mean temp. °C.	$(\varepsilon'/k) \div 1000$ uncorrected for Beckmann calibration	Temperature °C.	Beckmann reading uncorrected	Time of flow corrected for level	Mean temp. °C.	$(\varepsilon'/k) \div 1000$ uncorrected for Beckmann calibration
44.00	5.786 ± 0.000	178.71 ± 0.04			44.00	5.784 ± 0.000	180.33 ± 0.05		
45.00	4.774 ± 0.000	175.43 ± 0.03	44.50	1.845	45.00	4.794 ± 0.001	177.13 ± 0.03	44.50	1.823
46.00	3.771 ± 0.000	172.24 ± 0.02	45.50	1.856	46.00	3.794 ± 0.001	173.98 ± 0.03	45.50	1.820
47.00	2.771 ± 0.000	169.14 ± 0.03	46.50	1.854	47.00	2.775 ± 0.000	170.80 ± 0.04	46.50	1.848
48.00	1.785 ± 0.000	166.20 ± 0.05	47.50	1.847	48.00	1.782 ± 0.000	167.80 ± 0.03	47.50	1.833
48.00	4.916 ± 0.001	167.17 ± 0.02			48.00	4.902 ± 0.000	167.13 ± 0.05		
49.00	3.920 ± 0.000	164.26 ± 0.03	48.50	1.823	49.00	3.932 ± 0.000	164.27 ± 0.02	48.50	1.837
50.00	2.981 ± 0.000	161.53 ± 0.04	49.50	1.856	50.00	2.940 ± 0.001	161.42 ± 0.04	49.50	1.834
51.00	1.899 ± 0.000	158.58 ± 0.04	50.50	1.783	51.00	1.916 ± 0.000	158.53 ± 0.04	50.50	1.846
51.00	5.329 ± 0.001	158.46 ± 0.04			51.00	5.322 ± 0.001	158.29 ± 0.03		
52.00	4.332 ± 0.001	155.81 ± 0.01	51.50	1.782	52.00	4.309 ± 0.001	155.59 ± 0.02	51.50	1.794
53.00	3.325 ± 0.001	153.17 ± 0.03	52.50	1.798	53.00	3.318 ± 0.001	152.99 ± 0.02	52.50	1.802

of $(\varepsilon'/k)/1000$ together with the standard deviations as estimated (for groups of ten temperatures) from the differences between the rising and falling sequence values. The final accuracy of the results is seen to be about 0.012, which is satisfactory, even though it is higher than the corresponding figure for similar experiments with redistilled ethylene glycol (cf. also Table 2). The last column of Table 1(b) gives some values of the correction term $T^2\beta = T^2(\Delta\rho/\Delta T)$ estimated from the available standard density data, which however can barely be relied upon for the second decimal place in the correction.

Figure 1 shows a comparison of these measurements (upper curve) with the corresponding part of the graph for pure water (bottom curve) reproduced from Fig. 5 of the earlier work,[3] and a general similarity of the step-structure is apparent, except in the region of 32° to 40°C., where the data for water show a relatively gradual drop, which was attributed to the larger measuring interval of 2°C. The next step therefore was to repeat the measurements on water using $\Delta T = 1$ deg.C.

4. New Results with Thrice-distilled Water from 1°C. to 41°C.

Two experiments were performed with two different samples of water, each thrice distilled to minimize possible effects of trace impurities; each experiment was of course repeated with rising and falling temperature sequences. The mean corrected values of $(\varepsilon'/k) \div 1000$ for the first experiment are given against "Expt. I" in Table 2, together with the mean of standard deviations as estimated from

(i) the errors in the temperature differences ΔT and the flow time t, and (ii) the differences between the values of ε'/k obtained with the rising and falling temperature sequences. The values for "Expt. I" are plotted as the lowest full-line graph in Fig. 2 (solid circles); this graph runs essentially parallel to the earlier results with $\Delta T = 2$ deg. C. (broken line in top half of Fig. 2), except for the occurrence of an additional step at 35°C., indicated by the vertical arrow.

Since the data on water serve as a reference standard for all further work on aqueous solutions, it was desirable to improve the accuracy and detail of this data by taking the second set of measurements using the other sample of thrice-distilled water. The results are given in Table 2 under the label "Expt. II" and are plotted in the lower half of Fig. 2 with an upward displacement of 0.2 units of $(\varepsilon'/k)/1000$. There is satisfactory agreement between the graphs for "Expt. I" and "Expt. II", and the means of readings at corresponding temperatures in the two sets are plotted as triangles in the upper half of Fig. 2; the circles in this graph represent those readings of either set that have not been averaged because of too large a deviation in either temperature or energy. This graph as well as Table 2 clearly show that the measurements of $(\varepsilon'/k)/1000$ are sufficiently accurate (to $\pm$ 0.006) and closely spaced to bring out the fine details of the step structure; notably, the splitting of the previous long segment from 32° to 40° C. into two short steps (arrow 'A' in Fig. 2, top) bears out our earlier conjecture of the existence of such a fine-structure.[2,3] Also, traces of a narrow step of about 2 deg. C. width can be observed in the middle of the relatively slow drop at 17°C. (arrow B)
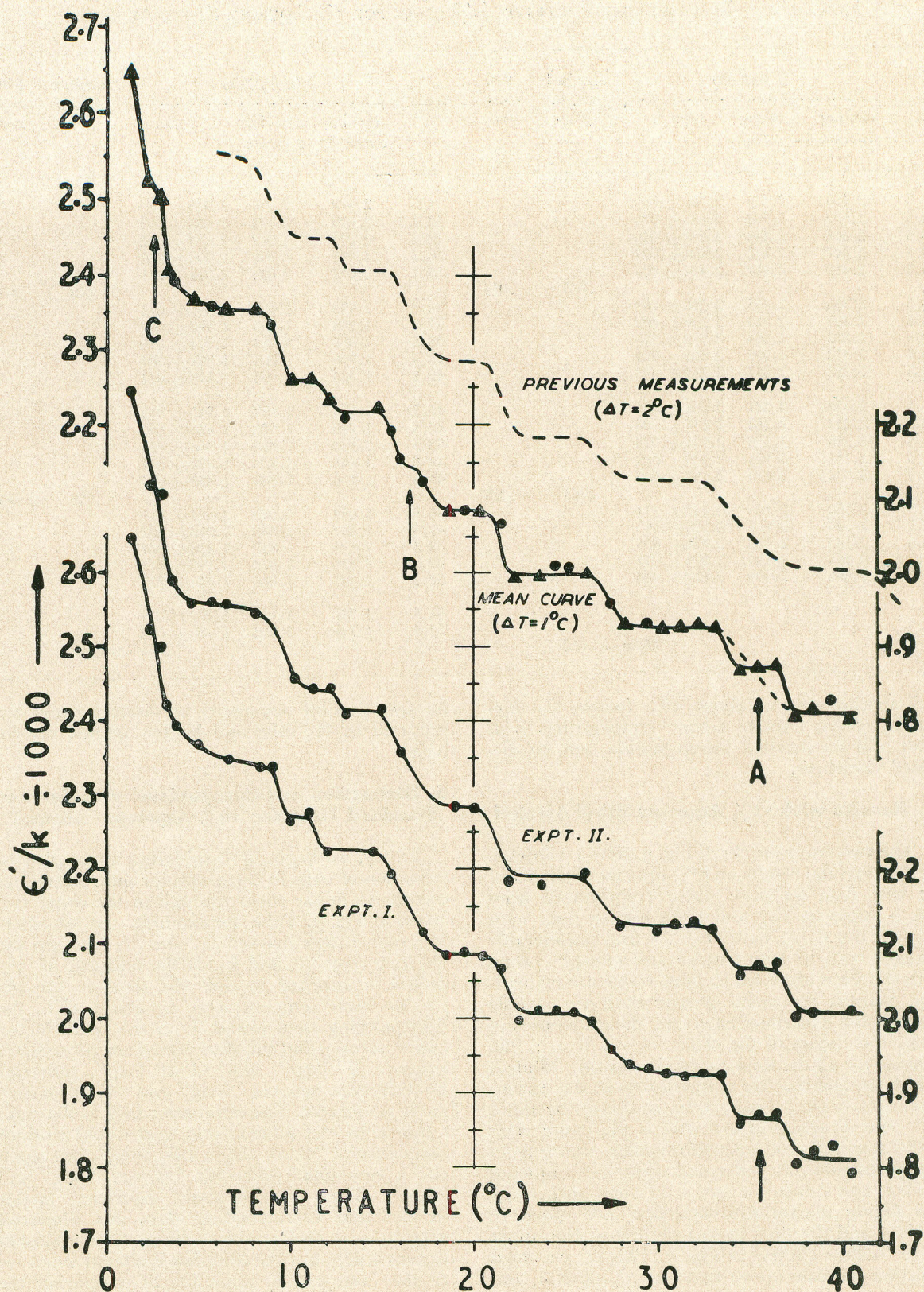
Fig. 2.—Graphs showing the new data obtained for thrice-distilled water, using a measuring interval of one degree C. The lower half shows the results of the two separate experiments, while the upper half shows the mean of the two (triangles and circles) compared with the earlier data (broken line, ordinates shifted up by 0.2 unit) obtained with $\Delta T = 2$ deg. C.

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Table 1(b).—Experimental Values of $(\varepsilon'/k)/1000$ for 5% Aqueous Ethyl Alcohol.

Temp. (°C).	$(\varepsilon'/k)/1000$			Standard dev. of group	$\dfrac{T2\beta}{1000}$	Temp. (°C.)	$(\varepsilon'/k)/1000$			Standard dev. of group	$\dfrac{T2\beta}{1000}$
	Heating sequence	Cooling sequence	Mean				Heating sequence	Cooling sequence	Mean		
11.5	2.486	2.526	2.506±.020			31.5	2.079	2.080	2.080±.000		
12.5	2.530	2.502	2.516±.014			32.5	2.079	2.073	2.076±.003		
13.5	2.468	2.448	2.458±.010			33.5	2.072	2.067	2.074±.002		
14.5	2.397	2.412	2.404±.007			34.5	1.997	1.996	1.996±.000		
15.5	2.412	2.417	2.414±.002			35.5	2.007	2.028	2.018±.011		
				.013	.014					.008	.035
16.5	2.386	2.405	2.396±.009			36.5	1.973	1.997	1.985±.012		
17.5	2.325	2.324	2.324∓.000			37.5	1.998	1.983	1.990±.007		
18.5	2.333	2.364	2.348±.016			38.5	1.964	1.984	1.974±.010		
19.5	2.352	2.305	2.328∓.024			39.5	1.916	1.901	1.908±.007		
20.5	2.328	2.337	2.332±.005			40.5	1.933	1.904	1.918±.014		
21.5	2.228	2.221	2.224±.004			41.5	1.926	1.899	1.912±.013		
22.5	2.232	2.242	2.237±.005			42.5	1.900	1.920	1.910±.010		
23.5	2.220	2.256	2.238±.018			43.5	1.920	1.892	1.906±.014		
24.5	2.152	2.126	2.139−.013			44.5	1.845	1.823	1.834±.011		
25.5	2.135	2.179	2.157±.022			45.5	1.8?6	1.820	1.838±.014		
				.013	.025					.013	.046
26.5	2.158	2.136	2.147±.011			46.5	1.854	1.848	1.851±.011		
27.5	2.140	2.113	2.126±.013			47.5	1.847	1.833	1.840±.007		
28.5	2.133	2.123	2.128±.005			48.5	1.8?3	1.837	1.830±.007		
29.5	2.105	2.128	2.116±.011			49.5	1.856	1.834	1.845±.011		
30.5	2.086	2.079	2.082±.004			50.5	1.783	1.846	1.814±.032		
						51.5	1.782	1.792	1.787±.005		
						52.5	1.798	1.802	1.800±.002		
			Mean = .013						Mean = .011		

and another one at about 3°C. (arrow C). Extension of this data to higher temperatures is in hand and its detailed interpretation will be discussed elsewhere.

5. Results with 11% Aqueous Ethyl Alcohol

The two lower graphs of Fig. 3 show a comparison between the results on 5% aqueous alcohol and the new data on pure water [reproduced from Fig. 2 (upto 41°C.) and from earlier data with $\Delta T = 1.5$ deg.C. (41°C. to 6°C.)], and considerable changes both in temperature and energy values from the steps observed in pure water are evident. The changes are much greater than are possible through the experimental errors, the differences in $(\varepsilon'/k)/1000$ being of the order of 0.1 to 0.3, the energies for all the steps having increased. While it is fairly certain that the temperatures at the discontinuities have altered more or less uniformly by about 3°C., the direction of this shift is not quite clear at this stage. To examine this further, the next set of experiments was performed using 11% aqueous alcohol, and values got for $(\varepsilon'/k)/1000$ with rising and falling temperature sequences are given in Table 3 and the final means plotted as the upper curve (hollow circles) in Fig. 3. This curve shows a further increase above that for 5% alcohol, and

the two possible sequences of displacements are indicated by the solid and broken arrows, respectively.

6. Discussion and Comparison with Earlier Standard Data for 10% Aqueous Alcohol

Firstly, we begin by considering a conspicuous succession of steps in the graph for pure water and attempt to follow them through in the other two curves of Fig. 3. Take, for example, the two short consecutive steps marked D_1 and D_2 bewteen the two long steps C_2 and E_1. If the addition of 5% alcohol is assumed to shift the steps to the left (i.e. to lower temperatures) by about 3°C., the corresponding steps would lie at the heads of the broken arrows, and this does reproduce the original sequence of "long, short, short, long", although the difference between "long" and "short" is now barely noticeable. The alternative shift to the right is shown by the solid arrows, and would produce a sequence of "short, short, long, long", but again with a very small difference between "long" and "short". These considerations somewhat favour the view that corresponding steps are displaced towards lower temperatures with increasing alcohol concentration, but the situation is altered when we try the (alternative) approach of comparing the

TABLE 2.—EXPERIMENTAL VALUES OF $(\varepsilon'/k)/1000$ OBTAINED FOR WATER USING $\Delta T = 1$ DEG. C.

Expt. I		Expt. II		Mean of I and II		Standard dev. for the group
Temperature (°C.)	$(\varepsilon'/k)/1000$	Temperature (°C.)	$(\varepsilon'/k)/1000$	Mean temp. (°C.)	$(\varepsilon'/k)/1000$	
1.3	2.648±.005	1.3	2.645±.004	1.30	2.646±.002	
2.3	2.524±.003	2.3	2.520±.003	2.30	2.522±.002	
2.9	2.501±.005	3.0	2.510±.005	2.95	2.506±.005	
3.2	2.412±.006	3.5	2.389±.003	3.35	2.405±.010	
3.8	2.391±.005	—	—	—	—	
5.0	2.367±.003	4.6	2.360±.004	4.80	2.364±.003	.006
—	—	5.7	2.360±.004	—	—	
6.6	2.346±.003	6.3	2.358±.004	6.45	2.352±.006	
8.3	2.362±.004	8.1	2.346±.004	8.20	2.354±.010	
9.0	2.337±.004					
10.0	2.263±.004	10.2	2.255±.004	10.10	2.259±.004	
11.0	2.278±.004	11.2	2.243±.003	11.10	2.260±.016	
12.0	2.215±.004	12.2	2.244±.004	12.10	2.230±.010	
—	—	13.0	2.208±.003	—	—	
14.5	2.223±.003	15.0	2.220±.003	14.75	2.222±.001	
15.5	2.191±.004	—	—	—	—	.007
—	—	16.0	2.156±.003	—	—	
17.2	2.126±.004					
18.5	2.083±.003	18.9	2.084±.003	18.70	2.084±.000	
19.5	2.089±.003	—	—	—	—	
20.5	2.083±.004	20.1	2.081±.004	20.30	2.082±.001	
21.5	2.067±.003	—	—	—	—	
22.5	1.996±.003	21.8	1.983±.003	22.15	1.990±.007	
23.5	2.012±.003	23.7	1.977±.003	23.60	1.994±.002	
24.5	2.014±.003	—	—	—	—	
25.5	2.009±.003					.009
26.5	1.984±.003	26.1	1.997±.004	26.30	1.990±.006	
27.5	1.958±.003	—	—	—	—	
28.5	1.938±.003	28.0	1.924±.005	28.25	1.931±.007	
29.5	1.932±.004	—	—	—	—	
30.5	1.926±.003	30.0	1.916±.004	30.25	1.921±.005	
31.5	1.922±.003	31.0	1.929±.004	31.25	1.926±.004	
32.5	1.927±.004	32.0	1.934±.003	32.25	1.930±.004	
33.5	1.927±.004	33.0	1.920±.003	33.25	1.924±.004	
34.5	1.859±.003	34.5	1.859±.003	34.50	1.859±.000	
35.5	1.873±.003	35.5	1.876±.003	35.50	1.874±.002	.005
36.5	1.872±.004	36.5	1.877±.004	36.50	1.874±.005	
37.5	1.806±.004	37.5	1.803±.004	37.50	1.804±.002	
38.5	1.822±.004	38.5	1.808±.003	38.50	1.815±.007	
39.5	1.837±.003	—	—	—	—	
40.5	1.793±.003	40.5	1.812±.004	40.50	1.802±.010	Overall mean S.D=.007

complete graphs with one another, taking both the length and depth of the steps into account, and looking for a probable sequential change with concentration. This procedure shows that better overall progression is obtained if we follow the solid arrows inclined to the right than if we follow the broken arrows. On this basis, we may conclude provisionally that a change of 10% in alcohol content involves an increase of 3°C to 5°C. in the temperatures for corresponding discontinuities. This is accompanied by an activation energy increase $\delta\varepsilon$, which can be estimated approximately as $\delta\varepsilon/\varepsilon = 0.16 \pm 0.02$.

The above analysis naturally prompts some speculation about the physical phenomena res-

ponsible for these shifts. As noted in an earlier paper[2] on the steps in ethylene glycol, the transition from one constant activation enregy level to the neighbouring one for any one liquid can be thought of as being similar in character to the well-known ferromagnetic $\rightleftharpoons$ paramagnetic transformation of the Weiss-Langevin domain theory of ferromagnetism. At low temperatures, there is perfect order over each separate domain, which is destroyed at the critical (Curie) temperature, above which the individual molecules (magnets) become randomly oriented subject to thermal motions. The presence of a series of such small pseudo-crystalline domain structures in the pure liquid, each with a different critical temperature, would fit the observed step-structure of the activa-
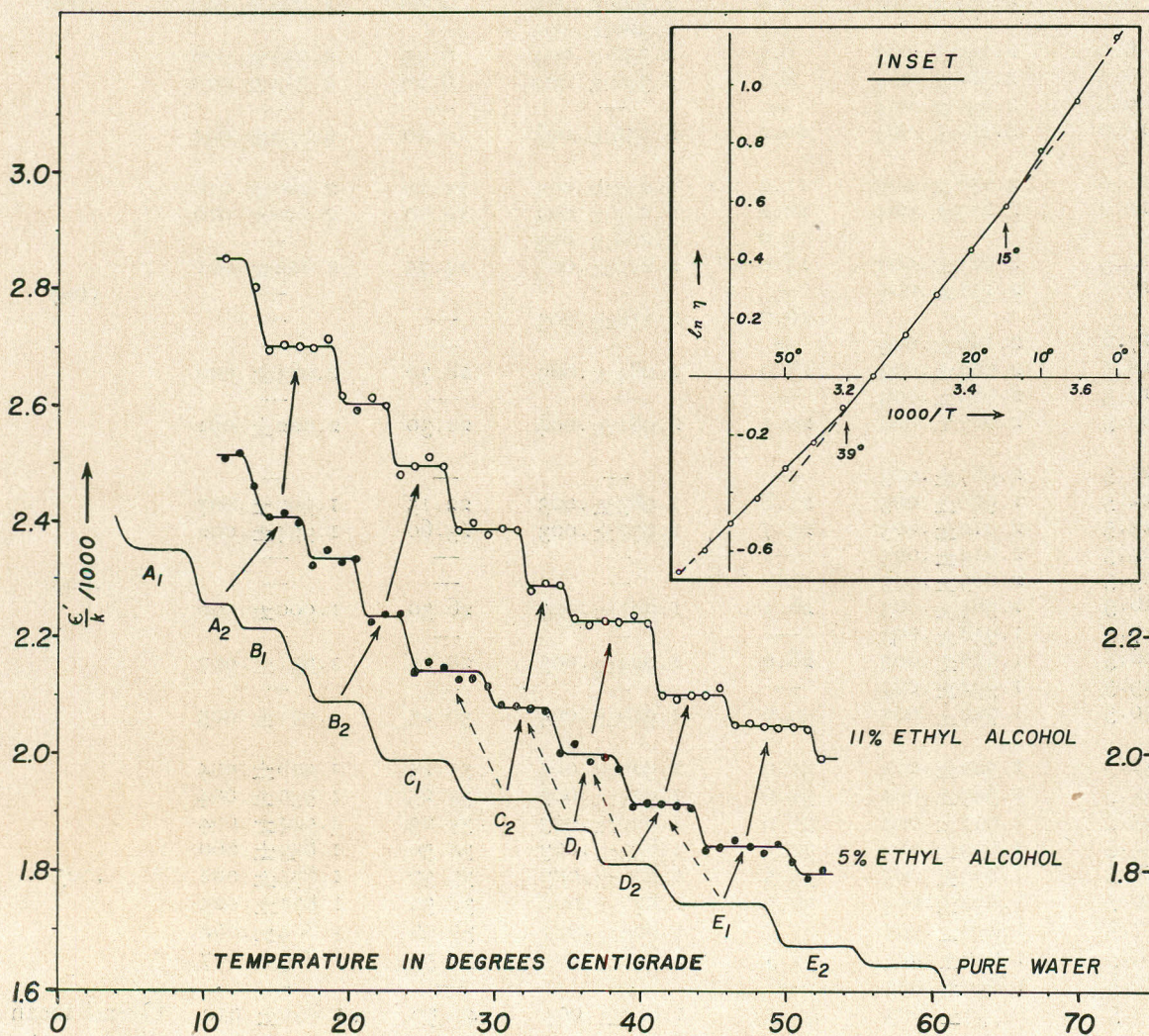

Fig: 3.—Comparison of the graph of $(\varepsilon'/k)/1000$ obtained for 11% alcohol (upper curve) with those for 5% alcohol and pure water, showing a systematic shift in the energy steps, as indicated by the solid arrows inclined to the right. The inset shows a ln η versus 1/T plot of the standard data for 10% alcohol, which exhibits sharp bends at 15°C. and 39°C., in agreement with the two largest steps in the $(\varepsilon'/k)/1000$ curve for 11% alcohol.

TABLE 3.—EXPERIMENTAL VALUES OF $(\varepsilon'/k)/1000$ FOR 11% AQUEOUS ETHYL ALCOHOL.

Temperature (°C.)	$(\varepsilon'/k)/1000$ Heating sequence	Cooling sequence	Mean	Standard dev. of group	Temperature (°C.)	$(\varepsilon'/k)/1000$ Heating sequence	Cooling sequence	Mean	Standard dev. of group
11.5	2.844	2.856	2.850 ± .006		31.5	2.378	2.389	2.384 ± .005	
12.5	2.842	2.870	2.856 ± .014		32.5	2.282	2.271	2.276 ± .005	
13.5	2.806	2.794	2.800 ± .006		33.5	2.300	2.282	2.291 ± .009	
14.5	2.702	2.683	2.692 ± .009		34.5	2.272	2.304	2.288 ± .016	
15.5	2.708	2.698	2.703 ± .005		35.5	2.240	2.224	2.232 ± .008	
				.012					.012
16.5	2.674	2.727	2.700 ± .027		36.5	2.215	2.226	2.220 ± .006	
17.5	2.716	2.678	2.697 ± .019		37.5	2.246	2.200	2.223 ± .017	
18.5	2.707	2.717	2.712 ± .005		38.5	2.250	2.200	2.225 ± .025	
19.5	2.608	2.621	2.614 ± .007		39.5	2.250	2.220	2.235 ± .015	
20.5	2.592	2.586	2.589 ± .003		40.5	2.224	2.220	2.222 ± .002	
21.5	2.618	2.606	2.612 ± .006		41.5	2.108	2.087	2.098 ± .010	
22.5	2.582	2.609	2.596 ± .004		42.5	2.088	2.097	2.092 ± .004	
23.5	2.489	2.462	2.476 ± .014		43.5	2.088	2.110	2.099 ± .011	
24.5	2.479	2.503	2.491 ± .012		44.5	2.076	2.120	2.098 ± .022	
25.5	2.512	2.504	2.508 ± .004		45.5	2.120	2.100	2.110 ± .010	
				.015					.014
26.5	2.499	2.484	2.492 ± .008		46.5	2.054	2.040	2.047 ± .007	
27.5	2.406	2.362	2.384 ± .022		47.5	2.070	2.030	2.050 ± .020	
28.5	2.372	2.420	2.396 ± .024		48.5	2.038	2.052	2.045 ± .007	
29.5	2.394	2.359	2.376 ± .018		49.5	2.040	2.044	2.042 ± .002	
30.5	2.390	2.380	2.385 ± .005		50.5	2.030	2.060	2.045 ± .015	
					51.5	2.030	2.050	2.040 ± .010	
					52.5	2.001	1.980	1.990 ± .010	
				Mean = .014					Mean = .013

tion energy versus temperature graph. The addition of small quantities of another component to the liquid would then be expected to produce small, regular changes in the energies and critical temperatures for the various series of domains, in agreement with the graphs of Fig. 3. For the further elaboration of these ideas, more detailed experiments are planned on the water-alcohol and other binary systems.

Since the water-alcohol system has been studied extensively by previous workers, it was thought likely that the earlier viscosity data might show some evidence of the two deepest steps (of depth 0.15 and 0.13 unit, respectively) observed at 13.5°C. and 41°C. in the curve for 11% aqueous alcohol in Fig. 3. Accordingly, Table 4 gives the viscosity data in centipoises for 10% ethyl alcohol (by weight) obtained from the International Critical Tables[6] and Landolt-Boernstein Tables,[7] while the inset to Fig. 3 is a plot of mean $\ln \eta$ against $1/T$ for this data. It is seen that the graph does break up approximately into three straight lines, with quite conspicuous kinks at 15 ± 2°C., and 39 ± 2°C., in good agreement with the two deepest steps observed by us for 11% alcohol. The error in the experimental data in Table 4 is believed to be something of the order of ± 0.3%, i.e. 0.003 in $\ln \eta$, which is apparently sufficient to obscure the remaining shallower steps to be seen in the graphs of Fig. 3 for $(\varepsilon'/k)/1000$. Further experiments with other alcohol concentrations are being conducted for a fuller elucidation of the observed phenomena.

TABLE 4.—EARLIER STANDARD VISCOSITY DATA FOR 10% AQUEOUS ETHYL ALCOHOL.

Temperature °C.	0	5	10	15	20	25	30	35	40	45	50	55	60	65	70
Int. Critical	3.125	—	2.162	—	1.548	1.328	1.153	—	.896	—	.725	—	.602	—	.509
Landolt-Boernstein	3.331	2.577	2.179	1.792	1.538	1.323	1.160	1.006	.907	.812	.734	.663	.609	.554	.514
Mean $\ln \eta$	1.166	.946	.755	.583	.434	.282	.145	.002	−.104	−.225	−.315	−.417	−.502	−.597	−.670

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