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

Part II.—Further Measurements on the Activation Energy of Viscous Flow for Aqueous Ethanol in the Concentration Range of 0 to 5%

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A detailed examination of the concentration dependence of the jumps in E_η for several aqueous solutions from 0% to 5% ethanol is undertaken at increments of nearly 0.9% ethanol. E_η is obtained by using the Andrade equation after differentiation, *viz.*

$$E_\eta/R = \Delta\ln\eta/\Delta\left(\frac{1}{T}\right) = -T^2\Delta\ln\eta/\Delta T$$

For studying the course of the movements of these energy jumps as a function of alcohol concentration, a chart is prepared for the various energy jumps, which are classified as large, medium or small compared to mean value of $(\Delta E/R)/1000 = 0.07$. The shifts of these jumps with the concentration changes are mostly smooth, in agreement with the ideas advanced earlier, but there is evidence for branching of these discontinuities into pairs at certain alcohol concentrations. This is accompanied by appearance and disappearance of certain jumps, so that in these regions the detailed chart looks substantially different from the earlier one based on data at interval of about 2% ethanol.

Introduction

The existence of sharp jumps in the activation energy of viscous flow E_η has been established on a firm footing in the case of several liquids, such as water,[1] ethylene glycol,[2] light hydrocarbons[3] and mineral oils.[4] Similar jumps were found in a series of experiments on dilute aqueous ethanol[5] and it was confirmed that E_η remains sensibly constant over certain temperature ranges and then sharply drops from one stage to the next. It was noted, that in the concentration range from 2.5% to 30% alcohol, these jumps occur at intervals of 4°C. to 8°C., and the magnitude of ΔE at each jump is of the order of 0.1 to 0.3 cal./mole. To further investigate the character of these jumps, the concentration range from 0% to 11% has been examined by Ahsanullah and Qurashi[6] (1965) by working with three more solutions of intermediate concentrations, namely 2.5%, 6.9% and 9.2%, so as to trace out the course of these jumps as a function of concentration. It appeared possible that these movements of the jumps might be discontinuous in character, especially in the region of 26°C. to 42°C. and for 2.5% to 6% ethanol solutions.

Lately, the derivatives of refractive index dn/dt, and of coefficient of dilatation, in addition to that of viscosity, have been the subject of investigation in this laboratory, and it was observed in Part I of the present series of papers that the temperatures at the minimum of (-dn/dt) values for five solutions of ethanol in water were quite close to the sharp jumps in E_η of that particular concentration, thus establishing a degree of correspondence between these two phenomena. Tentative charts, each containing series of graphs (Fig. 1) showing the variation of temperature for a particular energy jump (and minimum observed in -dn/dt) were prepared for 3% to 11% ethanol. This generally confirmed the earlier results, but the concentration intervals used were fairly large, *viz.*, of the order of 2% ethanol, thus leaving room for ambiguity in several regions. In order to further elucidate these phenomena and the nature of these transitions or discontinuities, it was considered worthwhile to undertake a detailed study of the jumps of E_η in the concentration range of 0 to 5% ethanol. The present communication describes some accurate measurements with dilute aqueous ethanol solutions covering the whole range of 0 to 5% in six increments of nearly 0.9% alcohol each. New activation energy measurements have been made on 0.9%, 1.8%, 3.5% and 4.1% ethanol solutions, each set being performed with a temperature interval of 1°C. between successive observations.

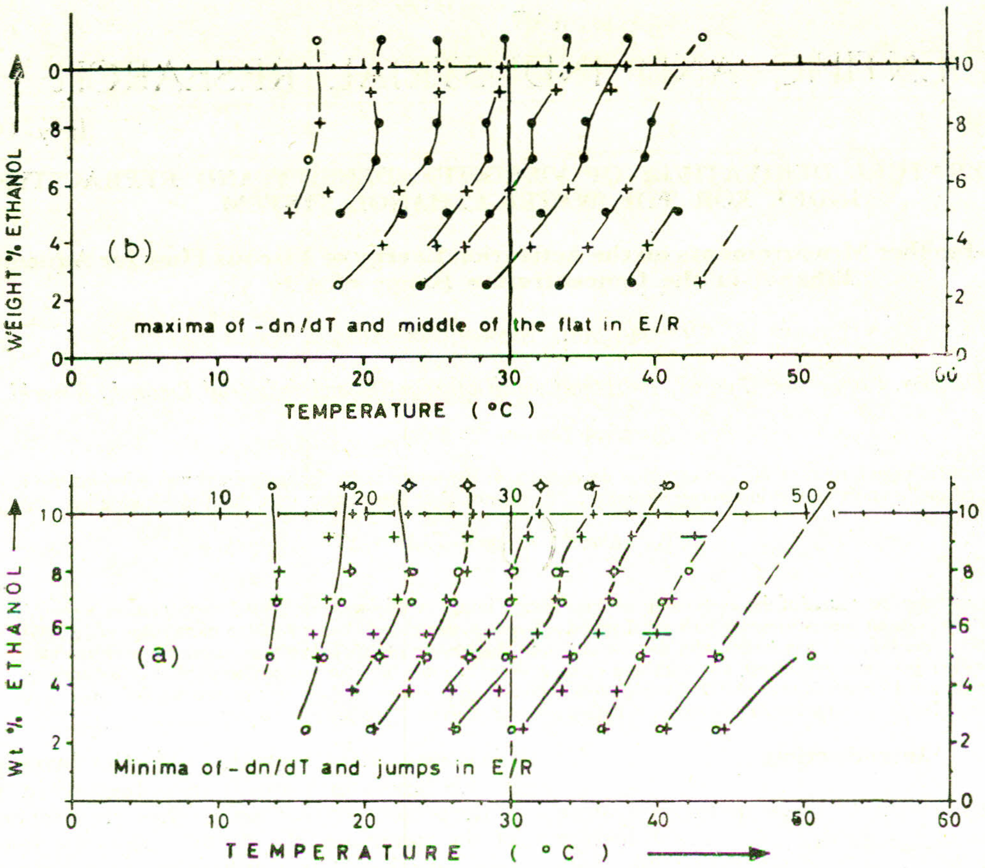

Fig. 1.—Reproduction of the plot of jumps in E and minima in (-dn/dt) from the earlier work of Qureshi, Haider and Qurashi, for some ethanol solutions from 2% to 11%. (a) Temperature-concentration charts, showing the dependence of a particular minimum of (-dn/dt) and corresponding energy jumps on the concentration of the alcohol. The hollow circles are for the temperature obtained from the jumps in E/R and the crosses are for the temperature for the minima of (-dn/dt). (b) Corresponding charts for the maxima of (-dn/dt) and middle points of the regions of constant energy. The crosses are for the maxima of (-dn/dt) and solid circles are for the mean of the values from dn/dt and E/R graphs. The graphs of Figs. 1(a) and (b) show anomalies in region of 26°C. to 42°C. and for the portion near 3.5% ethanol solution.

Experimental Technique

The experimental procedure is essentially the same as adopted before for the $E\eta$ measurements on water and glycol, and discussed in detail for dilute alcohol by Ahsanullah and Qurashi.[6] Contrary to the usual practice of measuring the slope of the tangent at various points in question on the plot of $\ln\eta$ against $1/T$, the value of $E\eta$ is determined by measuring the kinematic viscosity with high precision at close temperature intervals; this interval is nearly 1°C. in the present case. (This differential technique has the advantage of eliminating the uncertainty in drawing tangents as well as the error in the calibration of stop watches and adjustment of liquid level after every reading). The activation energy $E\eta$ is obtained from the differential of Andrade equation:

$$\eta = A \exp E\eta/RT$$

$$i.e\, E\eta/R = \Delta \ln\eta/\Delta\left(\frac{1}{T}\right) = -T^2\Delta\ln\eta/\Delta T = -T^2\Delta\ln(\nu\times\rho)/\Delta T$$

$$= -T^2\Delta\ln\nu/\Delta T + T^2\beta = \frac{E\nu}{R} + T^2\beta$$

where η is dynamic viscosity, ρ is the density and β is the coefficient of dilatation of the liquid. $T^2\beta$ forms a small slowly-varying correction term.

The kinematic viscosities are obtained by measuring, with a calibrated stop watch reading to 0.1 second, the time of flow four to six times through a U-Tube Viscometer No. "1" (constant 0.00401) of British Standard Specifications, supported vertically by a rigid clamp in a thermostat giving a temperature stability of ±0.002°C. or better. The actual temperature is read by ordinary mercury thermometer graduated to one-tenth of a degree, while the interval ΔT is recorded over six degrees with a Beckmann differential thermometer, calibrated previously by intercalibration method. The height of the liquid meniscus at equilibrium above the fiducial mark on the large bulb of the viscometer is read by cathetometer to 0.001 cm. and appropriate correction is applied to flow time. Since the time of flow ranges from 200 to 600 seconds, and is read to ±0.01 second, all the above measures ensure a reproducibility of 1 in 40,000 or better, in the final value of viscosity.

The water content of each solution is checked and rechecked at various stages, especially at the beginning and at the end of each experiments by density and viscosity measurements, carried out at two to three different temperatures. When working at the higher temperatures, a ballast bottle, connected to the wide limb of the viscometer, was immersed inside the bath and held some of the particular solution used in the viscometer.[1] This enables control of the evaporation of the test liquid by setting up a dynamic vapour equilibrium.

Results on 0.9% and 1.8% of Aqueous Ethanol

It was considered desirable to explore first the region between 0% and 2.5% ethanol content, and for this purpose solutions containing 0.9% and 1.8% alcohol by weight were prepared by adding measured quantity of absolute ethanol to thrice-distilled conductivity water and were subjected to viscosity determination. Since the ethanol in these solutions is liable to evaporation to a significant extent at higher temperatures, resulting in significant change in the ethanol percentage, counter-measures were adopted by (i) using the ballast bottles mentioned earlier (ii) checking the alcohol content at different stages, so that overall deviation in the concentration during the whole course of experiments may not exceed ±0.05% ethanol. The dilute solution containing 0.9% alcohol was subjected to flow activation energy measurements at the interval of 1°C. in the temperature range of 10 to 60°C., and Table 1(a) contains the values of E/R÷1000 for rising and falling sequences deduced from the Beckmann readings, temperatures °C. and time of flow (corrected for level). The E/R ÷1000 values are represented by the lower curve drawn through the solid circles of the Fig. 2, where the full line graph for pure water is shown shifted downward relative to the vertical scale by 0.2 unit of E/R $\times 10^{-3}$. There are a succession of the steps at nearly 4.5°C. interval from 10° to 60°C. with average step depth of 0.09 unit of E/R÷1000 while r.m.s. deviation is ±0.004 units.

TABLE 1(a).—MEASURED ACTIVATION ENERGIES E/R÷1000 = -($T^2\Delta$ ln $\nu/\Delta T$)/1000 FOR 0.9% AQUEOUS ETHANOL SOLUTION.

Temperature °C.	E/R ÷ 1000 = -T^2 (Δ ln ν/ΔT)/1000		
	Heating sequence	Cooling sequence	Mean E/R ÷ 1000
10.50	2.306±0.003	2.313±0.003	2.310±0.003
11.50	2.294±0.003	2.305±0.003	2.300±0.005
12.50	2.298±0.003	2.292±0.003	2.295±0.003
13.50	2.317±0.003	2.302±0.003	2.310±0.008
14.50	2.206±0.003	2.213±0.003	2.210±0.003
15.50	2.204±0.003	2.207±0.003	2.205±0.002
16.50	2.218±0.003	2.231±0.003	2.225±0.007
17.50	2.186±0.003	2.176±0.003	2.181±0.005
18.50	2.073±0.003	2.080±0.003	2.076±0.004
19.50	2.103±0.003	2.098±0.003	2.100±0.003
20.50	2.092±0.004	2.097±0.004	2.094±0.003
21.50	2.116±0.004	2.103±0.004	2.109±0.007
22.50	2.101±0.004	2.109±0.004	2.105±0.004
23.50	2.072±0.004	2.078±0.004	2.075±0.003
24.50	1.996±0.004	1.983±0.004	1.990±0.006
25.50	2.006±0.004	1.995±0.004	2.001±0.005
26.50	1.999±0.004	2.009±0.004	2.004±0.005
27.50	2.000±0.004	1.993±0.004	1.997±0.003
28.50	1.987±0.004	1.994±0.004	1.991±0.004
29.50	2.003±0.004	1.998±0.004	2.001±0.003
30.50	1.999±0.005	1.990±0.005	1.995±0.005
31.50	1.894±0.005	1.905±0.005	1.899±0.006
32.50	1.903±0.005	1.897±0.005	1.900±0.003
33.50	1.893±0.005	1.908±0.005	1.901±0.007
34.50	1.904±0.005	1.896±0.005	1.900±0.004
35.50	1.901±0.004	1.912±0.004	1.906±0.006
36.50	1.803±0.004	1.796±0.004	1.799±0.003
37.50	1.802±0.004	1.809±0.004	1.806±0.004
38.50	1.816±0.004	1.805±0.004	1.811±0.006
39.50	1.783±0.004	1.792±0.004	1.788±0.004
40.50	1.769±0.005	1.764±0.005	1.767±0.003
41.50	1.775±0.005	1.783±0.005	1.779±0.004
42.50	1.789±0.005	1.782±0.005	1.786±0.003
43.50	1.782±0.005	1.779±0.005	1.881±0.003
44.50	1.723±0.005	1.736±0.005	1.729±0.004
45.50	1.730±0.004	1.717±0.004	1.723±0.007
46.50	1.725±0.004	1.734±0.004	1.729±0.005
47.50	1.731±0.004	1.739±0.004	1.735±0.004
48.50	1.726±0.004	1.714±0.004	1.720±0.006
49.50	1.730±0.004	1.739±0.004	1.334±0.004
50.50	1.638±0.005	1.626±0.005	1.632±0.004
51.50	1.600±0.005	1.609±0.005	1.605±0.005
52.50	1.601±0.005	1.610±0.005	1.606±0.005
53.50	1.609±0.005	1.602±0.005	1.606±0.004
54.50	1.634±0.005	1.619±0.005	1.627±0.008
55.50	1.609±0.005	1.600±0.005	1.604±0.004
56.50	1.570±0.005	1.584±0.005	1.577±0.006
57.50	1.632±0.005	1.619±0.005	1.625±0.007
58.50	1.554±0.005	1.567±0.005	1.561±0.006
59.50	1.507±0.005	1.513±0.005	1.510±0.003

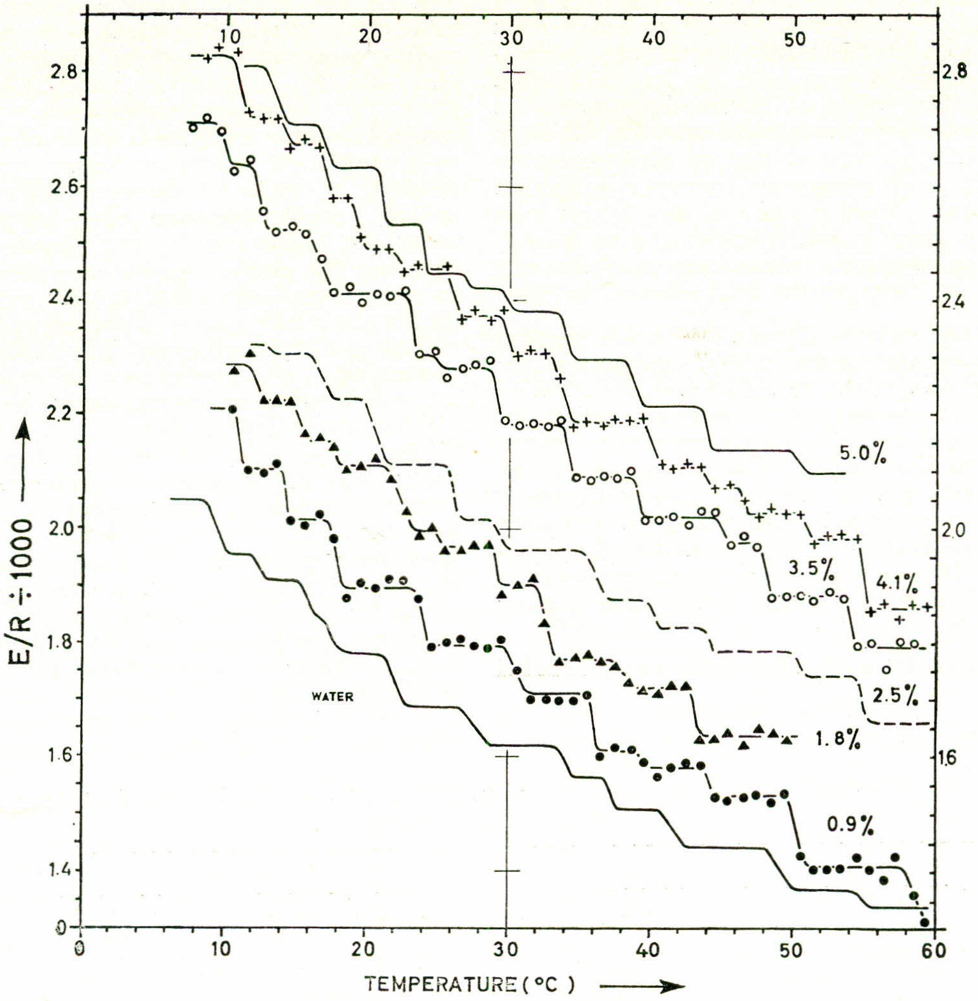

Fig. 2.—Plots of E/R 1000 against temperature for various concentrations of ethanol solutions, each shifted 0.1 unit upwards above the lower concentration. The scale is correct for the broken-line curve in the middle of the figure, which represents 2.5% solutions of the earlier data. The lowest full-line curve for pure water (i.e. 0% ethanol) is also reproduced from the earlier work, and the curve drawn through the solid circles, shifted 0.1 unit above this, is for 0.9% ethanol, while that through the triangles and shifted 0.2 units above the curve for water is for 1.8% ethanol solutions.

The curve for 3.5% ethanol is drawn through the hollow circles, while that through the crosses (0.1 unit above this) is the curve for 4.1% alcohol solution. The curve for 5% ethanol from the earlier work is indicated by the full-line at the top (shifted 0.3 units above that for 2.5% solution).

Table 1(b) shows the measured values for 1.8% solutions, both for heating and cooling sequences against the temperature and their standard deviation. These E_η values also have an r.m.s. scatter of the order of ±0.005 units and are plotted as triangles (shifted up 0.1 above the curve for 0.9% alcohol). Each of these steps extends over approximately 4.0°C., with average drop of 0.07 unit of (E/R)/1000 between steps. We may conjecture that this decrease in the temperature interval is due to appearance of certain sub-steps. The movement of some of the main steps can be readily traced in Fig. 2 from pure water through 0.9% and 1.8% upto 2.5% ethanol for which the broken line graph is plotted one unit above that for 1.8%.

TABLE 1(b).—MEASURED ACTIVATION ENERGIES $E/R \div 1000 = -T^2 (\Delta \ln \nu/\Delta T)/1000$ FOR 1.8% AQUEOUS ETHANOL SOLUTIONS, IN THE RANGE OF 10 TO 51 °C.

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
10.50	2.380±0.003	2.368±0.003	2.374±0.006	31.50	2.019±0.005	2.010±0.005	2.015±0.005
11.50	2.400±0.003	2.407±0.003	2.403±0.004	32.50	1.941±0.005	1.930±0.005	1.935±0.005
12.50	2.326±0.003	2.318±0.003	2.322±0.004	33.50	1.860±0.005	1.869±0.005	1.865±0.004
13.50	2.322±0.003	2.321±0.003	2.322±0.001	34.50	1.868±0.005	1.879±0.005	1.874±0.005
14.50	2.329±0.003	2.320±0.003	2.325±0.004	35.50	1.886±0.005	1.877±0.005	1.882±0.005
15.50	2.268±0.005	2.361±0.005	2.365±0.003	36.50	1.871±0.005	1.861±0.005	1.866±0.005
16.50	2.252±0.005	2.258±0.005	2.255±0.003	37.50	1.864±0.005	1.859±0.005	1.861±0.003
17.50	2.246±0.005	2.233±0.005	2.240±0.007	38.50	1.837±0.005	1.824±0.005	1.831±0.007
18.50	2.197±0.005	2.204±0.005	2.201±0.003	39.50	1.819±0.005	1.810±0.005	1.815±0.005
19.50	2.209±0.005	2.201±0.005	2.205±0.004	40.50	1.815±0.006	1.807±0.006	1.811±0.004
20.50	2.228±0.004	2.213±0.004	2.220±0.007	41.50	1.826±0.006	1.815±0.006	1.822±0.006
21.50	2.179±0.004	2.172±0.004	2.176±0.003	42.50	1.824±0.006	1.820±0.006	1.822±0.002
22.50	2.136±0.004	2.125±0.004	2.131±0.005	43.50	1.725±0.006	1.736±0.006	1.730±0.006
23.50	2.091±0.004	2.080±0.004	2.086±0.006	44.50	1.736±0.006	1.729±0.006	1.733±0.004
24.50	2.103±0.004	2.100±0.004	2.102±0.002	45.50	1.748±0.006	1.731±0.006	1.740±0.008
25.50	2.056±0.006	2.058±0.006	2.057±0.002	46.50	1.726±0.006	1.713±0.006	1.720±0.007
26.50	2.066±0.006	2.061±0.006	2.063±0.003	47.50	1.755±0.006	1.746±0.006	1.751±0.006
27.50	2.073±0.006	2.064±0.006	2.068±0.004	48.50	1.742±0.006	1.740±0.006	1.741±0.002
28.50	2.077±0.006	2.065±0.006	2.071±0.006	49.50	1.729±0.006	1.730±0.006	1.730±0.001
29.50	1.988±0.005	1.981±0.005	1.985±0.004	50.50			
30.50	2.006±0.005	1.995±0.005	2.015±0.006				

Note.—The deviations quoted with the overall means are half the differences between the values of $E/R \div 1000$ for the heating and cooling sequences.

Results with 3.5% and 4.1% Ethanol

To further trace out the movements of the energy jumps over the large gap between the previously reported data for solutions of 2.5% and 5% alcohol concentration, it was considered desirable to examine two more solutions in this concentration range. Aqueous ethanol of 3.5% and 4.1% concentration was prepared and used for the viscosity measurements with a thermal interval of 1°C. and the usual precautions, particularly against the evaporation of the test liquid. The flow activation energy values for the 3.5% ethanol solution, both for heating and cooling sequences, together with their r.m.s. deviations (estimated from those of flow time and temperature), are given in Table 2(a). The curve drawn through hollow circles represents the mean values of $E/R \div 1000$ for 3.5% dilute ethanol solution on vertical scale shifted 0.1 unit above 2.5% solution, while that shifted 0.2 units above through the corsses represents the 4.1% ethanol solution, both performed in the range of 7°C. to 60°C. The average step length is 4.4°C. and 3.7°C. with the mean drop of 0.08 and 0.075 units of $(E/R)/1000$.

Table 2(b) gives the Beckmann reading, corrected time of flow, mean temperature and calculated $(E/R)/1000$ values, together with their r.m.s. deviation (of the order of ±0.006) for 4.1% ethanol. For comparison purposes, the graph for 5,0% ethanol is reproduced from the earlier data and is represented, shifted 0.1 unit above 4.1% graph, by the full line in the top of Fig. 2.

Discussion

For understanding the exact course of the movements of the energy transition, as a function of concentration, a brief synopsis is given in Table 3. This Table gives the temperature at the various energy jumps or transitions, and their depths in terms of $(E/R)/1000$. This covers the range of 0% to 5% ethanol concentration and the various jumps are classified as "large" "medium" or "small", using the mean value of $\frac{\Delta E}{R}/1000 = 0.07$. A plot of the temperatures at the jumps for these solutions versus the concentration is given in Fig. 3, where the circles stand for large jumps, triangles for medium, and crosses for small ones.

TABLE 2(a).—MEASURED ACTIVATION ENERGIES $E/R \div 1000 = -T^2 (\Delta \ln \nu/\Delta T)/1000$ FOR 3·5% w/w AQUEOUS ETHANOL SOLUTION IN THE RANGE OF 7°C TO 59°C.

Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln \nu/\Delta T))/1000$ Heating sequence	Cooling sequence	Overall mean	Temperature °C.	$E/R \div 1000 = -T^2 (\Delta \ln \nu/\Delta T)/1000$ Heating sequence	Cooling sequence	Overall mean
7.50	2.606±0.004	2.601±0.004	2.603±0.003	33.50	2.095±0.003	2.086±0.003	2.091±0.005
8.50	2.631±0.004	2.618±0.004	2.625±0.007	34.50	1.983±0.003	1.980±0.003	1.981±0.002
9.50	2.600±0.004	2.594±0.004	2.597±0.003	35.50	1.990±0.003	1.981±0.003	1.986±0.005
10.50	2.531±0.004	2.519±0.004	2.525±0.006	36.50	1.993±0.003	1.987±0.003	1.990±0.003
11.50	2.547±0.004	2.544±0.004	2.546±0.002	37.50	1.993±0.004	1.986±0.004	1.990±0.004
12.50	2.460±0.004	2.451±0.004	2.456±0.005	38.50	2.002±0.004	2.000±0.004	2.001±0.001
13.50	2.416±0.004	2.425±0.004	2.421±0.004	39.50	1.913±0.004	1.908±0.004	1.910±0.002
14.50	2.427±0.004	2.434±0.004	2.430±0.003	40.50	1.916±0.004	1.907±0.004	1.912±0.005
15.50	2.421±0.004	2.428±0.004	2.425±0.003	41.50	1.923±0.005	1.928±0.005	1.926±0.003
16.50	2.378±0.004	2.371±0.004	2.375±0.004	42.50	1.908±0.005	1.901±0.005	1.905±0.004
17.50	2.313±0.004	2.311±0.004	2.312±0.001	43.50	1.937±0.005	1.922±0.005	1.929±0.007
18.50	2.330±0.004	2.320±0.004	2.325±0.005	44.50	1.927±0.005	1.923±0.005	1.925±0.002
19.50	2.301±0.004	2.291±0.004	2.296±0.005	45.50	1.868±0.004	1.872±0.004	1.870±0.002
20.50	2.313±0.005	2.311±0.005	2.312±0.001	46.50	1.884±0.004	1.877±0.004	1.881±0.004
21.50	2.307±0.005	2.298±0.005	2.303±0.004	47.50	1.867±0.004	1.869±0.004	1.868±0.001
22.50	2.318±0.005	2.311±0.005	2.315±0.004	48.50	1.786±0.004	1.775±0.004	1.781±0.006
23.50	2.203±0.005	2.201±0.005	2.202±0.001	49.50	1.784±0.004	1.777±0.004	1.780±0.004
24.50	2.216±0.005	2.205±0.005	2.211±0.006	50.50	1.788±0.004	1.781±0.004	1.785±0.004
25.50	2.170±0.003	2.161±0.003	2.166±0.005	41.50	1.770±0.004	1.781±0.004	1.775±0.006
26.50	2.183±0.003	2.188±0.003	2.185±0.003	52.50	1.785±0.004	1.780±0.004	1.783±0.003
27.50	2.185±0.003	2.180±0.003	2.182±0.003	53.50	1.775±0.004	1.774±0.004	1.775±0.001
28.50	2.193±0.003	2.187±0.003	2.190±0.003	54.50	1.700±0.004	1.692±0.004	1.696±0.004
29.50	2.099±0.003	2.090±0.003	2.094±0.005	55.50	1.706±0.006	1.696±0.006	1.701±0.005
30.50	2.086±0.003	2.075±0.003	2.081±0.006	56.50	1.648±0.006	1.661±0.006	1.655±0.007
31.50	2.088±0.003	2.080±0.003	2.084±0.004	57.50	1.697±0.006	1.704±0.006	1.701±0.003
32.50	2.077±0.003	2.082±0.003	2.080±0.002	58.50	1.705±0.006	1.697±0.006	1.701±0.004

Several of these plotted points can be definitely linked together, as represented by the full lines, while other involve some ambiguity, and are joined by broken lines. In two regions, where part of the data is not available so far, the probable course of the jumps is indicated by dotted lines.

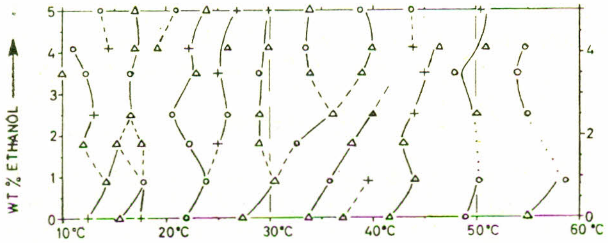

Fig. 3.—Chart showing the position of the jumps in the flow activation energy for several ethanol concentrations in the range of 0% to 5% ethanol. The various jumps are classified as large, medium or small (compared with the mean value of $\Delta(E/R)/1000 = 0.07$), and are plotted as circles, triangles and crosses, respectively. The full lines connecting some of the plotted points indicate the more or less definite movements of these jumps, and the broken lines stand for those parts involving some ambiguity. The dotted lines show the *possible* course of the jumps in two regions where the data is not available at present. Several new branches appear to develop in this chart.

A careful examination of this plot shows that the shift of these jumps with changes in concentration is mostly smooth in character, in agreement with the idea advanced earlier, but does not always follow the pattern in Fig. 1 based on the results of the previous communications. Two facts are clear; firstly, there is appearance and disappearance of certain steps accompanied by changes in the magnitude of the jump; secondly, the phenomena are rather complex in some regions where branching of the discontinuities with the variation of alcohol concentration takes place, particularly at the temperatures around 30°C. For instance, the jump in 0% (i.e. water) at 22.0°C. and 27.4°C. are branched with 0.9% solutions at 23.8°C. and 30.6°C. respectively. The two branches of first jump are going normally up to 5% ethanol, while for the second jump one branch goes more or less straight near 29°C. and the other is further branched at 2.5% solutions.

Table 2 (b).—Beckmann Readings, Flow Times and the Calculated Values of $(E/R)/1000 = -T^2(\Delta\ln\nu/\Delta T)/1000$ for 4.1% Aqueous Ethanol in the Range of 8°C. to 61°C.

	Heating sequence						Cooling sequence					
Tempe-rature °C.	Beckmann reading	Time of flow corrected for level	Mean tempe-rature. °C.	E/R ÷ 1000		Tempe-rature °C.	Beckmann reading	Time of flow corrected for level	Mean tempe-rature- °C.	E/R ÷ 1000		Mean E/R ÷ 1000
				Uncorrec-ted	Correc-ted					Uncorrec-ted	Correc-ted	
1	2	3	4	5	6	7	8	9	10	11	12	13
8.0	3.762±0.000	446.21±0.01				8.0	3.761±0.000	446.08±0.01				
			8.50	2.630	2.625±0.003				8.50	2.622	2.617±0.003	2.621±0.004
9.0	2.761±0.000	431.64±0.02				9.0	2.762±0.001	431.59±0.01				
			9.50	2.650	2.648±0.003				9.50	2.634	2.632±0.003	2.640±0.008
10.0	1.762±0.001	417.57±0.01				10.0	1.761±0.001	417.59±0.02				
			10.50	2.626	2.626±0.003				10.50	2.634	2.634±0.003	2.630±0.004
11.0	0.761±0.001	404.15±0.02				11.0	0.762±0.000	404.15±0.01				
11.0	4.072±0.000	404.42±0.01				11.0	4.076±0.000	403.40±0.01				
			11.50	2.517	2.521±0.005				11.50	2.532	2.536±0.005	2.528±0.008
12.0	3.072±0.001	392.05±0.02				12.0	3.072±0.001	391.91±0.02				
			12.50	2.518	2.513±0.005				12.50	2.535	2.530±0.005	2.521±0.009
13.0	2.072±0.000	380.14±0.01				13.0	2.076±0.000	379.97±0.01				
			13.50	2.522	2.520±0.005				13.50	2.525	2.523±0.005	2.521±0.002
14.0	1.071±0.001	368.59±0.02				14.0	1.074±0.001	368.45±0.02				
			14.50	2.476	2.473±0.005				14.50	2.466	2.463±0.005	2.468±0.005
15.0	0.072±0.000	357.70±0.01				15.0	0.073±0.000	357.62±0.01				
15.0	3.646±0.000	356.64±0.01				15.0	3.646±0.000	356.56±0.02				
			15.50	2.491	2.491±0.005				15.50	2.478	2.478±0.005	2.485±0.006
16.0	2.647±0.001	346.16±0.01				16.0	2.647±0.000	346.12±0.01				
			16.50	2.469	2.470±0.005				16.50	2.465	2.466±0.005	2.468±0.002
17.0	1.647±0.000	336.12±0.01				17.0	1.647±0.001	336.10±0.02				
			17.50	2.373	2.373±0.005				17.50	2.389	2.389±0.005	2.381±0.008
18.0	0.647±0.001	326.81±0.02				18.0	0.646±0.000	326.72±0.02				
18.0	5.041±0.001	327.54±0.01				18.0	5.042±0.000	327.41±0.01				
			18.50	2.377	2.382±0.005				18.50	2.373	2.378±0.005	2.380±0.008
19.0	4.042±0.000	318.52±0.01				19.0	4.042±0.000	318.41±0.01				
			19.50	2.321	2.321±0.005				19.50	2.313	2.313±0.005	2.317±0.004
20.0	3.042±0.001	310.00±0.00				20.0	3.043±0.000	309.94±0.02				
			20.50	2.285	2.285±0.005				20.50	2.297	2.297±0.005	2.291±0.006
21.0	2.042±0.000	301.89±0.01				21.0	2.043±0.000	301.80±0.01				
			21.50	2.286	2.286±0.005				21.50	2.294	2.294±0.005	2.290±0.004
22.0	1.042±0.000	294.04±0.02				22.0	1.041±0.000	293.92±0.01				
22.0	4.383±0.000	293.42±0.01				22.0	4.382±0.000	293.49±0.01				
			22.50	2.255	2.254±0.003				22.50	2.247	2.246±0.003	2.250±0.004
23.0	3.382±0.001	285.94±0.01				23.0	3.382±0.000	286.04±0.01				

(*Table Continued*)

1	2	3	4	5	6	7	8	9	10	11	12	13
			23.50	2.272	2.269±0.003				23.50	2.260	2.257±0.003	2.263±0.006
24.0	2.355±0.000	278.46±0.00				24.0	2.355±0.001	278.60±0.00				
			24.50	2.242	2.244±0.003				24.50	2.254	2.256±0.003	2.250±0.006
25.0	1.355±0.000	271.50±0.01				25.0	1.355±0.001	271.60±0.01				
			25.50	2.263	2.263±0.003				25.50	2.258	2.258±0.003	2.260±0.003
26.0	0.354±0.001	264.69±0.00				26.0	0.355±0.000	264.81±0.01				
26.0	5.045±0.001	264.86±0.01				26.0	5.044±0.001	265.35±0.01				
			26.50	2.158	2.160±0.005				26.50	2.168	2.170±0.005	2.165±0.005
27.0	4.045±0.000	258.57±0.01				27.0	4.044±0.000	259.02±0.01				
			27.50	2.184	2.179±0.005				27.50	2.194	2.189±0.005	2.184±0.005
28.0	3.045±0.000	252.41±0.01				28.0	3.044±0.001	252.81±0.01				
			28.50	2.169	2.163±0.005				28.50	2.177	2.171±0.005	2.167±0.004
29.0	2.043±0.001	246.46±0.00				29.0	2.045±0.000	246.84±0.00				
			29.50	2.180	2.186±0.005				29.50	2.172	2.178±0.005	2.182±0.004
30.0	1.045±0.000	240.69±0.00				30.0	1.042±0.001	244.04±0.01				
30.0	4.699.0±001	241.06±0.01				30.0	4.696±0.001	240.79±0.01				
			30.50	2.100	2.100±0.006				30.50	2.103	2.103±0.006	2.101±0.002
31.0	3.698±0.000	235.63±0.00				31.0	3.696±0.001	235.36±0.01				
			31.50	2.119	2.114±0.006				31.50	2.110	2.105±0.006	2.110±0.005
32.0	2.693±0.000	230.29±0.01				32.0	2.694±0.000	230.66±0.00				
			32.50	2.100	2.107±0.006				32.50	2.119	2.116±0.006	2.112±0.004
33.0	1.699±0.000	225.20±0.01				33.0	1.697±0.001	224.94±0.01				
			33.50	2.054	2.059±0.006				33.50	2.064	2.068±0.006	2.064±0.004
34.0	0.698±0.001	220.33±0.01				34.0	0.698±0.000	220.06±0.01				
34.0	4.546±0.000	220.10±0.00				34.0	4.546±0.000	220.17±0.01				
			34.50	1.981	1.981±0.006				34.50	1.970	1.970±0.006	1.976±0.006
35.0	3.544±0.000	215.54±0.01				35.0	3.545±0.001	215.63±0.01				
			35.50	1.983	1.983±0.006				35.50	1.991	1.991±0.006	1.987±0.004
36.0	2.546±0.001	211.11±0.01				36.0	2.545±0.000	211.17±0.00				
			36.50	1.983	1.983±0.006				36.50	1.977	1.977±0.006	1.980±0.003
37.0	1.546±0.000	206.79±0.00				37.0	1.547±0.000	206.87±0.00				
			37.50	1.993	1.997±0.006				37.50	1.981	1.985±0.006	1.991±0.006
38.0	0.546±0.001	262.56±0.01				38.0	0.546±0.000	202.67±0.01				
38.0	4.535±0.000	202.92±0.01				38.0	4.567±0.000	203.17±0.00				
			38.50	1.990	1.990±0.005				38.50	1.984	1.984±0.005	1.987±0.003
39.0	3.573±0.001	198.96±0.01				39.0	3.567±0.001	199.06±0.01				
			39.50	1.990	1.987±0.005				39.50	2.000	1.997±0.005	1.992±0.006
40.0	2.568±0.000	194.97±0.00				40.0	2.567±0.000	195.03±0.00				
			40.50	1.915	1.915±0.005				40.50	1.905	1.905±0.005	1.910±0.005
41.0	1.568±0.001	191.21±0.00				41.0	1.565±0.001	191.29±0.01				
			41.50	1.908	1.906±0.005				41.50	1.902	1.900±0.005	1.903±0.003
42.0	0.571±0.000	187.58±0.01				42.0	0.567±0.000	187.51±0.00				

(*Continued*)

(*Table Continued*)

1	2	3	4	5	6	7	8	9	10	11	12	13
42.0	5.013±0.001	187.60±0.01				42.0	5.011±0.001	187.46±0.01				
			42.50	1.916	1.917±0.006				42.50	1.903	1.905±0.006	1.912±0.008
43.0	4.012±0.000	184.02±0.00				43.0	4.011±0.000	183.91±0.00				
			43.50	1.900	1.900±0.006				43.50	1.910	1.910±0.006	1.905±0.005
44.0	3.015±0.001	180.57±0.01				44.0	3.011±0.001	180.44±0.01				
			44.50	1.880	1.878±0.006				44.50	1.866	1.864±0.006	1.871±0.007
45.0	1.978±0.001	177.11±0.00				45.0	1.978±0.000	177.03±0.00				
			45.50	1.880	1.884±0.006				45.50	1.872	1.876±0.006	1.880±0.004
46.0	0.923±0.000	173.69±0.01				46.0	0.920±0.000	173.61±0.01				
46.0	4.774±0.000	173.46±0.00				46.0	4.975±0.001	173.40±0.01				
			46.50	1.850	1.850±0.006				46.50	1.840	1.840±0.006	1.845±0.005
47.0	3.929±0.001	170.21±0.01				47.0	3.936±0.000	170.20±0.00				
			47.50	1.824	1.823±0.006				47.50	1.816	1.815±0.006	1.819±0.004
48.0	2.927±0.000	167.21±0.01				48.0	2.919±0.001	167.17±0.01				
			48.50	1.840	1.837±0.006				48.50	1.836	1.833±0.006	1.835±0.002
49.0	1.901±0.001	164.18±0.00				49.0	1.893±0.000	164.22±0.00				
			49.50	1.826	1.829±0.006				49.50	1.818	1.821±0.006	1.825±0.004
50.0	0.841±0.000	161.15±0.01				50.0	0.843±0.001	161.24±0.00				
50.0	5.036±0.001	161.26±0.00				50.0	5.035±0.000	161.09±0.00				
			50.50	1.812	1.817±0.008				50.50	1.828	1.833±0.008	1.825±0.008
51.0	4.000±0.000	158.40±0.01				51.0	3.999±0.001	158.20±0.01				
			51.50	1.772	1.772±0.008				51.50	1.776	1.776±0.008	1.774±0.002
52.0	2.937±0.002	155.61±0.01				52.0	2.935±0.000	155.39±0.01				
			52.50	1.792	1.792±0.008				52.50	1.776	1.776±0.008	1.784±0.008
53.0	1.878±0.000	152.85±0.00				53.0	1.878±0.001	152.66±0.01				
			53.50	1.786	1.781±0.008				53.50	1.780	1.775±0.008	1.778±0.003
54.0	0.833±0.001	150.20±0.00				54.0	0.843±0.000	150.04±0.00				
54.0	5.208±0.002	150.15±0.02				54.0	5.205±0.001	150.02±0.01				
			54.50	1.780	1.784±0.008				54.50	1.772	1.776±0.008	1.880±0.004
55.0	4.173±0.000	147.60±0.00				55.0	4.170±0.000	147.48±0.00				
			55.50	1.669	1.664±0.008				55.50	1.660	1.655±0.008	1.660±0.005
56.0	3.139±0.001	145.26±0.01				56.0	3.138±0.001	145.16±0.01				
			56.50	1.676	1.674±0.008				56.50	1.670	1.668±0.008	1.671±0.003
57.0	2.069±0.000	142.88±0.01				57.0	2.074±0.001	142.82±0.01				
			57.50	1.635	1.640±0.008				57.50	1.634	1.639±0.008	1.640±0.001
58.0	1.000±0.001	140.47±0.00				58.0	1.000±0.000	140.55±0.00				
58.0	4.774±0.001	141.77±0.00				58.0	4.172±0.000	141.71±0.00				
			58.50	1.673	1.673±0.006				58.50	1.661	1.661±0.006	1.667±0.006
59.0	3.776±0.000	139.63±0.01				59.0	3.775±0.001	139.59±0.01				
			59.50	1.665	1.665±0.006				59.50	1.657	1.657±0.006	1.661±0.004
60.0	2.785±0.001	137.56±0.00				60.0	2.774±0.000	137.51±0.00				
			60.50	1.654	1.656±0.006				60.50	1.664	1.666±0.006	1.660±0.006
61.0	1.780±0.000	135.39±0.00				61.0	1.784±0.001	135.49±0.00				

TABLE 3.—COMPARISON OF THE OBSERVED TEMPERATURES (°C.) FOR THE JUMPS OF E/R÷1000, AND THE MAGNITUDE OF THE JUMPS FOR VARIOUS AQUEOUS ETHANOL SOLUTIONS FROM 0% TO 5% ETHANOL.

Concentration of ethanol in water														
0% Ethanol. ((i.e. purewater)	1. Temperature of jumps in (E/R)/1000		12.4	15.5	17.5		22.0	27.4	33.8	37.1	41.6		49.0	55.0
	2. Depth of jump.		0.04	0.07	0.06		0.09	0.07	0.06	0.06	0.06		0.08	0.05
0.9% ethanol	1. Temperature of jumps in (E/R)/1000		14.2		17.8		23.8		30.6	35.8	39.5	44.1	50.2	58.8
	2. Depth of jump.		0.09		0.12		0.10		0.09	0.10	0.03	0.05	0.12	0.13
1.8% ethanol	1. Temperature of jumps in (E/R)/1000		12.0	15.2	17.6		22.2	25.0	29.0	32.6	38.6			
	2. Depth of jump		0.06	0.07	0.05		0.11	0.03	0.07	0.13	0.05			
2.5% ethanol	1. Temperature of jumps in (E/R)/1000		13.0		16.6		20.6	26.0	29.1	36.2	40.0	44.0	50.2	55.0
	2. Depth of jump		0.02		0.08		0.12	0.10	0.05	0.09	0.06	0.04	0.04	0.09
3.5% ethanol	1. Temperature of jumps in (E/R)/1000	10.0	12.2		16.6		23.0	25.0	29.0	34.0	39.0	45.0	48.0	54.0
	2. Depth of jump.	0.07	0.12		0.11		0.11	0.02	0.10	0.09	0.07	0.05	0.10	0.09
4.1% ethanol	1. Temperature of jumps in (E/R)/1000	11.0	14.4		17.0	19.2	22.2	26.0	29.9	33.5	40.0	43.9	46.5	51.0
	2. Depth of jump.	0.11	0.04		0.10	0.09	0.03	0.08	0.07	0.13	0.03	0.04	0.04	0.06
5% ethanol	1. Temperature of jumps in (E/R)/1000		13.6		17.0	20.9	23.9	26.9	28.8	33.9	38.3	43.8	50.4	
	2. Depth of jump.		0.10		0.08	0.11	0.08	0.02	0.04	0.08	0.09	0.09	0.03	

In order to decide the precise position and nature of these branchings, further investigations on the intermediate concentrations are necessary so as to trace out fully the course of each of these discontinuities, as was done in the case of some concentrated ethanol solutions.[8] The experiments on some more concentrations are in hand and will be reported later.

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