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INFLUENCE OF ETHYLENE GLYCOL CONCENTRATION ON THE ACTIVATION ENERGY TRANSITIONS OF LIQUID WATER

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The study of concentration dependence of the jumps in $E\eta$ for a number of aqueous solutions from 0% to 9.8% ethylene glycol is undertaken at increments of nearly 2% glycol. $E\eta$ is obtained by using the Andrade equation after differentiation, viz.

$$E\eta/R = \Delta \ln \eta / \Delta(1/T) = T^2 \Delta \ln \eta / \Delta T$$

For examining the course of the movements of the activation energy jumps as a function of concentration a chart is prepared for the various energy jumps. It is found that the shifts of these jumps with the change of concentration are mostly smooth, except, the region between 16°C to 30°C, where there is appearance and disappearance of certain steps with the change in magnitude of the jump.

Introduction

The previous measurements on flow activation energy,[1–4] derivatives of dilatation[5] and refractive index[6,7] have shown the existence of discontinuities or anomalies, probably associated with the presence of structural transitions of some kind in the case of number of pure liquids and aqueous solutions. In the case of water–ethanol system, the discontinuities are found to be the functions of both temperature and concentration of solute. It has also been observed that the transition of these discontinuties are mostly uniform in character, but does not always follow the uniformity in some regions, where there is appearance and disappearance of certain steps with the changes in magnitude of the jump.[4] Now, in order to clear up this point and to obtain further information on the character of structural transitions of liquid water associated with these discontinuities, another aqueous system such as water–glycol has been taken up for study. Some accurate work has already been done on the flow activation energy of pure ethylene glycol.[2] The present communication describes similar measurements with dilute aqueous ethylene glycol solutions, covering the concentration range of 0% to 10% ethylene glycol (by weight) at intervals of about 2%.

Experimental Technique

The experimental technique is essentially the same as described for dilute alcohol by Ahsanullah and Qurashi.[3] The activation energy of viscous flow ($E\eta$) is measured with small temperature intervals $\Delta T = 1$°C, by use of the differential method which is based on the differential of the Andrade quation, viz.

$$\begin{aligned} E\eta / R &= \Delta \ln \eta / \Delta(1/T) = -T^2 \Delta \ln \eta / \Delta T \\ &= -T^2 \Delta \ln \upsilon / \Delta T - T^2 (\Delta \rho / \Delta T)/\rho \\ &= E\upsilon / R + T^2 \beta. \end{aligned}$$

where ρ is the density, ν the kinematic viscosity, η the dynamic viscosity ($= \upsilon \times \rho$) and β is the coefficient of dilatation (the term $T^2\beta$ forms a small slowly varying correction factor which can be applied to the final $E\eta/R$ values). An analysis of basic differential technique has been made (Ahsanullah[8]) and found fully adequate for the study of small scale variation in $E\eta$.

The time of flow are measured by a U-tube viscometer no. 1 of B.S.S. pattern to an accuracy of ±0.02 sec with a calibrated stop-watch. Townson and Mercer thermostat is used in which Beckmann differential thermometer never showed a variation of more than 0.002°C in the temperature range studied. Correction for the change of equillibrium level of the liquid in the viscometer are usually applied, and the evaporation losses at high temperature (above 35°C) are diminished by keeping a ballast bottle device well immersed in the thermostat as fully described by Qurashi and Ahsanullah.[1] The errors due to variation of viscometer constants with temperature due to thermal expansion of viscometer and variation of precise magnetude of the differential Beckmann thermometer scale due to expulsion of the excess mercury at each resetting after 5°C, are also considered.

Measurements on 4.5% and 9.8% Ethylene Glycol in Water by Weight

The water–ethylene glycol solutions are prepared by adding a calculated quantity of pure redistilled glycol to thrice distilled water in a stoppered flask and shaking thoroughly. The glycol percentages are then checked by the measurement of density, and also by viscosity measurement at a suitable temperature during the main experiment. The first series of measurements are carried out with 4.5% and 9.8% solutions (by weight) which have viscosity nearly 2% and 4% higher than water at the corresponding temperature, and were expected to show some departures in the flow activation energy and may give a fair idea about the region between 0% to 10% ethylene glycol. The experimental values of $10^{-3}\ E\eta/R$ for 4.5% and 9.8% for increasing and decreasing temperature sequences together with the overall mean are shown in Tables 1(a) and 1(b), together with the standard deviation calculated from the scatter of the repeated measurements of flow times and temperatures. The mean values of $10^{-3}\ E\eta/R$ of each solutions are plotted as hollow circles in Fig. 1. The graph for 4.5% and 9.8% solutions show the occurence of a series of sharp discontinuities in $10^{-3}\ E\eta/R$, of magnitude 0.1 and 0.15 respectively on the average (i.e. about ten times

TABLE 1(a).—EXPERIMENTAL VALUES OF $E\eta$ FOR 4.5% AQUEOUS ETHYLENE GLYCOL OBTAINED WITH $\Delta T = 1°C$.

Temp (°C)	$(E\eta/R) \div 1000$ Increasing temp. sequence	Decreasing temp. sequence	Overall mean	Standard deviation of the group of ten
7.50	2.452±0.007	2.428±0.009	2.440±0.012	
8.50	2.449±0.007	2.440±0.009	2.444±0.004	
				0.012
9.50	2.409±0.007	2.431±0.009	2.420±0.011	
10.50	2.399±0.009	2.381±0.008	2.390±0.009	
11.50	2.358±0.009	2.333±0.008	2.346±0.013	
12.50	2.293±0.009	2.307±0.008	2.300±0.007	
13.50	2.287±0.010	2.263±0.006	2.275±0.012	
14.50	2.279±0.010	2.253±0.006	2.266±0.013	
				0.010
15.50	2.272±0.012	2.268±0.006	2.270±0.002	
16.50	2.266±0.010	2.280±0.006	2.273±0.006	
17.50	2.254±0.006	2.266±0.007	2.260±0.006	
18.50	2.219±0.006	2.180±0.007	2.199±0.019	
19.50	2.123±0.006	2.164±0.007	2.144±0.020	0.020
20.50	2.116±0.008	2.184±0.006	2.150±0.034	
22.50	2.130±0.008	2.136±0.006	2.133±0.003	
23.50	2.136±0.008	2.130±0.006	2.133±0.003	
24.50	2.049±0.005	2.043±0.008	2.046±0.003	
25.50	2.026±0.005	2.071±0.008	2.048±0.023	
				0.011
26.50	2.048±0 005	2.055±0.008	2.051±0.004	
27.50	2.051±0.005	2.044±0.008	2.048±0.009	
28.50	2.043±0.009	2.058±0.007	2.050±0.008	
29.50	2.043±0.009	2.030±0.007	2.036±0.006	
30.50	2.024±0.012	1.968±0.010	1.996±0.028	0.017
31.50	1.940±0.012	1.979±0.010	1.959±0.019	
32.50	1.972±0.009	1.952±0 006	1.962±0.010	
33.50	1.941±0.009	1.944±0.006	1.942±0 002	
34.50	1.940±0.009	1.941±0.006	1.940±0.001	
35.50	1.952±0.007	1.910±0.005	1.930±0.020	0.008
36.50	1.934±0.007	1.942±0.005	1.938±0.004	
37.50	1.880±0.007	1.868±0.005	1.874±0.006	
38.50	1.867±0.005	1.864±0.008	1.866±0.002	
39.50	1.852±0.005	1.906±0.008	1.878±0.028	
40.50	1.835±0.005	1.801±0.008	1.818±0.017	0.023
41.50	1.786±0.006	1.855±0.009	1.820±0.035	
42.50	1.825±0.006	1.847±0.009	1.836±0.011	
43.50	1.817±0.006	1.814±0.009	1.816±0.003	
44.50	1.801±0.007	1.824±0.004	1.812±0.012	0.013
45.50	1.813±0.007	1.828±0.004	1.820±0.008	
46.50	1.836±0.007	1.779±0.004	1.807±0.028	
47.50	1.767±0.007	1.761±0.004	1.764±0.003	
48.50	1.741±0.009	1.762±0.007	1.752±0.011	
49.50	1.743±0.009	1.765±0.007	1.754±0.011	0.010
50.50	1.743±0.009	1.745±0.007	1.744±0.001	
51.50	1.744±0.011	1.754±0.008	1.749±0.005	
52.50	1.764±0.011	1.742±0.008	1.753±0.011	
53.50	1.684±0.011	1.666±0.008	1.675±0.009	
54.50	1.690±0.013	1.666±0.009	1.678±0.012	0.013
55.50	1.658±0.013	1.683±0.009	1.670±0.013	

Overall mean standard deviation=0.014.

TABLE 1(b).—MEASURED ACTIVATION ENERGIES $(E/R) \div 1000 = -(T^2 \Delta \ln \nu / \Delta T)/1000$ FOR 9.8%. AQUEOUS ETHYLENE GLYCOL SOLUTION.

Temp (°C)	$(E/R) \div 1000 = -(T^2 \Delta \ln \nu / \Delta T)/1000$ Corrected for Beckmann error — Heating sequence	Cooling sequences	Mean$(E/R) \div 1000$	Standard deviation of the group of ten.
10.50	2.410±0.007	2.471±0.005	2.440±0.030	
11.50	2.482±0.010	2.406±0.006	2.444±0.038	
12.50	2.366±0.007	2.382±0.002	2.374±0.008	
13.50	2.385±0.007	2.356±0.011	2.370±0.014	
14.50	2.371±0.009	2.366±0.008	2.369±0.003	
15.50	2.361±0.007	2.349±0.012	2.355±0.006	0.016
16.50	2.311±0.005	2.350±0.008	2.340±0.010	
17.50	2.327±0.003	2.315±0.011	2.339±0.012	
18.50	2.252±0.005	2.222±0.011	2.237±0.015	
19.50	2.242±0.004	2.226±0.005	2.234±0.008	
20.50	2.189±0.006	2.181±0.004	2.185±0.004	
21.50	2.187±0.007	2.190±0.005	2.188±0.002	
22.50	2.171±0.009	2.163±0.004	2.167±0.004	
23.50	2.207±0.014	2.173±0.004	2.190±0.017	
24.50	2.200±0.013	2.154±0.007	2.177±0.023	0.025
25.50	2.188±0.007	2.085±0.004	2.138±0.050	
26.50	2.081±0.007	2.162±0.005	2.121±0.041	
27.50	2.156±0.004	2.065±0.006	2.110±0.045	
28.50	2.135±0.003	2.111±0.005	2.123±0.012	
29.50	2.089±0.010	2.038±0.006	2.063±0.025	
30.50	2.025±0.004	2.092±0.003	2.058±0.034	
31.50	2 059±0.003	2.020±0.005	2.040±0.020	
32.50	2 095±0.005	1.976±0.007	2.035±0.060	
33.50	2.091±0.004	1.980±0.008	2.035±0.055	
34.50	2.068±0.008	2.022±0.008	2.045±0.023	0.034
35.50	1.980±0.008	1.927±0.008	1.953±0.026	
36.50	1.919±0 008	1.926±0.007	1.923±0.003	
37.50	1.930±0 010	1.890±0.006	1.910±0.020	
38.50	1.955±0.010	1.901±0.005	1.928±0.028	
39.50	1.892±0.007	1.928±0.014	1.910±0.018	
40.50	1.944±0.005	1.908±0.008	1.926±0.018	
41.50	1.950±0.006	1.900±0.006	1.925±0.026	
42.50	1.900±0.010	1.940±0.005	1.920±0.020	
43.50	1.905±0.004	1.925±0.005	1.915±0.010	
44.50	1.840±0.007	1.810±0.006	1.825±0.015	0.024
45.50	1.865±0.006	1.805±0.005	1.835±0.030	
46.50	1.838±0 008	1.802±0.005	1.820±0.018	
47.50	1.820±0.009	1.800±0.006	1.810±0.010	
48.50	1.835±0.010	1.744±0.009	1.789±0.045	
49.50	1.811±0.009	1.802±0.009	1.807±0.005	
50.50	1.791±0.007	1.763±0.004	1.777±0.014	
51.50	1.759±0.007	1.844±0.005	1.801±0.043	
52.50	1.854±0.005	1.736±0.009	1.795±0.059	0.048
53.50	1.792±0.008	1.745±0.010	1.768±0.023	
54.50	1.675±0.012	1.798±0.008	1.736±0.062	

Overall means standard deviation=0.030.

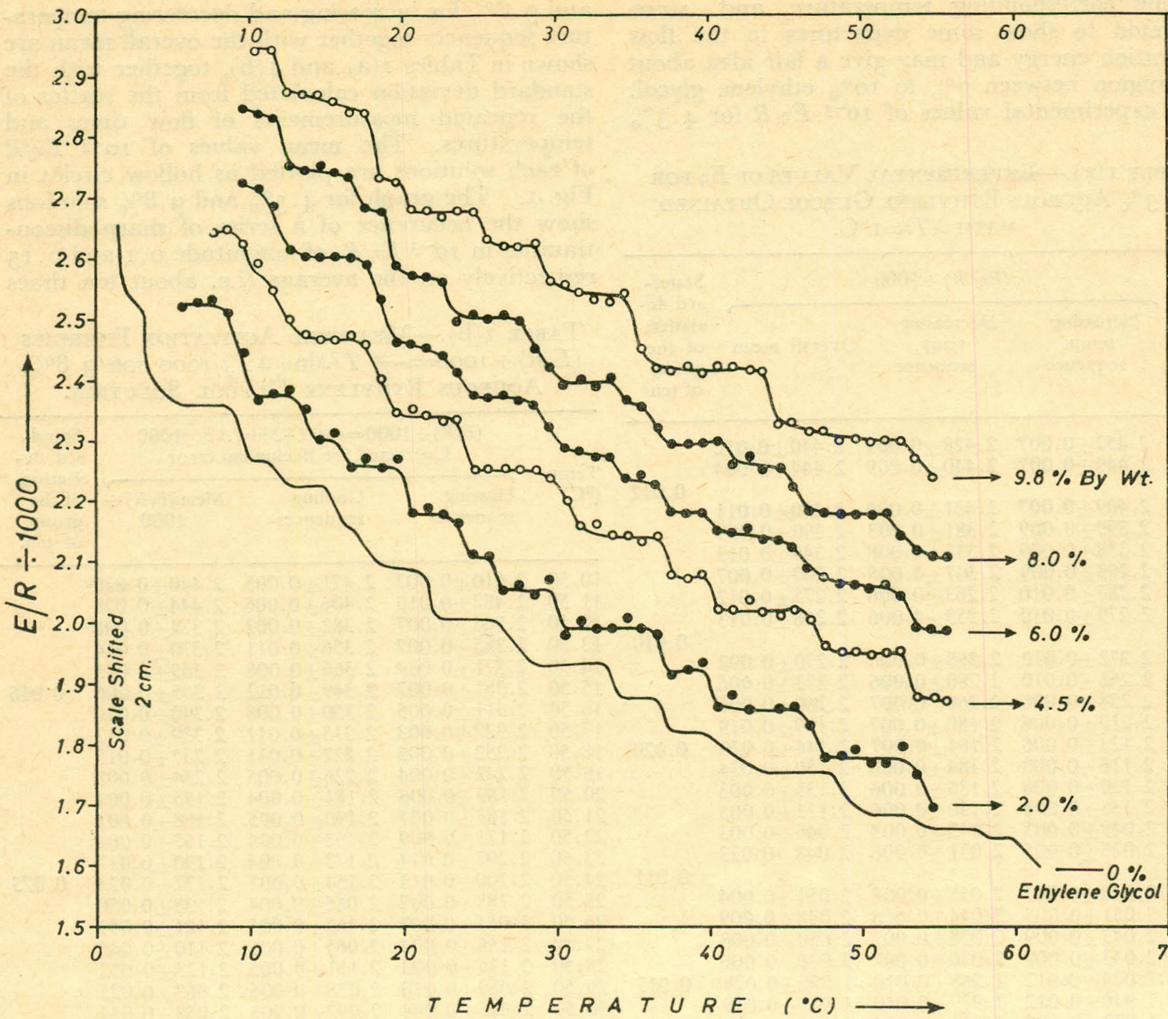

Fig. 1.—Plots of $(E / R) \div 1000$ against temperature for various concentrations of ethylene glycol solutions, each shifted 0.1 unit upwards above the lower concentration. The lowest fullline curve for pure water (0% glycol) is reproduced from earlier work.

the standard deviation of each point) with regions of constant $10^{-3}\ E_\eta/R$ between them. The three graphs of Fig. 1 (the lowest graph is for pure water, reproduced from an earlier communication), show a correspondence in the occurence of discontinuity, but considerable changes in the depth of the jumps, the energy values and the temperatures of discontinuities (with respect to pure water) are evident. The energy values of the steps increased considerably by the addition of glycol and the temperature at the discontinuities are also altered somewhat. In order to study the magnitude and nature of these transitions taking place in the jumps or steps as the concentration of ethylene glycol is increased, it is necessary to interpolate measurements with intermediate concentrations up to 9.8% glycol. Since there is only 2% increase in $10^{-3}\ E_\eta/R$ for the addition of 5% ethylene glycol, it was considered sufficient to explore the region between 0% to 9.8% at intervals of approximately 2% glycol by weight in the first instance. This enables one to get useful information about the magnitude and the precise transitions of the discontinuities taking place with the change of concentration of ethylene glycol.

Results for Intermediate Concentrations, and Discussion of Results

Accordingly, measurements of $10^{-3}\ E_\eta/R$ are carried out with 2%, 6% and 8% glycol solutions in the temperature range from 5°C to 55°C, at an intervals of 1°C. The detailed experimental data for 2% ethylene glycol solution for both increasing and decreasing temperature sequences

TABLE 2(a).—BECKMANN READINGS, FLOW TIMES AND CALCULATED VALUES OF $(E/R)\div 1000 = -T^2(\Delta \ln \upsilon/\Delta T)/1000$ FOR 2% SOLUTION OF AQUEOUS ETHYLENE GLYCOL IN THE RANGE OF 5°C–55°C, WITH $\Delta T = 1$°C.

Heating sequence					Cooling sequence				
Temp °C	Beckmann reading	Time of flow in sec corrected for level	Mean temp	(*E* / *R*)÷1000 corrected	Temp °C	Beckmann reading	Time of flow in sec corrected for level	Mean temp	(*E* / *R*)÷1000 corrected
1	2	3	4	5	6	7	8	9	10
5.00	0.126±0.001	408.94±0.03			5.00	0.132±0.001	407.73±0.01		
			5.50	2.392±0.007				5.50	2.448±0.003
6.00	1.126±0.001	396.53±0.04			6.00	1.137±0.002	395.01±0.00		
			6.50	2.418±0.005				6.50	2.429±0.005
7.00	2.129±0.001	384.42±0.00			7.00	2.141±0.001	382.88±0.03		
			7.50	2.399±0.001				7.50	2.458±0.005
8.00	3.129±0.001	372.88±0.00			8.00	3.135±0.001	371.18±0.01		
			8.50	2.368±0.002				8.50	2.451±0.005
9.00	4.121±0.001	362.00±0.01			9.00	4.130±0.002	359.94±0.02		
			9.50	2.362±0.005				9.50	2.328±0.004
10.00	5.121±0.001	351.45±0.02		—	10.00	5.125±0.000	349.65±0.01		
10.00	0.821±0.001	351.95±0.01			10.00	0.879±0.001	350.26±0.04		
			10.50	2.272±0.004				10.50	2.252±0.007
11.00	1.828±0.001	342.08±0.02			11.00	1.878±0.002	340.60±0.02		
			11.50	2.281±0.004				11.50	2.267±0.005
12.00	2.828±0.001	332.58±0.02			12.00	2.866±0.002	331.31±0.01		
			12.50	2.255±0.004				12.50	2.306±0.005
13.00	3.827±0.002	323.52±0.00			13.00	3.873±0.001	322.01±0.03		
			13.50	2.256±0.002				13.50	2.244±0.004
14.00	4.874±0.001	314.35±0.02			14.00	4.871±0.002	313.35±0.01		
14.00	3.014±0.001	312.40±0.02			14.00	3.012±0.002	312.33±0.01		
			14.50	2.198±0.004				14.50	2.198±0.007
15.00	4.015±0.002	304.20±0.01			15.00	4.016±0.001	304.11±0.05		
15.00	0.326±0.001	304.86±0.01			15.00	0.323±0.002	305.02±0.04		
			15.50	2.220±0.003				15.50	2.198±0.007
16.00	1.329±0.001	296.82±0.01			16.00	1.331±0.001	297.02±0.01		
			16.50	2.168±0.002				16.50	2.139±0.004
17.00	2.327±0.001	289.26±0.00			17.00	2.326±0.001	289.58±0.02		
17.00	2.327±0.001	289.46±0.01			17.00	2.326±0.002	289.58±0.03		
			17.50	2.169±0.004				17.50	2.166±0.006
18.00	3.327±0.002	282.12±0.02			18.00	3.324±0.001	282.26±0.01		
18.00	3.328±0.001	282.41±0.00			18.00	3.330±0.001	281.89±0.01		
			18.50	2.164±0.002				18.50	2.149±0.004
19.00	4.323±0.001	275.35±0.01			19.00	4.328±0.001	274.87±0.03		
			19.50	2.153±0.003				19.50	2.161±0.004
20.00	5.325±0.001	268.50±0.01			20.00	5.331±0.001	268.00±0.01		
20.00	0.032±0.001	268.58±0.03			20.00	0.036±0.001	268.43±0.02		
			20.50	2.083±0.006				20.50	2.070±0.005
21.00	1.027±0.002	262.20±0.02			21.00	1.028±0.001	262.11±0.02		

(*Continued*)

Table 2(a) (*continued*)

1	2	3	4	5	6	7	8	9	10
			21.50	2.111±0.008				21.50	2.063±0.004
22.00	2.032±0.001	255.87±0.05			22.00	2.027±0.002	255.96±0.00		
			22.50	2.070±0.006				22.50	2.074±0.004
23.00	3.032±0.001	249.88±0.01			23.00	3.028±0.002	249.95±0.01		
			23.50	2.055±0.006				23.50	2.063±0.004
24.00	4.036±0.002	244.09±0.04			24.00	4.031±0.001	244.14±0.01		
			24.50	2.030±0.007				24.50	1.990±0.006
25.00	5.034±0.002	238.57±0.01			25.00	5.034±0.001	238.70±0.02		
25.00	0.983±0.002	238.73±0.04			25.00	0.986±0.000	238.67±0.01		
			25.50	2.010±0.007				25.50	2.007±0.003
26.00	1.983±0.001	233.41±0.02			26.00	1.982±0.001	233.38±0.02		
26.00	1.361±0.001	233.12±0.08			26.00	1.363±0.001	233.10±0.04		
			26.50	1.944±0.011				26.50	1.958±0.003
27.00	2.360±0.001	228.13±0.04			27.00	2.363±0.000	228.07±0.00		
			27.50	1.946±0.008				27.50	1.979±0.005
28.00	3.358±0.001	223.28±0.04			28.00	3.361±0.001	223.14±0.05		
			28.50	1.974±0.006				28.50	1.942±0.005
29.00	4.362±0.001	218.47±0.01			29.00	4.361±0.000	218.30±0.00		
			29.50	1.966±0.006				29.50	1.956±0.006
30.00	5.358±0.001	213.85±0.04			30.00	5.363±0.001	213.85±0.06		
30.00	0.493±0.001	213.26±0.04			30.00	0.492±0.000	213.37±0.00		
			30.50	1.887±0.006					1.868±0.002
31.00	1.488±0.002	208.96±0.01			31.00	1.491±0.000	209.08±0.03		
31.00	3.879±0.002	209.27±0.07			31.00	3.877±0.001	209.25±0.01		
			31.50	1.902±0.005				31.50	1.907±0.005
32.00	4.878±0.001	205.03±0.03			32.00	4.878±0.002	204.99±0.02		
32.00	2.496±0.001	204.89±0.00			32.00	2.487±0.002	205.16±0.02		
			32.50	1.898±0.005				32.50	1.872±0.006
33.00	3.493±0.001	201.78±0.04			33.00	3.492±0.001	201.07±0.03		
			33.50	1.888±0.008				33.50	1.889±0.004
34.00	4.489±0.001	196.80±0.04			34.00	4.492±0.001	197.07±0.00		
			34.50	1.897±0.005				34.50	1.920±0.002
35.00	5.490±0.001	192.89±0.00			35.00	5.490±0.001	193.08±0.00		
35.00	0.708±0.001	192.47±0.00			35.09	0.709±0.001	192.50±0.03		
			35.50	1.880±0.002				35.50	1.892±0.003
36.00	1.710±0.001	188.70±0.01			36.00	1.710±0.000	188.71±0.00		
			36.50	1.881±0.006				36.50	1.873±0.004
37.00	2.711±0.001	185.04±0.04			37.00	2.710±0.001	185.06±00.4		
			37.50	1.809±0.006				37.50	1.806±0.007
38.00	3.709±0.001	181.61±0.02			38.00	3.710±0.000	181.63±0.04		
			38.50	1.817±0.003				38.50	1.816±0.007
39.00	4.710±0.001	178.24±0.00			39.00	4.709±0.000	178.27±0.05		
			39.50	1.810±0.002				39.50	1.860±0.006
40.00	5.707±0.001	174.98±0.01			40.00	5.706±0.000	174.92±0.03		

(*Continued*)

Table 2(a) *(continued)*

1	2	3	4	5	6	7	8	9	10
40.00	0.688±0 001	174 88±0.00			40.00	0.683±0.002	175.11±0.05		
			40.50	1.742±0.003				40.50	1.783±0.011
41.00	1.685±0 001	171.82±0.02			41.00	1.691±0.002	171.94±0.04		
			41.50	1.795±0.004				41.50	1.760±0.006
42.00	2.686±0 001	168.73±0.01			42.00	2.691±0.000	168.91±0.02		
			42.50	1.732±0.004				42.50	1.781±0.004
43.00	3.685±0.001	165.82±0.02			43.00	3.697±0.001	165.90±0.02		
			43.50	1.796±0.005				43.50	1.771±0.004
44.00	4.687±0.001	162 87±0.02			44.00	4.692±0.001	163.01±0.01		
			44 50	1.809±0 003				44.50	1.748±0.004
45.00	5.688±0.001	159.97±0.00			45.00	5.682±0.001	160.30±0.00		
45.00	0.958±0 001	160 33±0 02			45.00	0.964±0.002	160.35±0.03		
			45.50	1.735±0.007				45.50	1.786±0.004
46.00	1.956±0.002	157.62±0 04			46.00	1.958±0.001	157.57±0.00		
			46.50	1.717±0 006				46.50	1.752±0.002
47.00	2.958±0.002	154.99±0 00			47.00	2.959±0.001	154.89±0.01		
47.00	2.958±0.001	154.91±0 01			47.00	2.954±0.001	154.71±0.04		
			47.50	1.680±0.004				47.50	1.668±0.009
48.00	3.954±0 001	152.41±0 03			48.00	3.954±0.001	152.22±0.06		
			48.50	1.708±0.007				48.50	1.652±0.008
49.00	4.956±0.002	149.91±0.03			49.00	4.958±0.001	149.80±0.03		
			49.50	1.690±0.005				49.50	1.694±0.007
50.00	5.954±0.001	147.50±0 00			50 00	5.959±0.001	147.38±0.05		
50.00	0.357±0.001	148.00±0.01			50.00	0.352±0.001	147.94±0.00		
			50.50	1.682±0.004				50.50	1.677±0.002
51.00	1.354±0.002	145.65±0.01			51.00	1.365±0.001	145.56±0.01		
			51.50	1.661±0.006				51.50	1.672±0.020
52.00	2.364±0.002	143.35±0.03			52.00	2.356±0.001	143.29±0.00		
			52.50	1.676±0.007				52.50	1.709±0.003
53.00	3 361±0 002	141.11±0.02			53.00	3.356±0.002	141.00±0.01		
			53.50	1.602±0.005				53.50	1.696±0.005
54.00	4.365±0 001	139.00±0.01			54 00	4.364±0.001	138.76±0.02		
			54.50	1.615±0.004				54.50	1.576±0.004
55.00	5 363±0.002	137.00±0.01			55.00	5.368±0.001	136.73±0.01		

TABLE 2(b).—MEASURED ACTIVATION ENERGY OF 2% (BY WEIGHT) ETHYLENE GLYCOL IN WATER IN THE RANGE OF 5°C TO 55°C.

											Std. div. of the group
Mean temp (°C)	5.50	6.50	7.50	8.50	9.50	10.50	11.50	12.50	13.50	14.50	
Mean $(E_\eta/R)\div 1000$	2.419 ±0.027	2 424 ±0.005	2.428 ±0.030	2.410 ±0.041	2.345 ±0.017	2.262 ±0.010	2.274 ±0.007	2.280 ±0.026	2.250 ±0.006	2.198 ±0.000	0.019
Mean temp ("C)	15.50	16.50	17.50	18.50	19.50	20.50	21.50	22.50	23.50	24.50	
Mean $(E_\eta/R)\div 1000$	2 209 ±0.011	2.154 ±0.014	2.168 ±0.002	2.156 ±0.007	2.157 ±0.002	2.076 ±0.006	2.086 ±0.023	2.072 ±0.002	2.059 ±0.004	2.010 ±0.020	0.011
Mean temp (°C)	25.50	26.50	27.50	28.50	29.50	30.50	31.50	32.50	33.50	34.50	
Mean $(E_\eta/R)\div 1000$	2.008 ±0 001	1.951 ±0.007	1.962 ±0 016	1.943 ±0.031	1.963 ±0.000	1.878 ±0.010	1.904 ±0.002	1.885 ±0.013	1.889 ±0.000	1.908 ±0.012	0.011
Mean temp (°C)	35.50	36.50	37.50	38.50	39.50	40.50	41.50	42.50	43.50	44.50	
Mean $(E_\eta/R)\div 1000$	1.886 ±0.007	1.877 ±0.004	1.808 ±0.002	1.817 ±0.000	1.835 ±0.023	1.762 ±0.021	1.778 ±0.018	1.756 ±0.025	1.784 ±0.013	1.768 ±0.050	0.020
Mean temp (°C)	45.50	46.50	47.50	48.50	49.50	50.50	51.50	52.50	53.50	54.50	
Mean $(E_\eta/R)\div 1000$	1.760 ±0.025	1.734 ±0.017	1.674 ±0.007	1.680 ±0.028	1.692 ±0.002	1.679 ±0.002	1.666 ±0.005	1.692 ±0 016	1.649 ±0.047	1.595 ±0.019	0.020

TABLE 2(c).—MEASURED ACTIVATION ENERGY OF ETHYLENE GLYCOL IN WATER IN THE TEMPERATURE RANGE FROM 9° TO 56°C.

											Standard of group.
Ethylene glycol in water 6% by weight											
Mean temp (°C)	9.50	10.45	11.52	12.55	13.50	14.45	15.45	16.50	17.45	18.50	
Mean $(E\eta/R) \div 1000$	2.422 ±0.006	2.412 ±0.012	2.381 ±0.005	2.312 ±0.013	2.302 ±0.004	2.300 ±0.007	2.300 ±0.008	2.301 ±0.013	2.288 ±0.005	2.233 ±0.007	0.010
Mean temp (°C)	19.50	20.50	21.40	22.50	23.50	24.50	25.50	26.50	27.50	28.50	
Mean $(E\eta/R) \div 1000$	2.160 ±0.009	2.160 ±0.011	2.154 ±0.006	2.140 ±0.014	2.113 ±0.008	2.073 ±0.007	2.071 ±0.008	2.074 ±0.005	2.068 ±0.006	2.060 ±0.013	0.010
Mean temp (°C)	29.50	30.50	31.50	32.50	33.50	34.50	35.50	36.50	37.50	38.50	
Mean $(E\eta/R) \div 1000$	2.021 ±0.004	1.985 ±0.007	1.980 ±0.010	1.970 ±0.008	1.970 ±0.003	1.935 ±0.012	1.940 ±0.006	1.924 ±0.005	1.880 ±0.003	1.877 ±0.006	0.007
Mean temp (°C)	39.50	40.50	41.50	42.50	43.50	44.50	45.50	46.50	47.50	48.50	
Mean $(E\eta/R) \div 1000$	1.877 ±0.003	1.852 ±0.005	1.840 ±0.007	1.852 ±0.004	1.835 ±0.002	1.830 ±0.010	1.820 ±0.006	1.787 ±0.003	1.770 ±0.005	1.760 ±0.004	0.006
Mean temp (°C)	49.50	50.50	51.50	52.50	53.50	54.50	55.50				
Mean $(E\eta/R) \div 1000$	1.760 ±0.007	1.753 ±0.009	1.758 ±0.014	1.742 ±0.008	1.690 ±0.017	1.688 ±0.006	1.683 ±0.015				0.012
Ethylene glycol in water 8% by weight											Standard of group.
Mean temp (°C)	9.50	10.40	11.50	12.50	13.50	14.50	15.50	16.50	17.50	18.50	
Mean $(E\eta/R) \div 1000$	2.446 ±0.006	2.434 ±0.003	2.428 ±0.007	2.349 ±0.004	2.337 ±0.021	2.350 ±0.013	2.335 ±0.012	2.330 ±0.015	2.280 ±0.010	2.273 ±0.007	0.012
Mean temp (°C)	19.50	20.52	21.53	22.56	23.53	24.50	25.50	26.40	27.50	28.50	
Mean $(E\eta/R) \div 1000$	2.180 ±0.005	2.171 ±0.007	2.168 ±0.000	2.156 ±0.002	2.098 ±0.008	2.109 ±0.002	2.100 ±0.007	2.105 ±0.015	2.092 ±0.006	2.052 ±0.021	0.008
Mean temp (°C)	29.53	30.60	31.50	32.50	33.50	34.50	35.50	36.50	37.50	38.50	
Mean $(E\eta/R) \div 1000$	2.016 ±0.011	1.986 ±0.008	2.005 ±0.004	1.984 ±0.017	2.006 ±0.012	1.962 ±0.009	1.954 ±0.014	1.920 ±0.008	1.894 ±0.009	1.894 ±0.006	0.012
Mean temp (°C)	39.50	40.50	41.50	42.50	43.50	44.50	45.50	46.50	47.50	48.50	
Mean $(E\eta/R) \div 1000$	1.897 ±0.012	1.896 ±0.022	1.861 ±0.015	1.878 ±0.009	1.851 ±0.012	1.854 ±0.015	1.821 ±0.021	1.780 ±0.004	1.780 ±0.020	1.773 ±0.008	0.017
Mean temp (°C)	49.50	50.50	51.50	52.50	53.60	54.70	55.50				
Mean $(E\eta/R) \div 1000$	1.775 ±0.024	1.772 ±0.014	1.775 ±0.015	1.736 ±0.007	1.714 ±0.007	1.703 ±0.005	1.705 ±0.005				0.013

Table 3.—Comparison of the Observed Temperatures (°C) for the Jumps of $(E\eta/R) \div 1000$, and the Magnitude of the Jumps for Various Aqueous Ethylene Glycol Solutions from 0% to 9.8% Glycol by Weight.

Concentration of glycol in water		1	2	3	4	5	6	7	8	9	10	11
0% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	9.5	12.4	15.5	17.5	22.0	27.4	33.8	37.1	41.6	49.0	55.0
	Depth of jumps	0.08	0.04	0.07	0.06	0.09	0.07	0.06	0.06	0.06	0.08	0.05
2% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	9.3	13.4	16.0	20.0	23.7	26.0	30.1	36.7	40.0	46.6	53.7
	Depth of jumps	0.14	0.06	0.04	0.07	0.05	0.04	0.06	0.07	0.05	0.07	0.07
4.5% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	9.3	11.8		18.0	24.0	30.2		37.0	40.0	46.6	52.8
	Depth of jumps	0.05	0.08		0.11	0.08	0.08		0.05	0.05	0.06	0.07
8% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	11.6		17.6		23.5	29.0	34.2	36.8	40.5	46.2	53.0
	Depth of the jumps	0.10		0.11		0.07	0.07	0.04	0.05	0.04	0.07	0.05
8% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	11.8		17.0	18.8	23.0	28.2	34.3	36.1	41.0	45.2	52.2
	Depth of jumps	0.07		0.04	0.08	0.04	0.09	0.03	0.05	0.04	0.07	0.07
9.8% glycol	Temperature of jumps in $(E\eta/R) \div 1000$	12.2		17.8	20.0	25.0	29.0	35.0			44.2	52.2
	Depth of jumps	0.06		0.09	0.04	0.04	0.06	0.11			0.10	0.07

are shown in Table 2(a). The means of flow activation energy values for 2.0%, 6.0% and 8.0% glycol, for increasing and decreasing temperature sequences together with standard deviation (estimated from the difference between the increasing and decreasing temperature sequence values) are shown in Table 2(b) and 2(c), and plotted as solid circles in Fig. 1. The scale of each graph is shifted two units on the vertical scale from the solid line for pure water. The average step length is found to be of the order 4.5°C, with a mean drop of approximately 0.12. The analysis of the experimental graphs suggests that there is appearance and disappearance of certain steps as the concentration of glycol is increased. To examine this point further, and to follow more precisely the transitions of the jumps or steps as the glycol concentration increases, a comprehensive table (Table 3) is prepared showing the comparison of the observed temperature (°C) for jumps in $10^{-3}\ E\eta/R$, and the magnitude of the jumps for various aqueous ethylene glycol solutions from 0% to 9.8% glycol (by weight). This comparison is explicitly shown in the temperature concentration graphs of Fig. 2. The jumps are classified as large, medium and small, and plotted as circles, triangles and crosses respectively. This classification is based on the mean value of $\Delta E/100R = 0.07$. The graphs of Fig. 2, exhibit clearly that the behaviour of the various discontinuities is

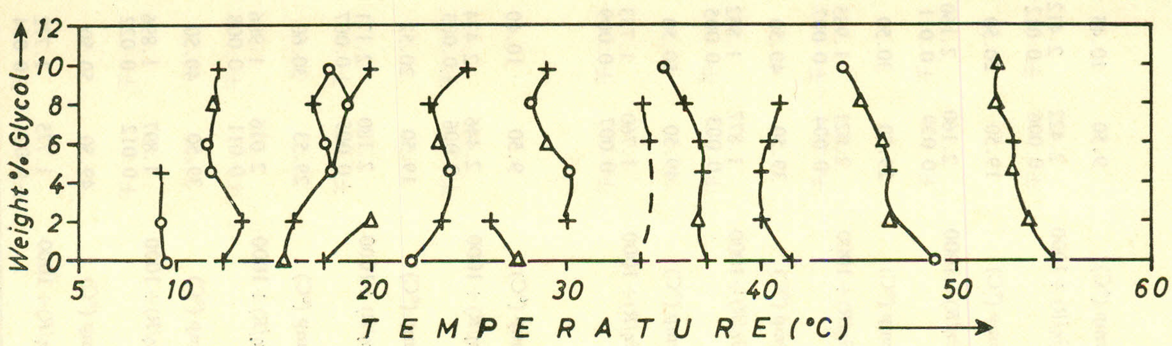

Fig. 2.—Chart showing the position of the jumps in the flow activation energy for several glycol concentrations in the range of 0% to 9.8% glycol. The full lines connecting some of the plotted points indicate more or less definite movements of these jumps, and the broken line stand for those parts involving some ambiguity.

mostly uniform, except the region between 16°C to 30°C, where the situation seems to be a bit erratic. In this region, there is appearance and disappearance of certain steps with the change in magnitude of the jump, in agreement with the earlier result obtained with water–ethanol system.[4] For instance, the jumps in 0% (water) at 17.5°C and 27.4°C disappeared beyond 2% glycol, while a new jump appeared at 30.0°C and going uniformly up to 9.8% glycol. It is possible that the aggregates of solute and solvent molecules are not uniformly distributed in solution. They may be concentrated or forbidden in certain region. The consequence of this effect might lead to larger association or agregation of solute and solvent molecules. And the cooperative structural breaking up and reforming may possibly occur at a larger temperature interval than expected, which leads to the disappearance of certain steps in certain regions, but the fundamental influence of water structure persists in solutions. To study these facts further, it is proposed to extend the measurements to higher concentrations, using closer intervals of 1% glycol concentration.

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