INVESTIGATION OF THE CHARACTER OF THE JUMPS IN ACTIVATION ENERGY OF VISCOUS FLOW IN PURE LIQUIDS AND SOLUTIONS. PART IV

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Further study of the bulk and the boundary-induced effect in the activation energy jumps observed in pure liquids and aqueous solutions was undertaken by determining the flow activation energy of dilute aqueous solutions of ethylene glycol, using three viscometers of different capillary bore. It has been confirmed that the whole phenomena of discontinuity observed in pure liquids and aqueous solutions are more or less equally dependent on the two basic causes viz. bulk aggregation and boundary-layer, and the latter does not extend much beyond 0.4 mm i.e. 400μ. The results show that almost half of the observed jumps, i.e. those at 15°C, 22°C, 27°C and 42°C, are *not* affected substantially by changing the diameter or by additions of glycol up to 15%, and can be presumed to be definite bulk phenomena.

1. Introduction

Detailed studies on the influence of temperature and of concentration of foreign molecules on the activation energy jumps observed in pure water[1] were undertaken in these laboratories, with a number of aqueous systems, such as water–ethanol,[1,2] water–sodium chloride[3,4] and water–ethylene glycol.[5] In the course of these studies, it has been tentatively observed that the jumps or discontinuity found in the structural properties of water are functions of the temperature and the concentration of the foreign molecules. The movements of these jumps with concentration are found to be more or less uniform in character, but in certain regions there is appearance, disappearance and even coalescence of some of the steps, with a change in magnitude of the jumps. The manifestation of such characteristic features in the structural properties of liquid water clearly shows that the observed phenomena may be the result of more than one isolated cause or a combination of them. It is, therefore, necessary to make a full investigation of the character and the origins of these jumps.

Some preliminary investigation has already been done by Qurashi and his coworkers[6,7] by making a synoptic analysis of the refractrometric measurements on water–ethanol systems taken with grazing and nongrazing incidence, and also by viscometric measurements taken with viscometers of different capillary diameters. It was found that in the range from 20°C to 50°C only the activation energy jumps at 22°, 27°, 42° and

48°C could be definitely considered as authentic anomalies in the bulk properties of water, while the rest are induced or augmented by the glass–liquid interfacial bondary. Further experimental investigation has, therefore, been carried out by extending the measurements on flow activation energy of pure water, as well as by carrying out these measurements with another aqueous system, namely water–ethylene glycol, using three viscometers of different capillary diameters.

2. Measurements with Pure Water

Accurate activation energy data on pure water at one degree intervals in the range from 20° to 50°C, using two viscometers of capillary bore 0.50 mm and 0.71 mm, have already been reported and discussed in the earlier communication.[6] Graphical comparison of the two separate sets of data brought out the fact that the additional jumps at 34°C and 37°C appearing in the data obtained with the finer viscometer of capillary bore of 0.50 mm are largely smoothed out with the use of the wider bore. This significant development is now followed up by (a) extending down to 10°C the measurements previously carried out with the viscometer of capillary bore of 0.71 mm, and (b) making further redeterminations of E_η for pure water in the range of 10°–45°C, using a still wider viscometer of capillary bore 0.88 mm. The redetermination of E_η could not be made over the whole range from 10° to 50°C, because of the significant increase of experimental error in the measurement of times of flow, and the consequent individual error in $(E_\eta/R) \div 1000$, due to very small flow times above 40°C.

The results obtained with the wider viscometer of capillary bore 0.88 mm are plotted as solid circles in the lowest set of three graphs of Fig. 1, for comparison with the similar data (partly reported earlier[6]) obtained with viscometers of capillary bores of 0.50 mm and 0.71 mm, which are plotted as hollow circles and vertical crosses respectively. The three plots are successively shifted vertically by 0.1 unit of $(E\eta/R) \div 1000$. The graphical comparison of Fig. 1 shows that, out of nine jumps observed in the data obtained with the finer viscometer of 0.50 mm capillary bore, the jumps at 12°, 15°, 22°, 27°, 42° and 48°C appear distinctly in the data obtained with the viscometer of capillary bore 0.71 mm. An inflection point at 34°C is still clearly visible in this
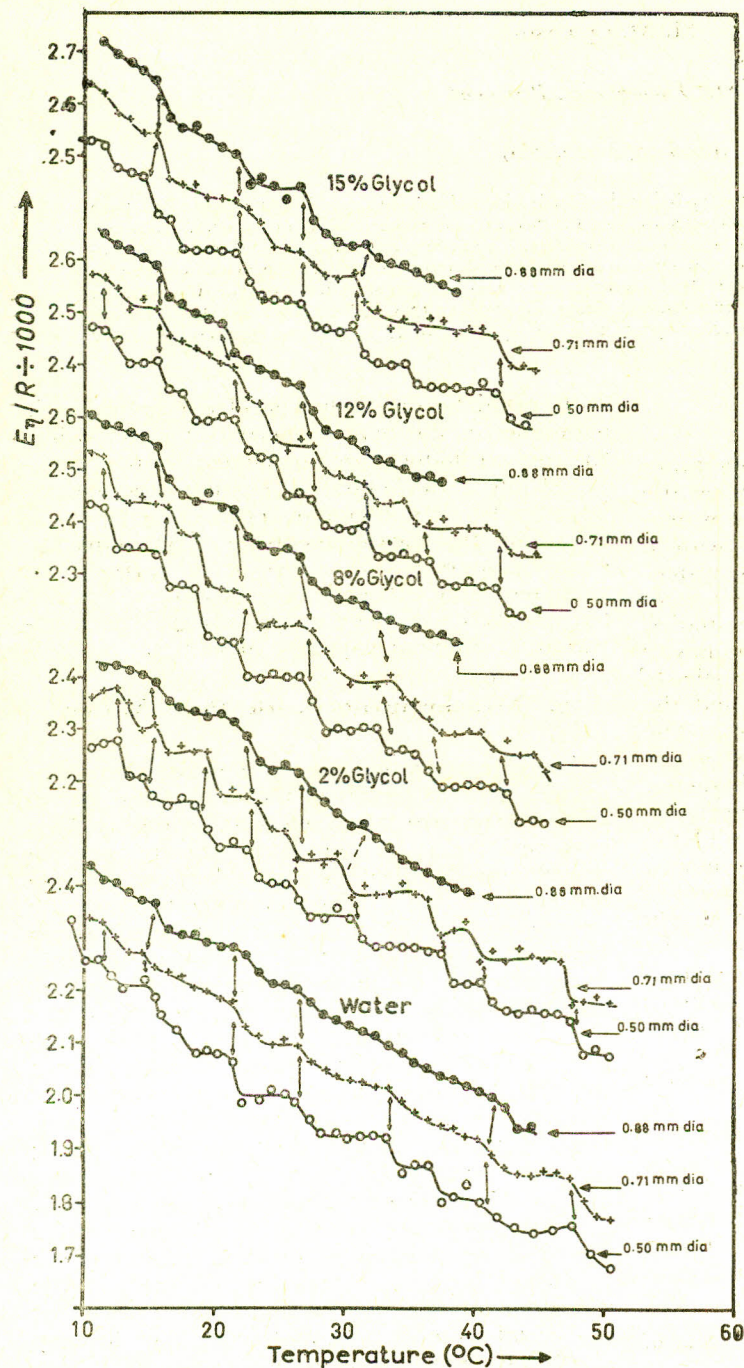

Fig. 1.—The plots of activation energy data for 0, 2, 8, 12 and 15% ethylene glycol by weight, as obtained with three different viscometers of capillary bores 0.50, 0.71 and 0.80 mm. These are plotted as hollow circles, vertical crosses and solid circles, respectively.

data. Proceeding further, the jumps at 12°C and 34°C have disappeared in the data obtained with the viscometer of capillary bore 0.88 mm. This shows that the jumps at 15°, 22°, 27° and 42°C in the temperature range from 10° to 45°C are unaffected by the capillary diameter up to 0.9 mm and this confirms the presumption of their being bulk effects.

3. Measurements with Water–Glycol System

Some measurements of $E\eta$ for aqueous solutions of 2%, 6%, 8% and 9.8% glycol by weight were already reported in an earlier communication.[5] These are, therefore, extended by (i) redetermining the values of $E\eta$ for 2%, 6%, 8% and 9.8% by the use of viscometers of capillary bore of 0.50 mm and 0.80 mm as against the viscometer of capillary bore 0.71 mm previously used, and (ii) new determination of $E\eta$ for 12% and 15% glycol by weight in the temperature range from 10°C to 45°C, using all the three viscometers (of capillary bores 0.50 mm, 0.71 mm and 0.88 mm, respectively). The results obtained in this way are plotted in the upper four sets of curves of Fig. 1 for 2%, 8%, 12% and 15% glycol by weight.

A synopsis of the temperatures and the corresponding depths of $E\eta$ jumps for 0, 2, 6, 8, 9.8, 12 and 15% glycol by weight, as measured with three viscometers of different capillary bore are shown in Table 1 (a–g). The last row of each section of Table 1 indicates the average depth of a particular jump calculated from the graph of each solution as measured with the three viscometers. The nine jumps originally found in water with the finer viscometer are numbered as 1 to 9, while the rest of the data on dilute glycol are given corresponding numbers. The bracketted asterisks in the table indicate that the particular jump is missing with the increasing viscometer sizes. It is clearly seen from the table that the depths of some of the jumps do *not* change appreciably with the increasing viscometer capillary bore up to 0.88 mm. One can see very clearly from Table 1 that in all the seven concentrations of glycol so far studied from 0% to 15%, the jumps at 15°, 22°, 27°, 42°, and most possibly 48°C, are unaffected by the capillary diameter. This means that almost 50% of the total number of jumps observed in water in the temperature range from 10° to 50°C are associated with the bulk aggregation effect. The disappearing jumps at temperature 11°, 17°, and 37°C can be considered to be associated witht he boundary-layer effect.

The above synoptic analysis is further visualized in the graphs of Fig. 2, where the temperatures of the jumps, as observed with three different viscometers, are separately plotted against the concentration of ethylene glycol. The hollow
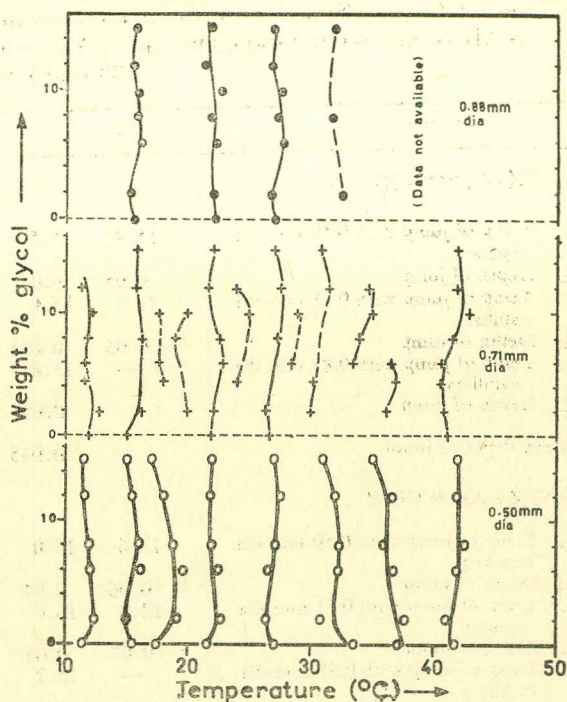

Fig. 2.—The graphs for temperature of the jumps as observed with the three different viscometers, each separately plotted against the concentration of ethylene glycol. The hollow circles, crosses, and solid circles represent the results obtained with viscometers of capillary bore 0.50, 0.71 and 0.88 mm, respectively.

circles, vertical crosses and the solid circles represent the results obtained with viscometers of capillary bore of 0.50, 0.71 and 0.88 mm, respectively. It is at once seen from the graphs of Fig. 2 that some of the jumps are unstable and very sensitive to changes in the viscometer. These jumps are displaced, separated, and finally disappear with the increasing viscometer diameter, while the rest are found to be unaffected by the capillary diameter. For example, the jumps around the temperatures 18° and 37°C observed with viscometer of capillary bore 0.50 mm are displaced and separated when measured in the wider viscometer of bore 0.71 mm; and finally disappear when measured in the widest viscometer of capillary bore 0.88 mm. On the other hand, the jumps at 15°, 22° and 27°C remain unaffected throughout the whole range of capillary diameters up to 0.88 mm.

4. Discussion and Conclusion

From the analysis of Table 1 and Figs. 1 and 2, it can be concluded that the jumps at temperatures 15°, 22° and 27°C in the range from 10° to 40°C are definitely stable and unaffected by boundary-layer effect. The jumps at 12° and 42°C are found to be stable up to the capillary diameter of

TABLE I (a–g).—SYNOPSIS OF TEMPERATURES OF $E\eta$ JUMPS FOR DILUTE ETHYLENE GLYCOL (0–15%) AS MEASURED WITH THREE DIFFERENT VISCOMETERS OF CAPILLARY BORES 0.50 mm, 0.71 mm AND 0.88 mm RESPECTIVELY.

No. of jump	1	2	3	4	5	6	7	8	9
(a) 0% Ethylene Glycol (i.e. Water)									
1. Temp of jump with 0.50 mm dia capillary	11.4	15.5	17.5	21.6	27.0	33.4	37.2	41.8	48.0
2. Depth of jump	0.05	0.06	0.05	0.07	0.07	0.05	0.05	0.05	0.07
1. Temp of jump with 0.71 mm dia capillary	11.9	15.0	—	21.9	26.6	33.8	—	41.5	47.8
2. Depth of jump	0.05	0.025		0.08	0.07	0.05		0.05	0.07
1. Temp of jump with 0.88 mm dia capillary	—	15.8	—	22.4	27.0	—	—	42.2	(data not available)
2. Depth of jump		0.05		0.06	0.04			0.035	
Mean depth of jump		0.045		0.070	0.060			0.045	(0.070)
(b) 2% Ethylene Glycol									
1. Temp of jump with 0.50 mm dia capillary	12.6	15.0	19.0	22.8	26.4	30.8	37.8	41.0	47.8
2. Depth of jump	0.06	0.04	0.08	0.06	0.05	0.05	0.05	0.05	0.06
1. Temp of jump with 0.71 mm dia capillary	12.8	16.0	20.0	22.5	26.2	30.2	36.2	40.7	47.4
2. Depth of jump	0.07	0.05	0.08	0.08	0.05	0.06	0.08	0.06	0.07
1. Temp of jump with 0.88 mm dia capillary	—	15.2	—	22.0	26.6	32.4 (inflection)	—	(data not available)	
2. Depth of jump		0.05		0.08	0.05	0.03			
Mean depth of jump		0.047		0.073	0.050	(0.047)		(0.055)	(0.065)
(c) 6% Ethylene Glycol									
1. Temp of jump with 0.50 mm dia capillary	12.3	16.0	19.5	22.2	26.5	32.2	36.7	42.4	
2. Depth of jump	0.06	0.05	0.08	0.07	0.08	0.04	0.06	0.06	
1. Temp of jump with 0.71 mm dia capillary	11.4	—	17.6	22.6	28.5	33.5	36.6	40.4	
2. Depth of jump	0.08		0.12	0.08	0.06	0.035	0.035	0.03	
1. Temp of jump with 0.88 mm dia capillary	—	16.0	—	22.1	27.7	—	—	41.8	
2. Depth of jump		0.07		0.08	0.05				
Mean depth of jump		(0.060)		0.077	0.063			0.043	
(d) 8% Ethylene Glycol									
1. Temp of jump with 0.50 mm dia capillary	12.0	16.0	18.8	22.0	27.2	32.4	36.0	42.4	
2. Depth of jump	0.07	0.07	0.09	0.06	0.09	0.04	0.05	0.06	
1. Temp of jump with 0.71 mm dia capillary	11.8	16.4	19.0	22.6	27.5	34.0	(?)	41.6	
2. Depth of jump	0.07	0.05	0.08	0.05	0.10	0.10		0.04	
1. Temp of jump with 0.88 mm dia capillary	—	15.8	—	21.8	27.2	31.6 (inflection)	—	data not available.	
2. Depth of jump		0.08		0.07	0.04	0.02			
Mean pepth of jump		0.067		(0.060)	0.077	(0.053)		(0.050)	
(e) 9.8% Ethylene Glycol									
1. Temp of jump with 0.71 mm dia capillary	11.6	15.4	17.7 (20.0)	— (25.0)	28.4	34.6	—	43.4	
2. Depth of jump	0.06	0.03	0.11 (0.04)		(0.05) 0.07	0.10		0.08	
1. Temp of jump with 0.88 mm dia capillary	—	15.8	—	22.6	27.6		—	42.6	
Depth of jump		0.05		0.07	0.05			0.06	
Mean depth of jump		0.04			0.06			0.07	

No. of jump	1	2	3	4	5	6	7	8	9
(f) 12% *Ethylene Glycol*									
1. Temp of jump with 0.50 mm dia capillary	11.6	15.6	18.0	21.8	25.0	27.4	32.0	36.6	42.0
2. Depth of jump	0.07	0.05	0.05	0.05	0.07	0.05	0.05	0.05	0.05
1. Temp of jump with 0.71 mm dia capillary	11.2	15.6	—	21.7	(24.0)	27.6	31.6	34.8	42.0
2. Depth of jump	0.05	0.05		0.05	(0.06)	0.05	0.03	0.03	0.04
1. Temp of jump with 0.88 mm dia capillary		15.4	—	21.0	—	26.7	—	—	(data not available)
2. Depth of jump		0.06		0.04	0.065				
Mean depth of jump		0.053		0.047	0.055				(0.045)
(g) 15% *Ethylene Glycol*									
1. Temp of jump with 0.50 mm dia capillary	11.4	15.0	17.0	22.0	27.0	31.0	35.0		42.0
2. Depth of jump	0.05	0.055	0.05	0.07	0.04	0.06	0.03	0.03	0.05
1. Temp of jump with 0.71 mm dia capillary	—	15.6	—	22.1	27.0	31.0	—	—	42.0
2. Depth of jump		0.08		0.05	0.05	0.06			
1. Temp of jump with 0.88 mm dia capillary	—	15.6	—	21.8	26.8	13.8	—		0.05 (data not available)
2. Depth of jump		0.06		0.05	0.06	0.025			
Mean depth of jump		0.065		0.057	0.050	0.04			

0.71 mm, that at 42°C being also observed with 0 to 15% ethanol. Further data with the next higher viscometer could not be obtained with respect to these jumps. The other jumps at temperatures 18° and 37°C, which become unstable, separate and finally disappear with increasing capillary diameter, are definitely due to boundary-layer effect. The remaining jump at temperature 32°C is displaced and separated with viscometer of capillary bore of 0.71 mm, but partially reappears with the wider viscometer of capillary bore 0.88 mm (as shown by the broken line in Fig. 2, top). It may perhaps be considered the result of some combined influence of both boundary-layer and bulk aggregation effect.

Now, it can be said with considerable certainty that the whole phenomenon of the occurrence of discontinuity in the temperature variation of various properties of water and aqueous solution, is mostly dependent on the two basic origins, viz. boundary-layer and bulk aggregation in the liquid. From the upper graphs of Fig. 2, it is also clear that the boundary-layer effect does *not* extend much beyond 0.8/2 mm, i.e. 400μ, and there is a critical depth of liquid surface or boundary-layer (~400μ) beyond which surface-induced structural effects practically disappear. This corresponds to thickness of a million molecules and bears comparison with the data from the refractometric measurements. It is hoped to throw further light on the critical depth of boundary layer in some future communication.

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