

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

Part III.—Experimental Differentiation of the Jumps Induced by Boundary-Layer Effects

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In view of the conflicting opinions regarding the nature and interpretation of the discontinuous jumps observed in the flow activation energy of water, a critical synoptic analysis is made of the refractometric measurements and dilute aqueous ethanol solution and pure water taken at grazing and nongrazing incidence. This leads to the result that only 35% of all the observed minima in (dn/dT) can correspond to genuine bulk anomalies, while the rest are induced or augmented by the glass-liquid interfacial boundary of 0 to 1 mm thickness.

This interpretation is confirmed by some preliminary measurements taken with (i) a different viscometer in a different laboratory, and (ii) a viscometer having a wider capillary. The boundary-induced anomalies are found to be very sensitive to changes in the viscometer, and to (gradually) disappear with increasing diameter. It is shown that in the range of 20°C to 50°C, only the activation jumps at 22°C, 27°C, and 42°C can be considered as authentic anomalies in the bulk properties of water.

Introduction

As a result of a series of investigations, involving accurate differential measurements of the flow activation energy, E_η , and the temperature derivative of refractive index, i.e. dn/dT , it has been possible to show the existence of a series of jumps in E_η occurring at various well-defined temperatures in several hydroxylic liquids,^{1,2} aqueous solutions,^{3,4} and even straight-chain hydrocarbons.^{5,6} While these results suggest the presence of certain type of molecular aggregation in these liquids, it is desirable (a) to study the characteristics of these jumps in detail, and (b) to compare with corresponding studies in other fields, before a complete picture can be obtained of the origin and nature of these aggregates or clusters within the liquid. Accordingly, in Part I of the present series of communications,⁷ an attempt was made to examine the sharpness of the E_η jumps by carrying out some especially refined measurements of $E_\eta = RT^2 \Delta \ln \eta / \Delta T$, with a measuring interval ΔT as small as 0.3 degree C for pure water and 0.2 degree C for 10% aqueous ethanol solution in the temperature range 12°C to 43°C. It was found (cf. Fig. 1) that the mean width of the steep part of the four jumps measured in case of pure water was 0.25 degree C, while a mean width of 0.19 degree C was obtained in case of 10% aqueous ethanol, so that the measured widths of all these jumps are in fact nearly equal to the corresponding measuring interval, ΔT . Thus the natural or

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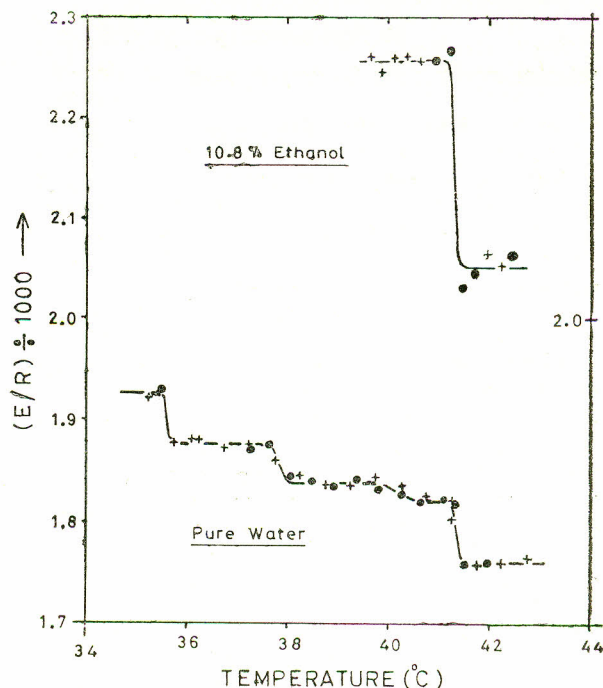


Fig. 1.—Reproduction of a part of the previously reported, measurements of flow activation energy E_η with small measuring intervals of 0.2°C to 0.3°C, showing the sharp and narrow character of the jumps for pure water and 10.8% aqueous ethanol solution.

inherent width of these E_η jumps is considerably less than 0.2 degree C, and it was concluded that

the observed jumps can be considered as discontinuous changes in E_η .

Comparison of the E_η data with measurements of dn/dT brings out the result that each jump (or oscillation) in E_η is in general associated with a corresponding minimum^{8,9} in $(-dn/dT)$ thus confirming that all the E_η jumps or other anomalies are real phenomena and *not* the result of chance or cumulative errors of measurement, etc. While our work on dilute aqueous solutions has received confirmation from the E_η measurements of Kirgintsev and his coworkers¹⁰ on fairly concentrated solutions of $Sr(NO_3)_2$, NH_4NO_3 , KCl , etc., yet many authorities have tended to doubt the existence of discrete energy states or discrete aggregation in liquids. On the experimental side, Falk and Kell¹¹ have concluded that the spectroscopic absorption data on water do not show evidence of discontinuous behaviour, but some recent work¹² in the U.K. on the shift of the absorption maximum of the iodide ion in aqueous solution indicates a series of small discontinuities at temperatures close to those of the E_η jumps observed by Qurashi and his coworkers.

From the marine scientists has come evidence for the presence of anomalies in the properties of water at several definite temperatures, and Drost-Hansen¹³ has, on the basis of a study of surface tension and other properties, postulated discontinuities at temperatures close to 15°C, 30°C, 45°C, and 60°C, i.e. approximately every 15 degrees C. This would be a little less than half the number of E_η jumps found by Qurashi and his coworkers in the corresponding temperature range, and so opens up the possibility of some of these observed jumps having a different origin from the others. In fact, Korson, Drost-Hansen and Millero,¹⁴ have in a recent re-determination of the viscosity of water gone to the other extreme of doubting the reality of all the E_η jumps so far observed in case of water. Nevertheless, they feel that these may be a result of interfacial effects, and go on to suggest that thermal anomalies in other bulk properties of water should *not* be discounted. It is therefore important to make an attempt to critically re-examine the data on various types of measurements, and to see what specific experiments can distinguish between the interface-induced component and the bulk aggregation component in the observed anomalies in E_η and other properties of water.

Analysis of the Data on dk/dT and dn/dT for Aqueous Solutions and Water

In case of pure water, some accurate data are available on dn/dT as well as on dk/dT , and a

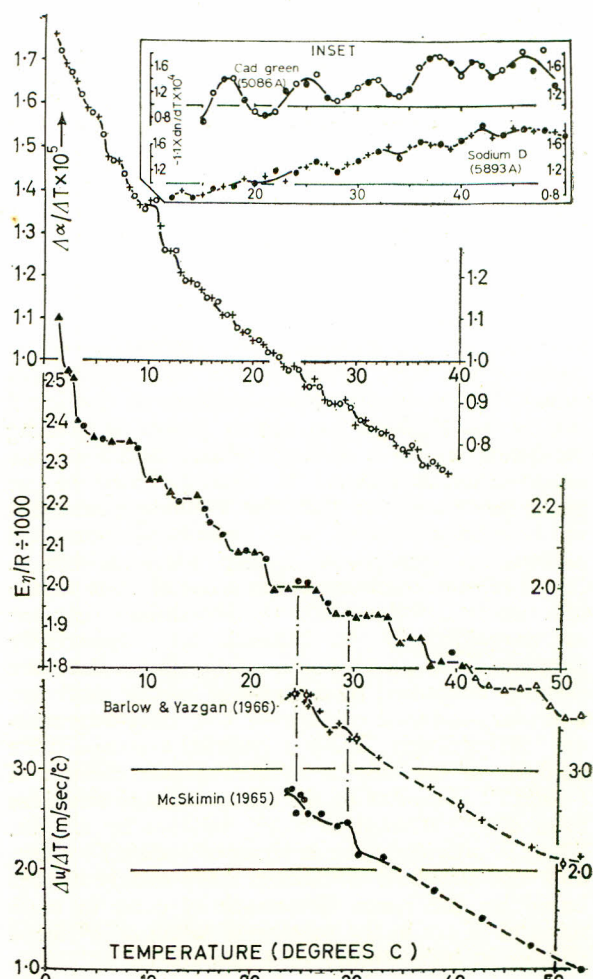


Fig. 2.—Comparison of the temperature derivatives of (i) ultrasonic velocity, u , (ii) coefficient of dilation, α , and (iii) refractive index, n , (inset) of water, with the flow activation energy, E_η , plotted as triangles and circles, showing that at least two E_η jumps between 20°C and 35°C are associated with a bulk anomaly.

comparison of these has been made with the E_η jumps in Part II of this paper,¹⁵ from which it appears (cf. Fig. 2), that at least two of these (one at 27°C and one of those at 22°C and one of those at 22°C and 34°C) correspond to maxima of dk/dT , and therefore involve III-order anomalies in the thermodynamic parameters of water. Because the values of K are based on measurements of ultrasonic velocity, u , which were made in cells 7 to 12 mm thick, and so presumably free from any boundary-layer effects, this would suggest that some of these jumps in E_η do correspond to discontinuities or III-order anomalies in aggregation and therefore the bulk properties of water.

The measurements of dn/dT on water and aqueous solutions show a series of minima equal to the number of jumps or anomalies in E_T . Since refractive index, n , is a bulk property, this at first sight shows that *all* these jumps should correspond to a bulk property of the liquids, but a closer look at the details of the technique of refractive index measurement is more revealing. It was observed,⁹ when corresponding solutions were measured on the Pulfrich and the V-Block refractometers, that the amplitudes of many of the maxima and minima in dn/dT are 2 to 4 times larger in the Pulfrich data. An examination of the paths of the light beams in the two instruments shows (Fig. 3) that the beam incident on the liquid cell in the Pulfrich instrument passes at grazing incidence within a distance of 0.1 mm from the liquid-glass interface. It should therefore be much more sensitive than the V-Block instrument to boundary-induced or boundary-augmented molecular aggregation taking place within a liquid layer of thickness of the order of a few tenths of a mm. It follows that the oscillations that are *not* magnified in the Pulfrich are apparently genuine bulk phenomena, while those that are *definitely* magnified by a factor of two or more are boundary-induced or at least boundary-augmented. Accordingly, Table 1 presents a comparative analysis of the depths of the various minima of $(-dn/dT)$ observed in six dilute ethanol solutions from 0.2% ethanol to 1.3% ethanol by weight. These depths are given in terms of $(-dn/dT) \times 10^4$, and the standard deviations ρ are nearly 0.025, based on the r.m.s. deviations of 0.03 to 0.05 minutes of arc in the measured values of $\Delta\theta$ for a change in temperature of 2 degrees C.

A systematic analysis of this table can be made by assuming as a working basis that depths differing on the two instruments by $1.5 \times \rho$ (i.e. 0.04) or less may be considered as invariant, while those that differ from each other by more than $3 \times \rho$ (i.e. 0.075) can be considered to be definitely dependent on the thickness of the boundary layer traversed by the incident beam. Using these criteria, we find that, out of the forty measured in Table 1, the thirteen minima marked with an asterisk are independent of the refractometer used, and may therefore be considered as genuine bulk phenomena in these solutions. Two more, namely that at 39.4°C in 0.21% ethanol and that at 34.5°C in 1.26% ethanol, show a slightly larger variation 0.05 to 0.06) between the two instruments, but the depth is in each case smaller with the Pulfrich refractometer and so these two may also be considered as bulk anomalies. The overall sums of the depths of these fifteen minima are nearly the same with either of the two refractometers.

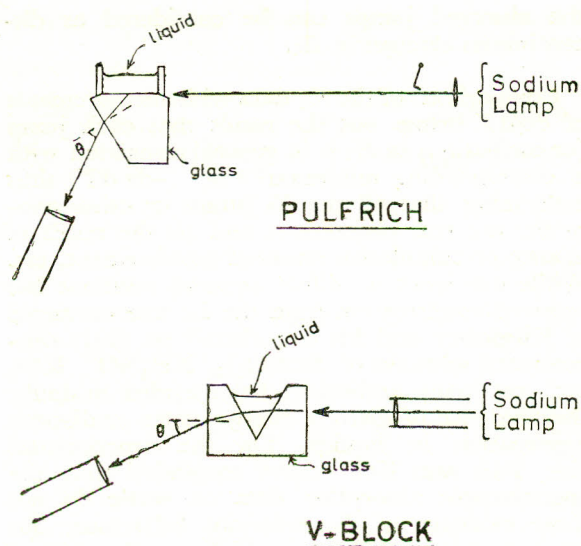


Fig. 3.—Sketch showing the light-path through the measuring cell and prism in the Pulfrich and V-Block refractometers. The grazing incidence in the Pulfrich arrangement makes the incident beam pass only a fraction of a mm away from the glass-liquid interface.

Similarly, another thirteen minima are found to fit the second criterion, i.e. difference $> 3\rho$, and in each case the Pulfrich gives the greater depth. These minima are therefore *definitely enhanced* in the Pulfrich measurements, and are marked with a letter "P" in Table 1; their depths with the Pulfrich are $2\frac{1}{2}$ to 5 (average $3\frac{1}{2}$) times those measured with the V-Block refractometer. Thus, something like 33% to 38% of the total number of observed minima appear to be genuine bulk anomalies, while another 33% are strongly augmented by the liquid-glass boundary effects, and are thus fairly definitely *not* bulk phenomena. The remaining 30% could belong to either type, or else be of an intermediate nature. It is interesting to note that if the same behaviour exists in case of pure water, then only three of the nine E_T (or dn/dT) anomalies observed between 10°C and 50°C would be genuine bulk phenomena.

To identify these in case of pure water, we make in Table 2, a comparison of our measurements of $(-dn/dT)$ obtained with the two refractometers. This comparison shows that the depths of the four minima at 20.8°C, 24.2°C, 27.8°C, and 43.2°C are probably independent of the measuring instrument, while those at 39.0°C and 48.9°C are definitely enhanced $2\frac{1}{2}$ times in case of the Pulfrich refractometer data. This partly fits in with the analysis for 0.2% ethanol solution in Table 1, and we can conclude that the $(-dn/dT)$ minima at 28°C and 21°C correspond almost certainly to anomalies in the bulk properties of

TABLE I.—SYNOPSIS OF DATA ON DEPTHS OF MINIMA IN $(-dn/dT)$ FOR DILUTE ETHANOL, AS MEASURED WITH THE V-BLOCK AND PULFRICH REFRACTOMETERS.

0.21% ethanol	Temp (°C)	(17.7)	22.0	25.5	28.7	31.8	35.5	39.4	43.7	
	Depth	{	V-Block	..	—	.06	.04	.04	.08	.07	.10	.1
			Pulfrich	..	—	.08	.10	.07	.04	.06	.05	.07
				—	*	—	*	*	*	—	*	
0.41% ethanol	Temp (°C):			(17.5)	21.0	25.6		30.4	34.6	38.8	43.2	
	Depth	{	V-Block	..	—	.1	.05		.03	.10	.03	.03
			Pulfrich	..	—	.16	.12		.04	.11	.16	.18
				—	—	—		*	*	—	P	
0.60% ethanol	Temp (°C):			(18.0)	22.8	(26)		29.0	33.4	39.7	44.6	
	Depth	{	V-Block	..	—	.04	(?)		.06	.06	.11	.05
			Pulfrich	..	—	.06	.05		.17	.18	.16	.13
				—	*	—		P	P	—	P	
0.78% ethanol	Temp (°C):			(19.0)	23.1		27.2	29.6	34.2	38.9	43.2	
	Depth	{	V-Block	..	.05	.03		.03	.06	.04	.05	.08
			Pulfrich	..	.11	.14		.04	.14	.12	.12	.19
				—	P		*	P	P	—	P	
1.05% ethanol	Temp (°C):	(19.3)	23.8		(27)	30.4	34.2	37.5	41.4	
	Depth	{	V-Block	..	.03	.05		.05	.05	.06	.11	.08
			Pulfrich	..	.16	.16		.02	.13	.12	.09	.07
				P	P		*	P	—	*	*	
1.26% ethanol	Temp (°C):	(19.0)	23.4	25.5		30.0	34.5	39.2	43.6	
	Depth	{	V-Block	..	.03	.05	.08		.10	.11	.08	.07
			Pulfrich	..	.08	.08	.18		.13	.05	.27	.14
				—	—	P		*	—	P	—	

 TABLE 2.—COMPARISON OF THE DEPTHS OF $(-dn/dT)$ MINIMA OBSERVED IN PURE WATER ON THE V-BLOCK AND PULFRICH REFRACTOMETER.

Temp (°C)	20.8	24.2	27.8	33.5	39.0	43.2	48.9	
Depth	{	V-Block05	.06	.06	.07	.06	.08	.07
		Pulfrich05	.04	.11	.14	.14	.12	0.18
				*	*	*	—	P	*	P	

water. This agrees very well with the conclusions arrived at from the analysis of ultrasonic measurements^{15,16} of dk/dT , and shows that (i) the $(-dn/dT)$ minima of invariant depth are indeed associated with genuine anomalies in the bulk behaviour of water and aqueous solutions, and (ii) the analysis of Tables 1 and 2 can be used to pick out these anomalies.

Examination of the Boundary-induced Effects in the Activation Energy Data

It is also possible to make a rough estimate of the thickness of the liquid layer that will exhibit

the interfacial boundary effects that enhanced the minima. Going back to the sketches of Fig. 3, it is clear that, whereas the incident beam passes within 0.1 mm of the glass-liquid boundary in the Pulfrich instrument, the beam in the hollow of the V-Block traverses path-lengths varying from 0 at the apex to about 8 mm near the surface of the liquid. If the boundary-induced order or domain-formation persists up to a distance δ mm away from this interface, then only a fraction $2\delta/8 = \delta/4$ of the height of the beam passing through the V-Block will be subject to this boundary-induced effect. It follows that the ratio of the depths of corresponding minima measured

with the Pulfrich and V-Block instruments will be approximately $1:\delta/4$, i.e. $4/\delta$. Comparing this with the observed mean ratio of $3\frac{1}{2}$, we get $4/\delta=3.5$, whence $\delta=4/3.5=1.1$, (1)

which indicates that the boundary-induced effects probably extend up to distances of a mm or so away from the glass-liquid boundary. If this is indeed the case, some indication of their existence should be observable in measurements of viscosity and the activation energy, E_η , carried out with viscometers having capillaries of different materials and various diameters, between 0.2 mm and 1 mm.

Accordingly, some preliminary experiments in this direction have already been carried out. For instance, it was decided to examine the effect of repetition of the measurements on water by a new observer (Z. Shaikh) in a different laboratory and using a new viscometer. The results obtained from two separate experiments in the temperature range of 20°C to 46°C are plotted as circles and crosses in Fig. 4(a). The temperatures at the six jumps observed are to be compared with the overall means of three series previously reported and collected in Table 3. It is seen that the three jumps observed at 31.2°C, 35.7°C and 44°C deviate by about 3 ± 1 degrees C from the corresponding means of 34.3°C, 37.2°C and 49°C, given in Table 3, thus suggesting that these jumps are very sensitive to changes of the boundary surface. The other three jumps at 22.6°C, 26.0°C, and 40.2°C in Fig. 4(a) are all within one degree C of the values in Table 3, and so can be accepted as being probably stable.

This lead was followed up by carrying out a redetermination of E_η at one-degree intervals in the range of 20°C to 50°C, using a viscometer with a capillary of bore 0.71 mm as against one of 0.50 mm used in the previously reported measurements. The results obtained with this viscometer are plotted as vertical crosses in Fig. 4(b) for comparison with the data previously reported by Ahsanullah and Qurashi, which are plotted as circles, the two plots being separated vertically by 0.1 unit of $E/R \div 1000$. The comparison brings out the fact that, while the two pairs of jumps at

22°C, 27°C, and 42°C, 49°C appear distinctly in the data with the wider viscometer, the others have already been largely smoothed out.

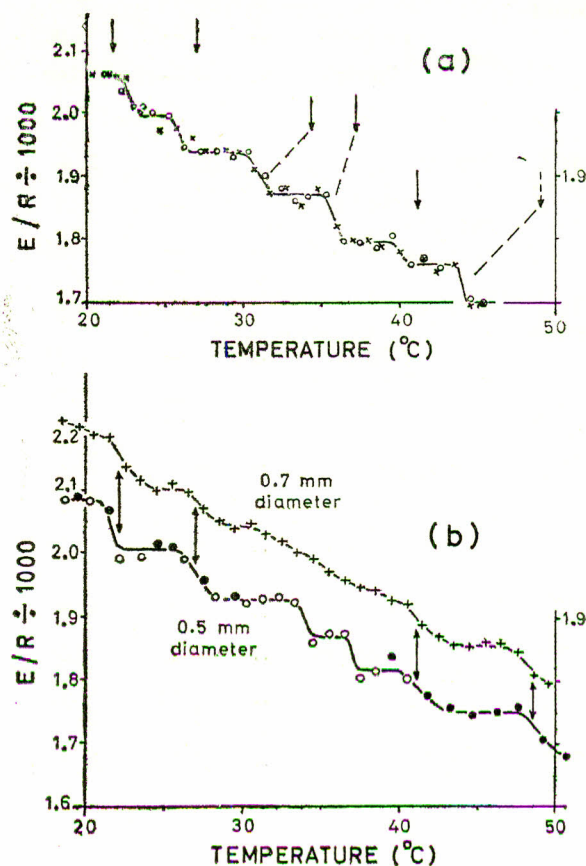


Fig. 4(a).—Probing measurements of flow activation energy for water, made with a new viscometer and a new observer from 20°C to 46°C, the circles being the means of two experiments. The mean graph shows that three of the jumps have shifted to temperatures lower by 3.5°C on the average than the earlier (reported) mean data indicated by the short vertical arrows.

Fig. 4(b).—Confirmatory experiments with a viscometer having a wider capillary, which results in the disappearance of about half the E_η jumps; those marked with the vertical double headed arrows appear to be invariant.

TABLE 3.—SYNOPSIS OF REPORTED MEASUREMENTS ON TEMPERATURES FOR E_η JUMPS.

Q & A (1961)	9.5	12.5	(16.5 ± 1.0)	21.8	26.6	(35 ± 1.5)	40.0	49.1
A, A & Q (1962)	9.3	12.4	15.5 17.5	22.0	27.4	33.8 37.1	41.8	—
Q & Q (1965)			—	21.1	(—)	35.7 38.0	41.4	
Mean	9.4	12.4	15.5 17.5	21.6	27.0	34.3 37.2	41.1	(49)
	±.1	±.1	±.3 ±.3	±.3	±.4	±.8 ±.5	±.8	

Conclusions

Comparing these findings with those of Fig. 4(a) and the analysis of Table 2, we conclude that in the range of 20°C to 50°C, only the three jumps at 22°C, 27°C and 42°C are the definitely stable ones, and may therefore be accepted as genuine bulk phenomena, while those at 49°C and 20°C are border-line cases, and may perhaps be partly genuine and partly boundary-augmented. This conclusion is in essential agreement with that obtained from the analysis of the data on ultrasonic velocities in Fig. 2, but only to some extent with the ideas of Drost-Hansen, because there is on the average one such bulk discontinuity every 11°C. The actual temperatures seem to depart considerably from his conjectured values of 15°, 30°C, 45°C, etc. The differences between the two sets of values are 7°C, 3°C, and 3°C respectively, giving an r.m.s. difference of 4.5 degrees C, which is well above the experimental errors of about one degree C.

It is hoped to follow up this preliminary investigation by more detailed experiments on activation energy measurements for polar and nonpolar liquids with capillaries of various diameters, and on refractive index measurements through various boundary layer thicknesses, as also of thermodynamic properties like dilatation, compressibility, etc. These studies are likely to throw more light on the extent to which surface-induced structural effects penetrate into the bulk of the liquid.

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