

## THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

### Part II.—The Temperature Dependence of the Viscosity of Hydroxylic Compounds. Preliminary Activation Energy Data on Glycerol and Ethylene Glycol

MOHAMMAD NASEEM\* AND MAZHAR MAHMOOD QURASHI

Central Laboratories, Pakistan Council of Scientific and Industrial Research, Karachi

#### Introduction

In Part I of this paper, some results were presented on the temperature variation of the viscosity of certain mineral oils over a range extending from 5°C. to 130°C.<sup>1</sup> In the final analysis, the measured viscosity was fitted to an Andrade-type equation,

$$\ln \eta = \ln A + \frac{\varepsilon}{kT}, \quad (1)$$

with variable  $\varepsilon$  and  $A$ ,  $\varepsilon$  being obtained from the derived relation

$$-T^2 \frac{d(\ln \eta)}{dT} = -\frac{T^2}{\eta} \frac{d\eta}{dT} = \frac{\varepsilon}{k} = \frac{E}{R}, \quad (2)$$

where  $\varepsilon$  measures the mutual potential energy between neighbouring molecular aggregates, and  $E$  is the same energy per mole,  $R$  being the gas constant and  $k$  the Boltzmann constant. The curves for  $E/R$  (or  $\varepsilon/k$ ) and  $\ln A$  against the absolute temperature  $T$  showed evidence for the existence of certain definite states of the liquids in which  $\varepsilon$  and  $A$  are constant, the transition between these states being gradual and smooth, as shown schematically in Fig. 1. However, since the mineral oils used in these experiments

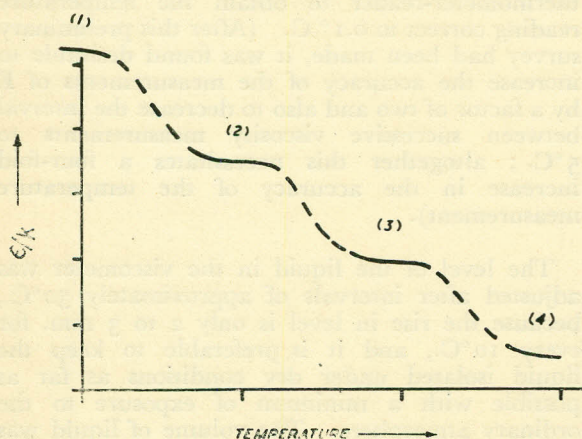


Fig. 1.—Schematic representation of segments in the curves of activation energy of viscous flow in mineral oils.

are known to be mixtures of several closely related hydrocarbons, the data obtained with them are not easy to interpret with certainty. In order to study the significance of this succession of definite states, and to correlate them with the behaviour of the molecular aggregates, it was therefore considered advantageous first to extend the observations to several pure liquids, especially those containing hydroxyl groups, capable of forming hydrogen bonds between adjacent molecules.

Ethylene glycol and glycerol are two readily available liquids of this type, glycol possessing two hydroxyls per molecule and glycerol three, thus providing considerable possibilities of a high degree of aggregation (chelation), especially at low temperatures not far above the melting points. The present communication deals with the preliminary results obtained with these two liquids, together with a discussion of the improvements in experimental technique that are necessary to obtain accurate measurements of the step-wise variation in the inter-aggregate potential energy.

#### Apparatus and Experimental Details

To obtain measurements of any worthwhile accuracy on the polyalcohols glycerol and ethylene glycol, two precautions must be taken: (a) the experimental liquid must be purified by repeatedly distilling and drying under reduced pressure, and (b) the entry of moisture from the atmosphere into the viscometer containing the liquid must be guarded against. The dryness of these liquids is particularly important, because their viscosity is extremely sensitive to dissolved water, *e.g.*, the presence of 0.1% water lowers the viscosity of glycerol by 2%, and of ethylene glycol by about  $\frac{1}{2}$ %. In order to keep the liquids as dry as possible during the viscometric readings, drying tubes were attached to each limb of the U-tube viscometers, which were of the British Standard Specifications pattern. Furthermore, a half-litre bottle with a special three-way stop-cock was used as a ballast tank (Fig. 2) and trap to prevent any water-vapour entering the viscometer due to a sudden release of the suction when the liquid is being sucked up into the upper bulb of the viscometer. The three-way stop-cock serves to

\* Present address: Kansas State University, Kansas.



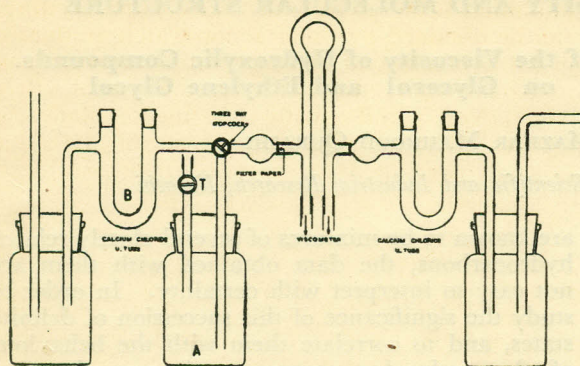


Fig. 2.—Sketch showing layout of water-vapour traps and ballast bottle for raising the liquid in the capillary limb of the viscometer

connect the left-hand limb of the viscometer either with (A) the half-litre bottle, or directly with (B) the drying tube. With the rubber tube connecting the two limbs of the viscometer pinched in the middle and the stop-cock in position 'A', a suitable quantity of air is sucked out of the bottle, after which the stop-cock T in the inlet to the bottle is closed. The liquid in the viscometer rises slowly in the left-hand limb, and when it is about 1 cm. above the upper mark, the three-way cock is turned to position 'B', thus isolating the ballast bottle and connecting the left-hand limb of the viscometer to the atmosphere through the drying tube. The pressure on the rubber connection at the top of the viscometer is also released, and the liquid flows down freely for the measurement of flow time. (The outer stop-cock T on the ballast bottle can be opened at leisure so as to bring the bottle to atmospheric pressure). With the above simple arrangement, it is possible to exercise very fine control over the rate of rise of liquid in the left-hand limb and at the same time to ensure that only dry air is introduced into the viscometer.

For measurements at high temperatures, the glycerol thermostatic bath designed for the work on lubricating oils, and described in Part I of this paper, is eminently suitable because it ensures temperature control to within one or two hundredths of a degree centigrade in the range of 70°C. to 250°C. For temperatures lower than 70°C., efficient stirring becomes difficult due to the high viscosity of the glycerol, and therefore a water-bath is preferable. The viscometer was supported vertically in the bath and a thermometer of appropriate range placed with its bulb close to the middle of the viscometer. Since the literature showed that previous experimental measurements of the viscosities of glycerol and ethylene glycol are limited to a few temperatures

between 0°C. and 50°C., the first step was to make a general survey of the variation of viscosity of these two liquids from room temperature to as high a temperature as is practicable without excessive oxidation or loss of the test liquid by evaporation. For this purpose, it was considered sufficient to measure the kinematic viscosity of the liquids at intervals of 10°C., and to calculate the value of the quantity,

$$-\frac{T^2}{1000} \frac{\Delta \ln \nu}{\Delta T} = \frac{E'}{R} / 1000, \quad (3)$$

in the middle of each ten-degree interval.  $E'$  differs from the energy  $E$  (cf. equation 2) by a small correction for the use of the kinematic viscosity  $\nu$ , in place of the dynamic viscosity  $\eta$ . From the calculations given in Appendix I of Part I of this paper, it is clear that

$$\frac{E}{R} = \frac{E'}{R} + T^2 \times \beta, \quad (4a)$$

where  $\beta$  is the coefficient of cubical expansion of the liquid at temperature  $T$ . Contrary to the usual practice of drawing graphs for  $\ln \eta$  against  $1/T$  and measuring their slope at various points, we have considered it better to calculate the activation energy,  $E$ , directly from successive observations. This method is preferable because it eliminates the uncertainties in drawing the tangent to a graph and enables a more reliable picture of the variation of  $E$  with temperature to be obtained.

Since an accuracy of about 2% in  $E$  was thought to be sufficient for the general survey, an ordinary thermometer graduated in degrees centigrade was used in conjunction with a magnifying thermometer-reader to obtain the temperature reading correct to 0.1°C. (After this preliminary survey had been made, it was found desirable to increase the accuracy of the measurements of  $E$  by a factor of two and also to decrease the interval between successive viscosity measurements to 5°C.; altogether this necessitates a four-fold increase in the accuracy of the temperature measurement).

The level of the liquid in the viscometer was adjusted after intervals of approximately 30°C., because the rise in level is only 2 to 3 mm. for every 10°C., and it is preferable to keep the liquid isolated under dry conditions as far as possible with a minimum of exposure to the ordinary atmosphere. The volume of liquid was adjusted so that at the beginning of this 30°-interval, the level was about 4 mm. below the mark, hence at the end of this interval it would be nearly the same height above the mark. The



correction for the variation of level with temperature and for the kinetic-energy term in the viscometer formula,

$$\nu = A t - \frac{B}{t},$$

was applied by means of the formula developed in Part I (Appendix I) of this paper, which is

$$-\frac{\Delta \ln \nu}{\Delta T} = -\frac{\ln(t_2/t_1)}{T_2 - T_1} \left( 1 + 2 \frac{B/A}{t^2} \right) + \frac{\alpha}{100} \frac{x_2 - x_1}{T_2 - T_1} \quad (4b)$$

where  $t_1$  and  $t_2$  refer to the times of flow at temperatures  $T_1$  and  $T_2$ , and  $x_1, x_2$  are the corresponding heights of the liquid level above the mark on the large bulb of the viscometer. The constant ' $\alpha$ ' is the percentage increase in time of flow produced by 1 cm. rise of the level above the mark, and it is nearly equal to 1.0 for the viscometers used in our work.

### Results with Glycerol

To begin with, the exploratory experiment was performed to determine the general variation of viscosity and of  $\frac{E'}{R} = -T^2 \frac{\Delta \ln \nu}{\Delta T}$  with temperature. For this purpose, redistilled glycerol was used and the times of flow in the appropriate viscometers were measured every 10°C. from room temperature (nearly 30°C.) upto 200°C. In this range of temperature, the viscosity fell from about 460 centistokes to 1.5 centistokes — a range of 1 : 300 — so that, the measurements had to be taken with two B.S.S. U-tube viscometers, namely Nos. 3 and 2. The data obtained are given in Table 1, and they show that  $\frac{E'}{R}/1000$  drops monotonically from over 7 at room temperature to about 3 at 200°C.

This table shows that if we measure  $\Delta T$  and  $\Delta \ln \nu$  accurate to one percent, the error in  $\frac{E'}{R}/1000$  will vary from about 0.10 at low temperatures to 0.04 at 200°C. However, it usually happens that the errors of measurement of both  $\Delta T$  and  $\Delta \ln \nu$  increase somewhat at higher temperatures, so that the error in  $\frac{E'}{R}/1000$  in the exploratory experiment may be taken to be *nearly uniform* at a figure of about 0.1 or a little lower. This exploratory experiment also showed that, although the times of flow in viscometer No. 2 at the highest temperatures are much less than one minute (the

minimum being 30 seconds), satisfactory accuracy can be obtained by using a stop-watch graduated in tenths of a second, thus permitting measurement to 0.02 second. In this way, the use of viscometers Nos. 1 and 0 with very fine capillaries, is avoided, thus reducing the chances of error due to small particles that may find their way accidentally into the experimental liquid.

For the more detailed measurements, redistilled glycerol was dried over sulphuric acid in a vacuum desiccator until bubbles ceased to rise from the glycerol. In this way, the water content of the glycerol can be kept well below 0.1%. Care was also taken when filling the viscometer to dry it by passing a stream of dry air through it. For each determination of viscosity, the bath was maintained at the desired temperature for fifteen to thirty minutes before the flow time was measured four to five times in succession. The temperature was also noted along with each measurement of the time of flow, and the mean values of both were used in the calculations. The observations were taken continuously between 25°C. and 210°C., using viscometer No. 3 from 25°C. to 75°C. and viscometer No. 2 from 70°C. upwards. In the lower temperature range, the viscometer was supported inside a standard electrically controlled water-bath with a temperature stability of 0.01°C., while for the higher temperature range the special glycerol thermostat was used. Table 2 gives the values of  $(-10 \Delta \ln \nu / \Delta T)$  calculated from the observed times of flow both with rising temperature sequence and falling temperature sequence. The agreement between the two sets of values is seen to be quite good, the standard deviation being about 1%. The individual deviations (from the mean) are given for values of  $\frac{E'}{R}/1000$  calculated from the corresponding means for  $-10 \Delta \ln \nu / \Delta T$ . The standard deviation for  $\frac{E'}{R}/1000$  is seen to be 0.04 in each of the two ranges of the table. The results are plotted in the upper graph of Fig. 3(b) and show the presence of steps of the kind envisaged in the introduction (Fig. 1), especially at the higher temperatures.

The corresponding plot of  $\ln \nu$  against  $1/T$  in Fig. 3(a) gives some idea of the improved discrimination obtained by calculating the values of  $E'/R$  from successive observations instead of trying to split up the curve for  $\ln \nu$  against  $1/T$  into a series of linear segments. (It is worth noting here that Benedick (private communication to Prof. Antonoff) has advocated the use of the first derivative,  $d\phi/dT$  to bring out the discontinuities



TABLE 1.—EXPLORATORY EXPERIMENT WITH REDISTILLED GLYCEROL.

Temp. (°C.) ..	35	45	55	65	75	85	95	105	115	125	135	145
$-10\Delta\ln v/\Delta T$ ..	0.744	0.657	0.572	0.506	0.441	0.398	0.338	0.318	0.285	0.252	0.223	0.200
$\frac{E'}{R}/1000$ ..	7.08	6.63	6.17	5.78	5.34	5.10	4.58	4.55	4.30	4.00	3.71	3.50
Temp. (°C.) ..	150	160	170	180	190							
$-10\Delta\ln v/\Delta T$ ..	0.193	0.187	0.170	0.147	0.142							
$\frac{E'}{R}/1000$ ..	3.46	3.51	3.34	3.02	3.04							

TABLE 2.—APPROXIMATE DATA FOR GLYCEROL FROM 30°C. TO 205°C.

Mean temp. in °C.	$-10\Delta\ln v/\Delta T$			$\frac{E'}{R}/1000 = \frac{T^2 \Delta\ln v}{1000\Delta T}$	Mean temp. in °C.	$-10\Delta\ln v/\Delta T$			$\frac{E'}{R}/1000 = \frac{T^2 \Delta\ln v}{1000\Delta T}$
	Rising	Falling	Mean			Rising	Falling	Mean	
30	0.794	0.786	0.790	7.26± .04	130	0.236	0.240	0.238	3.88± .02
35	0.741	0.732	0.7365	6.99± .04	135	0.235	0.227	0.231	3.85± .08
40	0.689	0.692	0.6905	6.78± .01	140	0.218	0.218	0.218	3.72± .01
45	0.651	0.659	0.655	6.62± .04	145	0.205	0.213	0.209	3.66± .07
50	0.615	0.605	0.610	6.37± .06	150	0.196	0.200	0.198	3.55± .03
55	0.563	0.563	0.563	6.08± .00	155	0.196	0.198	0.197	3.61± .01
60	0.544	0.546	0.545	6.05± .01	160	0.189	0.187	0.188	3.53± .01
65	0.516	0.512	0.514	5.88± .03	165	0.174	0.170	0.172	3.31± .04
70	0.472	0.466	0.469	5.52± .04	170	0.170	0.172	0.171	3.36± .01
75	0.453	0.466	0.4595	5.56± .07	175	0.168	0.172	0.170	3.42± .03
80	0.428	0.428	0.428	5.33± .00	180	0.154	0.156	0.155	3.18± .02
85	0.404	0.393	0.3985	5.11± .07	185	0.156	0.150	0.153	3.22± .07
90	0.378	0.386	0.382	5.04± .05	190	0.148	0.148	0.148	3.18± .00
95	0.354	0.358	0.356	4.82± .03	195	0.125	0.131	0.128	2.81± .07
100	0.331	0.324	0.3275	4.56± .05	200	0.128	0.124	0.126	2.82± .05
105	0.305	0.299	0.302	4.32± .04	205	0.124	0.123	0.123 <sub>5</sub>	2.82± .01
110	0.288	0.292	0.290	4.25± .02					
115	0.275	0.281	0.278	4.19± .05					
120	0.272	0.264	0.268	4.14± .06					
125	0.248	0.248	0.248	3.93± .00					
				Std. deviation = .04 <sub>2</sub>					Std. deviation = .04 <sub>1</sub>



in a measured property,  $\phi$ . Our technique of calculating  $-T^2 \frac{d \ln \nu}{dT} = -\frac{T^2}{\nu} \frac{d\nu}{dT}$  is better still because (a) it directly measures the energy, and (b) this function varies very slowly with the temperature,  $T$ , while the values of  $d\nu/dT$  are approximately proportional to  $\nu$ , and therefore

vary rapidly with temperature, thus making the identification and interpretation of the segments in the curve rather difficult. Even the function,  $\frac{d \ln \nu}{dT} = \frac{1}{\nu} \frac{d\nu}{dT}$ , is open to this objection, though in lesser degree). The magnitude of the difference in  $\frac{E'}{R}/1000$  between successive steps in Fig. 3(b)

lies between 0.15 and 0.3, which is 3 to 7 times the standard deviation of the individual points, and should therefore be significant. This, however, presupposes that other disturbances, such as thermometer error, are negligibly small. To check this point, and at the same time to obtain another set of observations of  $E'/R$ , a part of the experiment was repeated with another thermometer, also graduated to  $1^\circ\text{C}$ ., and therefore capable of being read to  $0.1^\circ\text{C}$ . The points obtained with this second thermometer in the range  $75^\circ\text{C}$ . to  $150^\circ\text{C}$ . are plotted in the lower graph of Fig. 3(b), which is labelled "Thermometer II" and is displaced downwards by 0.5 unit. The means of the two sets of observations are plotted in the upper curve of Fig. 4, the short vertical lines in which are equal to the estimated standard deviation. It is seen that, although the graphs obtained with two different thermometers show a number of similar variations, nevertheless

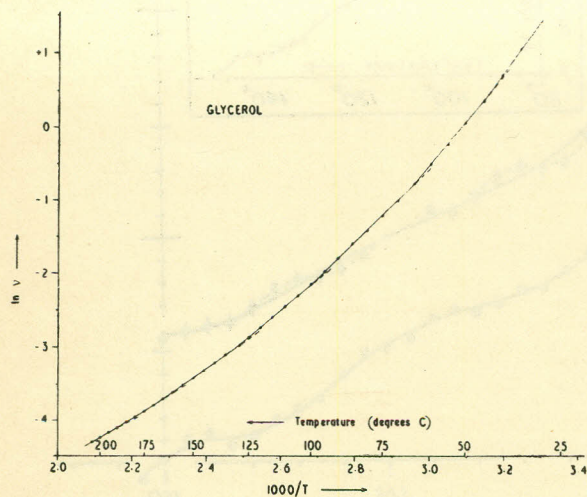


Fig. 3.—(a) Graph for  $\ln \nu$  against  $1000/T$  for glycerol between  $25^\circ\text{C}$ . and  $205^\circ\text{C}$ ., showing linear segments.

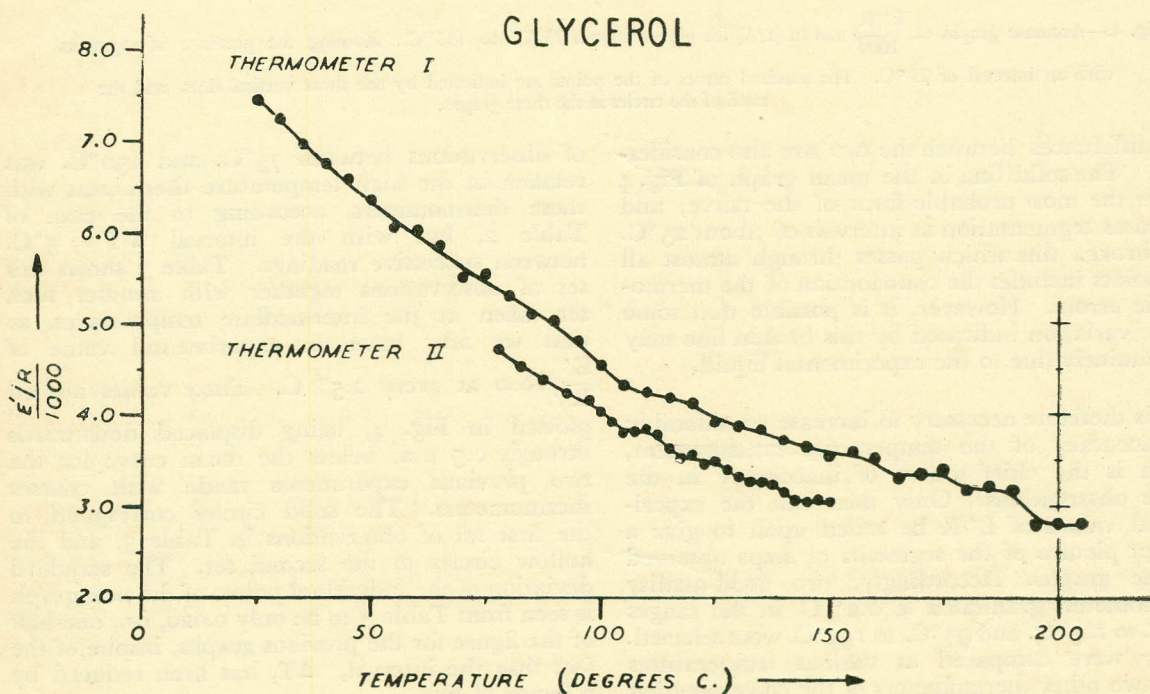


Fig. 3 (b).—Alternative graphs of activation energy,  $\frac{E'}{R}/1000$ , against temperature for glycerol, showing the presence of steps. The radius of the solid circles corresponds to the standard error.



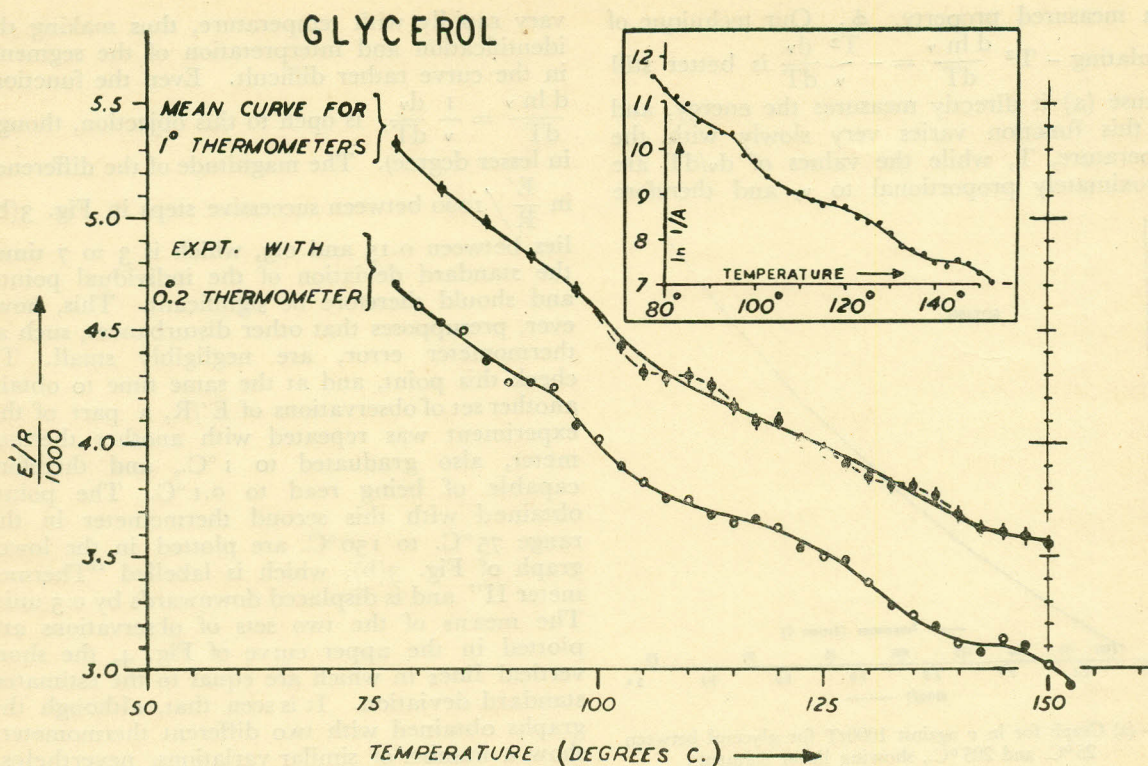


Fig. 4.—Accurate graphs of  $\frac{E'/R}{1000}$  and  $\ln(1/A)$  for glycerol from 75°C. to 155°C., showing the presence of segments with an interval of 25°C. The standard errors of the points are indicated by the short vertical lines and the radii of the circles in the three graphs.

the differences between the two are also considerable. The solid line in the mean graph of Fig. 4 shows the most probable form of the curve, and indicates segmentation at intervals of about 25°C. The broken line which passes through almost all the points includes the contribution of the thermometric errors. However, it is possible that some of the variation indicated by this broken line may be genuinely due to the experimental liquid.

It is therefore necessary to increase considerably the accuracy of the temperature measurement, which is the chief source of inaccuracy in the above observations. Only then can the experimental values of  $E'/R$  be relied upon to give a correct picture of the segments or steps observed in the graphs. Accordingly, two good-quality thermometers graduated to 0.2°C. in the ranges 45°C. to 105°C. and 95°C. to 155°C. were selected. (They were compared at various temperatures with two other thermometers of the corresponding ranges and the differences were found to be of the order of 0.01° to 0.03° C., indicating that the individual thermometers could be relied upon to somewhat better than this). The complete set

of observations between 75°C. and 150°C. was retaken in the high temperature thermostat with these thermometers, according to the plan of Table 2, but with the interval  $\Delta T = 5^\circ\text{C.}$  between successive readings. Table 3 shows this set of observations together with another such set taken at the intermediate temperatures, so that we now have an experimental value of  $\frac{E'}{R}/1000$  at every 2.5°C. These values are all plotted in Fig. 4, being displaced downwards through 0.5 unit below the mean curve for the two previous experiments made with coarser thermometers. The solid circles correspond to the first set of observations in Table 3, and the hollow circles to the second set. The standard deviation of the individual points of the new graph is seen from Table 3 to be only 0.020, *i.e.*, one-half of the figure for the previous graphs, in spite of the fact that the interval,  $\Delta T$ , has been reduced by a factor of two.

The new graph confirms the conclusions derived from the previous mean graph, and shows very clearly that the complete curve for  $E'/R$  against



TABLE 3.—MORE ACCURATE DATA FOR GLYCEROL FROM 75°C TO 150°C.

Mean temp. in °C.	$-10 \frac{\Delta \ln \nu}{\Delta T}$ (deviations are given x10 <sup>4</sup> )	$\frac{E'}{R} / 1000 = \frac{T^2 \Delta \ln \nu}{1000 \Delta T}$	Cor-rection $= \frac{T^2 \beta}{1000}$	$\ln \frac{1}{A}$ (cor-rected)	Mean temp. in °C.	$-10 \frac{\Delta \ln \nu}{\Delta T}$ (deviations are given x10 <sup>4</sup> )	$\frac{E'}{R} / 1000 = \frac{T^2 \Delta \ln \nu}{1000 \Delta T}$	Cor-rection $= \frac{T^2 \beta}{1000}$	$\ln \frac{1}{A}$ (cor-rected)
77.5	0.4226±13	5.21±0.02		11.55	75.0			0.067	
82.5	0.3980± 8	5.04±0.01		11.12	80.0	0.4088±20	5.11±0.03		11.28
87.5	0.373 <sub>1</sub> ± 8	4.86±0.01	0.074	10.58	85.0	0.3887±17	5.00±0.02		10.97
92.5	0.3560± 9	4.77±0.01		10.36	90.0	0.3605± 6	4.76±0.01		10.34
97.5	0.3322± 7	4.58±0.01		9.85	95.0	0.3499± 8	4.75±0.01		10.32
102.5	0.3110±11	4.40±0.02		9.38	100.0	0.3244± 4	4.52±0.01	0.082	9.73
107.5	0.2935±13	4.26±0.02		9.02	105.0	0.3030± 3	4.33±0.00		9.23
112.5	0.2814± 6	4.19±0.01	0.090	8.86	110.0	0.289 <sub>3</sub> ± 7	4.25±0.01		9.01
117.5	0.2725± 5	4.17±0.01		8.80	115.0	0.2756± 9	4.15±0.01		8.77
122.5	0.257 <sub>7</sub> ± 9	4.04±0.01		8.48	120.0	0.2669±12	4.13±0.02		8.71
127.5	0.248 <sub>1</sub> ±11	3.99±0.02		8.37	125.0	0.2517±10	4.00±0.02	0.099	8.36
132.5	0.229 <sub>2</sub> ± 7	3.78±0.01		7.84	130.0	0.2390±11	3.89±0.02		8.12
137.5	0.218 <sub>8</sub> ± 8	3.69±0.01	0.118	7.66	135.0	0.224 <sub>3</sub> ±13	3.74±0.02		7.76
142.5	0.206 <sub>6</sub> ± 6	3.57±0.01		7.38	140.0	0.211 <sub>7</sub> ± 3	3.61±0.01		7.46
147.5	0.203 <sub>3</sub> ±11	3.60±0.02		7.44	145.0	0.2074±10	3.63±0.02		7.51
152.5	0.188 <sub>3</sub> ±15	3.42±0.03		7.03	150.0	0.195 <sub>7</sub> ±14	3.51±0.02	0.137	7.23
		Std. deviation=0.020					Std. deviation=0.020		

temperature consists of a series of segments of the type sketched in Fig. 1, each segment covering a range of about 25°C. in temperature and 0.25 in  $\frac{E'}{R} / 1000$ . The various segments are apparently identical in shape, starting with a steep drop and ending with a practically horizontal portion as the temperature is raised. The degree of agreement between the two graphs of Fig. 4 is such as to confirm that the precision of the more accurate experiments (cf. Table 3) is enough to bring out correctly the general shape of these segments, while the previous experimental data contain a large proportion of random error, comparable with the magnitude of the effects being investigated.\*

Finally, with the data of Table 3, we can calculate the values of  $\ln 1/A$  using equation (1), thus

$$\ln \frac{1}{A} = \frac{e}{KT} - \ln \eta = \frac{E/R}{T} - \ln \eta \quad (5)$$

$E/R$  is obtained from Table 3, while the corresponding values of  $\ln \eta$  are readily derived from the observed times of flow. The results of the calculation are set out in columns 5 and 10 of Table 3, and are presented graphically in the inset of Fig. 4.  $\ln 1/A$  decreases monotonically with rise of temperature, and the graph is seen to have nearly the same shape as that for the energy,  $E$ ; this is due to the dominance of the first term on the right hand side of equation (5). The value of  $\ln 1/A$  decreases by about 1.4 in going from one segment to the next, so that  $A$  increases by a factor of  $\exp. (1.4) = 4$ . Bearing in mind that  $A$  is directly dependent on the concentration of the molecular aggregates in the liquid, this four-fold increase is suggestive of a corresponding diminution in size of the aggregates after each step of

\*There is however some indication in the points that the lower graph of Fig. 4 may actually involve some small variations with a smaller temperature interval than 25°C., but the decision for this must await still more accurate measurements.



25°C. However, further investigation is necessary before such an interpretation can be fully developed.

### Results with Ethylene Glycol

The curves of Fig. 4 provided sufficient encouragement for taking up the study of ethylene glycol, which has two hydroxyl groups instead of the three in glycerol. Although glycol has a much lower viscosity than glycerol, it can be expected to show effects similar to glycerol, possibly with somewhat different characteristics. One thing is certain, namely, that accurate measurements of  $\Delta \ln \nu / \Delta T$  will be more difficult, because, for a given  $\Delta T$ , the quantity  $\Delta \ln \nu$  is smaller for less viscous liquids, cf. the values of  $(-10 \Delta \ln \nu / \Delta T)$  at higher temperatures in Tables 2 and 3. To attain this accuracy, it was found expedient to take the observations every 5°C., as for glycerol, but to use a larger interval for  $\Delta T$ , viz., 10°C., for calculating  $\Delta \ln \nu / \Delta T$ . In this way the requisite accuracy can be obtained, although with the sacrifice of some of the detail in the variation of the energy  $E$ .

Since the viscosity of ethylene glycol is only a fraction of that of glycerol, viscometers must be used having finer capillaries than before. U-tube viscometer No. 2 was used from room temperature upto 90°C., at which temperature the time of flow fell to about three quarters of a minute, and U-tube viscometer No. 1 was used for the higher temperatures upto 160°C. Accurate measurements at temperatures higher than this were not feasible with our simple experimental arrangement because of errors introduced by excessive evaporation of glycol (boiling point = 198°C.). Distilled glycol was dried thoroughly over sulphuric acid in a vacuum desiccator and then introduced into the viscometer with suitable precautions against the absorption of moisture. The times of flow were measured at intervals of 5°C. as described in the previous section on glycerol, and the values of  $(-10 \Delta \ln \nu / \Delta T)$  and  $\frac{E'}{1000R} = \frac{-T^2 \Delta \ln \nu}{1000 \Delta T}$  were calculated with  $\Delta T = 10^\circ\text{C.}$  in order to obtain sufficient accuracy. The results are shown in Table 4, where the heading "Expt. I" refers to the first complete experiment performed with both rising and falling temperature sequences as in Tables 2 and 3. Due to the very small values of  $\Delta \ln \nu$  at the higher temperatures, the precision at these temperatures was still poor (due probably to evaporation effects) and therefore another complete set of observations was taken from 85°C. to 150°C. The data obtained from this are shown under the column headed "Expt. II".

By taking the mean values for the two experiments, an accuracy of about  $\pm 0.025$  was obtained in the measured value of  $\frac{E'}{R}/1000$  over the entire range of temperatures.

The final results are shown graphically in Fig. 5, which again shows very clearly the presence of the step-like segments of Fig. 1. The different steps are nearly as definite as those in the final curve of Fig. 4 for glycerol, except at the lower temperatures, where there is some lack of clarity. The essential differences between the results for the two liquids are that (a) the temperature interval between successive "steps" is about 15°C. for ethylene glycol as against 25°C. for glycerol, and (b) there is a corresponding decrease in the magnitude of the jump in energy for each step. It is worthwhile to consider for comparison the available data for ethyl alcohol, which has only one hydroxyl group per molecule. The lower graph of Fig. 5 is drawn from calculations made with the standard data of Thorpe (1894), Titani (1927), and others.<sup>2</sup> It shows a clear division into segments with a repetition interval of about 30°C., but, in contrast to the curves for glycerol and glycol, the "steps" are upwards instead of downwards. However from the general trend of the curve, it is reasonable to expect that at lower temperatures (*i.e.*, well below the boiling point) the graph for ethyl alcohol will become similar to those for glycol and glycerol. To check this point and to obtain more accurate data for the shape of the segments, it is proposed to study ethyl alcohol down to a few degrees above its freezing point.

### Discussion and Lines for Further Work

The above observations suggest that the arrangement of the step-like segments is characteristic of the liquid being studied and that it will be very interesting to study the laws governing the interval between successive steps, both as regards the energy difference,  $\Delta E$ , and the temperature difference. Such a study, if carried out for a number of related liquids, should give considerable insight into the mechanism responsible for the regular occurrence of these steps. It is worth noting here that Fig. 4 indicates that, at least for glycerol, the melting point (18°C.) will lie on the steep part of one of the earlier segments of the graph for  $E$  against temperature. This is in agreement with similar measurements on super-cooled liquids by Urazovski and Chernyavski, and suggests that the steep part of each segment corresponds to a structural transition. Since the interval,  $\Delta E/1000R$ , between successive segments is of the order of 0.15 for glycol and for



TABLE 4.—PRELIMINARY DATA FOR ETHYLENE GLYCOL FROM 30°C. TO 155°C.

Mean temp. in °C.	$-10\Delta \ln \nu/\Delta T$			$\frac{E'}{R}/1000 = -\frac{T^2}{1000} \frac{\Delta \ln \nu}{\Delta T}$	Mean temp. in °C.	$-10\Delta \ln \nu/\Delta T$			$\frac{E'}{R}/1000 = -\frac{T^2}{1000} \frac{\Delta \ln \nu}{\Delta T}$
	Expt. I	Expt. II	Mean			Expt. I	Expt. II	Mean	
30	0.388	—		$3.56 \pm .03$	105	0.180	0.175	0.177 <sub>5</sub>	$2.54 \pm .02$
35	0.367	—		$3.49 \pm .02$	110	0.175	0.171	0.173	$2.54 \pm .02$
40	0.344	—		$3.37 \pm .01$	115	0.155	0.162	0.1585	$2.39 \pm .04$
45	0.324 <sub>5</sub>	—		$3.28 \pm .01$	120	0.146	0.157	0.1515	$2.34 \pm .06$
50	0.308 <sub>5</sub>	—		$3.22 \pm .02$	125	0.1495	0.1515	0.150 <sub>5</sub>	$2.38 \pm .01$
55	0.291 <sub>5</sub>	—		$3.14 \pm .03$	130	0.144 <sub>5</sub>	0.142 <sub>5</sub>	0.143 <sub>5</sub>	$2.33 \pm .01$
60	0.277 <sub>5</sub>	—		$3.07 \pm .01$	135	0.135	0.135	0.135	$2.25 \pm .00$
65	0.285	—		$2.95 \pm .02$	140	0.127 <sub>5</sub>	0.1325	0.130	$2.22 \pm .03$
70	0.252	—		$2.96 \pm .02$	145	0.129	0.130	0.129 <sub>5</sub>	$2.26 \pm .01$
75	0.239 <sub>5</sub>	—		$2.90 \pm .03$	150	0.130 <sub>5</sub>	0.124 <sub>5</sub>	0.127 <sub>5</sub>	$2.27 \pm .04$
80	0.221	—		$2.75 \pm .03$	155	0.123 <sub>5</sub>	0.121 <sub>5</sub>	0.122 <sub>5</sub>	$2.24 \pm .01$
85	0.219	0.212	0.2155	$2.76 \pm .03$					
90	0.2085	0.2075	0.208	$2.74 \pm .01$					
95	0.197 <sub>5</sub>	0.198 <sub>5</sub>	0.198	$2.68 \pm .01$					
100	0.186 <sub>5</sub>	0.184 <sub>5</sub>	0.185 <sub>5</sub>	$2.58 \pm .01$					

Std. deviation of  $\frac{E'}{R}/1000$  is:—  
 (a) 0.02<sub>6</sub> from 30° to 80°C.  
 (b) 0.02<sub>5</sub> from 85°C. to 155°C.

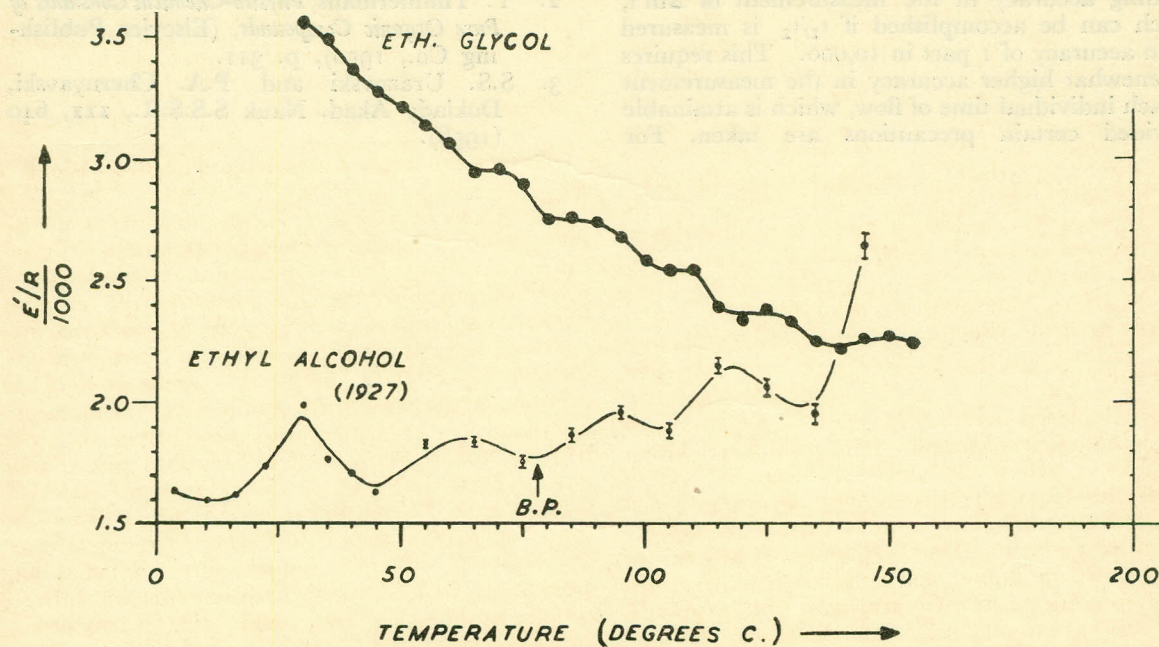


Fig. 5.—Graphs of  $\frac{E'}{R}/1000$  for ethylene glycol and ethyl alcohol below 150°C. The radii of the solid circles and the short vertical lines indicate the estimated standard deviations of the points in the two graphs.



ethyl alcohol, and the present measurements have a standard error of 0.026, it is clearly necessary to increase the accuracy still further before the dependence of  $\Delta E$  on temperature can be properly studied. Moreover, it will also be necessary to decrease the interval,  $\Delta T$ , between successive viscosity measurements ( $5^\circ\text{C}$ . for glycerol and  $10^\circ\text{C}$ . for glycol) to about  $2^\circ\text{C}$ . in order to obtain true representation of the variation of  $E$  from one step to the next. Such a decrease in the measuring interval,  $\Delta T$ , necessitates a further corresponding increase in the accuracy of the measurements of both temperature and time of flow.

Thus, if we wish to attain an accuracy of 0.01 in  $\frac{E}{R}/1000 \approx \frac{T^2 \Delta \ln t}{1000 \Delta T}$ , which has a value of  $4 \pm 2$ , we must measure both  $\Delta \ln t$  and  $\Delta T$  to an accuracy of  $1/2 \times 0.01/4$ , i.e., 0.12%, which requires an accuracy of better than 0.002 degrees centigrade in each temperature reading when the interval  $\Delta T$  is taken as  $2^\circ\text{C}$ . This degree of accuracy is attainable either with a Beckmann differential thermometer or with a platinum resistance thermometer. Of these two, the Beckmann thermometer is somewhat easier to handle and has the further advantage of a smaller bulb and a quicker response to temperature changes.

There remains the matter of obtaining a corresponding accuracy in the measurement of  $\Delta \ln t$ , which can be accomplished if  $t_1/t_2$  is measured to an accuracy of 1 part in 10,000. This requires a somewhat higher accuracy in the measurement of each individual time of flow, which is attainable provided certain precautions are taken. For

instance, if the time of flow is 300 seconds and readings are taken to 0.01 second (by estimation), an accuracy of 1 part in 30,000 is possible. Further details of the measurements will be discussed in Part III of this paper, which deals with the accurate experiments on ethylene glycol and their interpretation.

It is hoped in subsequent communications to present also the results obtained from equally accurate experiments on ethyl alcohol, glycerol, methyl alcohol, water, and mixtures of these liquids in various proportions. The experiments on mixtures are expected to be especially illuminating because of the control that can be exercised through the concentration parameter. Later on, it will be feasible to include non-polar liquids also within the framework of the investigation.

#### Acknowledgement

Grateful acknowledgement is made to Dr. Salimuzzaman Siddiqui and to Prof. G. Antonoff for their interest and encouragement, and to Mr. Salim Malik for help with some of the earlier experiments.

#### References

1. M.M. Qurashi, Pakistan J. Sci. Ind. Research, **1**, 116 (1958).
2. T. Timmermans, *Physico-Chemical Constants of Pure Organic Compounds*, (Elsevier Publishing Co., 1950), p. 311.
3. S.S. Urazovski and P.A. Chernyavski, Doklady Akad. Nauk S.S.S.R., **111**, 640 (1956).