SHORT COMMUNICATIONS

STUDIES IN THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part VI.—Evidence for Fine Structure in the Steps Observed in the Energy of Activation of Viscous Flow in Ethylene Glycol

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In previous communications of this series, well-defined steps were observed in the curves for temperature variation of activation energy of viscous flow in ethylene glycol[1] and water.[2] For water, the steps were found to be sharp (Fig. 1, lowest curve), while for ethylene glycol the drop from one step to the next was gradual, extending over about 5°C. (Fig. 1, uppermost curve). In an effort to resolve this discrepancy, it was considered worthwhile to examine the effect of reducing the measuring interval of 2.5°C. previously used for the measurements on ethylene glycol. This interval has been reduced to 1°C., and some preliminary results obtained with a redistilled commercial grade glycol are presented in this communication.

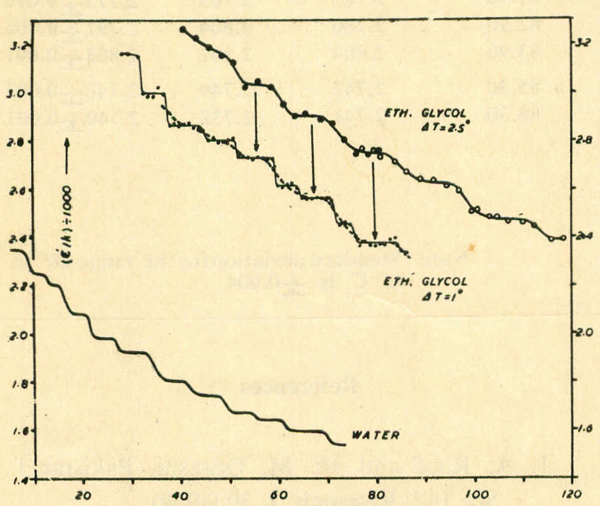

Fig. 1.—Showing the previously obtained data for ethylene glycol (large circles, uppermost curve) and for water (lowest curve), together with the now reported data obtained for ethylene glycol with a smaller measuring interval $\Delta T = 1°C$. (small circles, middle curve ; the ordinates being displaced downward by 0.4 unit).

The experimental arrangement and other details are the same as in the previously reported investigation on ethylene glycol, except that a better thermostat was used and the ballast bottle device for prevention of evaporation used in the measurements on water[2] was also incorporated. The viscosity was obtained from time of flow measurements made every 1°C., five degrees being covered with one setting of the calibrated Beckmann thermometer.

The results obtained with rising and falling temperature sequences, together with the mean values of $(\varepsilon'/k) \div 1000$, obtained at one-degree intervals in the range of 28°C. to 86°C. are given in Table 1. The means are plotted as small solid circles in Fig. 1 (the ordinates having been shifted downward by 0.4 units); the thin continuous line shows the best graph that can be drawn through these experimental points, the standard deviation of which is seen to be about 0.004 from a comparisonof the readings taken with rising and falling temperature sequences. The graph shows a succession of sharp steps occurring at slightly irregular intervals of nearly 6°C., which is to be contrasted with the 12°C. interval found in the previous results obtained by Rauf and Qurashi,[1] and shown in Fig. 1 by large (solid and hollow) circles.

The striking differences between the two graphs can be resolved by smoothing the new curve (for the commercial grade) over a range of 2.5°C., this being the value of the measuring interval used in the earlier experiments. This smoothed graph is shown approximately by the thick broken line curve in Fig. 1. This curve runs closely parallel to the earlier results of Rauf and Qurashi plotted in the upper curve, thus showing agreement between the two sets of results as regards both the temperatures at the steps and energy values of the flat portions. This agreement for the experiments on two grades of glycol with two different thermostats can be taken as proof that (i) the phenomena being observed are essential properties of the

TABLE 1.—VALUES OF ACTIVATION ENERGY ε'/K OF ETHYLENE GLYCOL (COMMERCIAL GRADE) OBTAINED WITH MEASURING INTERVAL Δ T=1 °C.

Mean temperature (°C.)	$\frac{\varepsilon'}{k} \div 1000 = -\frac{T^2}{1000} \times (\Delta \ln \nu / \Delta T)$ Heating sequence	Cooling sequence	Mean	Mean Temperature (°C.)	$\frac{\varepsilon'}{k} \div 1000 = -\frac{T^2}{1000} \times (\Delta \ln \nu / \Delta T)$ Heating sequence	Cooling sequence	Mean
28.40	3.563	3.562	3.562±0.000	60.00	3.014	3.018	3.016±0.002
29.60	3.559	3.563	3.561±0.002	61.00	3.005	3.013	3.009±0.004
31.70	3.551	3.548	3.550±0.002	62.00	3.021	3.025	3.023±0.002
32.70	33.98	3.400	3.399±0.001	63.00	3.025	3.033	3.029±0.004
33.80	3.386	3.387	3.386±0.000	64.00	3.012	3.004	3.008±0.004
34.90	3.385	3.389	3.387±0.002	65.00	2.972	2.964	2.968±0.004
35.90	3.425	3.428	3.426±0.002	66.00	2.963	2.962	2.962±0.001
36.90	3.400	3.396	3.398±0.002	67.00	2.960	2.966	2.963±0.003
38.10	3.265	3.272	3.268±0.004	68.00	2.965	2.975	2.970±0.005
39.00	3.270	3.274	3.272±0.002	69.00	2.960	2.974	2.967±0.007
40.00	3.256	3.268	3.262±0.006	70.00	2.973	2.967	2.970±0.003
41.00	3.268	3.276	3.272±0.004	70.50	2.968	2.965	2.967±0.001
42.00	3.280	3.276	3.278±0.002	71.00	2.962	2.956	2.959±0.003
43.00	3.255	3.261	3.258±0.003	72.60	2.845	2.858	2.852±0.006
44.00	3.260	3.251	3.256±0.005	73.70	2.875	2.857	2.866±0.009
45.00	3.245	3.250	3.248±0.002	74.70	2.856	2.857	2.856±0.000
45.00	3.202	3.208	3.205±0.003	75.70	2.810	2.807	2.808±0.001
47.00	3.208	3.220	3.214±0.006	76.60	2.768	2.761	2.765±0.003
48.00	3.191	3.200	3.196±0.004	77.70	2.777	2.790	2.784±0.006
49.00	3.196	3.204	3.200±0.004	78.90	2.769	2.770	2.770±0.000
50.00	3.203	3.213	3.208±0.005	79.90	2.767	2.763	2.765±0.002
51.00	3.216	3.212	3.214±0.002	80.90	2.771	2.775	2.773±0.002
52.00	3.134	3.142	3.138±0.004	81.90	2.782	2.763	2.773±0.010
53.00	3.140	3.136	3.138±0.002	82.90	2.780	2.804	2.792±0.008
54.00	3.128	3.138	3.133±0.005	83.90	2.804	2.802	2.803±0.001
55.00	3.131	3.119	3.125±0.006	85.30	2.742	2.749	2.746±0.003
56.00	3.128	3.140	3.134±0.006	86.30	2.741	2.738	2.740±0.001
57.00	3.133	3.127	3.130±0.003				
58.00	3.125	3.130	3.128±0.002				
59.00	3.115	3.123	3.129±0.004				

Note : Standard deviation for the range 28° to 59°C. is ±0.004

Note : Standard deviation for the range 60° to 86° C. is ±0.004

ehtylene glycol and (ii) the steps are influenced only in small measure by the impurities (in the two grades of glycol) or by the specific vibrations, etc., of the two thermostats. We may thus expect that the refined experiments on purified ethylene glycol using the measuring interval of 1°C. will yield results essentially similar to those of the middle curve of Fig. 1, i.e. a series of sharp well-defined steps like those observed in water.

These experiments are in hand and their results and interpretations will be communicated separately in a fuller paper.

References

1. A. Rauf and M. M. Qurashi, Pakistan J. Sci. Ind. Research, **2**, 30 (1959).

2 M. M. Qurashi and A. K. M. Ahsanullah (a) Pakistan J. Sci Ind. Research, **3**, 93 (1960), (b) British J. Appl. Phys., in press.