TEMPERATURE DEPENDENCE OF THE INTERMOLECULAR ACTIVATION ENERGY FOR FLOW IN LIQUIDS AND SOLUTIONS

Part III.—Periodicity of Activation Energy in Pure Benzene

A. K. M. AHSANULLAH, S. RAHMAT ALI AND MAZHAR M. QURASHI

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

(Received April 17, 1963)

As a sequel to the series of investigations leading to the discovery of jumps in the activation energy E_η for viscous flow of several hydroxylic liquids, it was considered worthwhile to undertake similar measurements on a few typical non-hydroxylic liquids. Some results for benzene are reported here, and a satisfactory degree of reproducibility has been obtained in working with two samples of pure benzene using a measuring interval $\Delta T = 1°C$.

Evidence of a nearly cyclic variation with an approximate period of 5°C. has been obtained in the range of 26° to 46°C., the peak-to-peak amplitude of $(E_\eta/R)/1000$ being 0.1, corresponding to changes in E_η of about 200 cal.mole.

1. Introduction

In previous communications on this subject, it has been shown that, with the use of a sufficiently small thermal interval of 1°-2°C., the activation energy measurements for several hydroxylic liquids[1,2] and aqueous alcohol[3] solutions show sharp, regularly-recurring jumps in activation energy, E_η. In an effort to throw further light on those phenomena, it was considered desirable to investigate the flow activation energy for some non-hydroxylic liquids such as the paraffin oils, benzene, etc. The present communication gives the results of some experiments carried out on benzene, which was previously found to exhibit an anomalous temperature variation[4] of the activation energy of mixing ΔG_m in solutions of heptane.

The measuring technique is the same as used in the previously reported experiments on flow activation energy of ethylene glycol,[2] where temperature control to 0.002°C. was maintained and the viscometer system was protected by drying tubes on either side. Three to five readings of flow-time were taken at each temperature, and the temperature intervals were measured on a fifth-degree thermometer in the preliminary experiment, and on a calibrated Beckmann differential thermometer in the later experiments. Values of E/R were calculated from the usual equation,

$$E_\eta/R = \Delta \ln \eta/\Delta(1/T) = -T^2 \Delta \ln \eta/\Delta T$$
$$= -T^2 \Delta \ln \nu/\Delta T - T^2 \beta$$

2. Preliminary Experiment

This experiment was of an exploratory character and therefore the measurements were taken from 30°C. to 50°C. at intervals of 2°C. The actual flow-times at the various temperatures are shown in Table 1, together with their standard deviations and the calculated values of E/R for the heating and cooling sequence. The overall means are given in the last column and these are seen to have an r.m.s. error of about 0.015, i.e. a little over 1%, which is quite satisfactory.

A plot of these results is shown in the lowest graph (triangles) of Fig. 1 marked Expt. I, and one can readily observe the two maxima at 33°C. and 45°C., the maximum-to-minimum variation being about 0.1 unit, i.e. seven times the r.m.s. error. A third max. is also noticeable near 38°C.

3. Experiments Using the Beckmann Thermometer

The second set of experiments was carried out at every degree centigrade using a Beckmann thermometer, and the calculations of E/R were made with a one-degree C. interval so as to obtain higher resolution. The results obtained are given in Table 2, where the last column gives the standard deviations as estimated (for groups of five temperatures) from the differences between the results for the heating and cooling sequences. A plot of this data labelled Expt. II is shown in the lower half of Fig. 1 as solid circles. The best curve drawn through these brings out quite clearly the three maxima observed in the preliminary experiment, as well as a series of others at intervals of about 4°C.

In an effort to obtain still more information about the character of these more or less cyclic variations in the activation energy, a third experiment was carried out, but the temperatures were selected in such a way that the plotted points would fall midway between the solid circles of Expt. II. The actual flow-times and Beckmann readings taken at various temperatures are recorded in Table 3, the other columns of which give the corresponding values of E/R calculated for

TABLE 1.—TEMPERATURE, TIME OF FLOW AND CALCULATED VALUES OF $E'/R \div 1000 = -T^2(\Delta \ln \nu/\Delta T)/1000$ FOR PURE BENZENE (ANALAR GRADE) USING $\Delta T = 2°C.$

Heating sequence				Cooling squence				Overall
Temp. (°C.)	Time of flow (sec.) corrected for level	Mean temp. (°C.)	$E'/R \div 1000$	Temp. (°C.)	Time of flow corrected for level	Mean temp. (°C.)	$E'/R \div 1000$	mean $E/R \div 1000$
30.73±0.01	868.40±0.10			30.73±0.01	868.30±0.08			
		31.36	1.14			31.36	1.12	1.13±0.01
32.00±0.00	854.96±0.20			32.00±0.01	855.00±0.10			
34.00±0.00	832.51±0.07	33.00	1.24	34.00±0.00	832.65±0.10	33.00	1.24	1.24±.000
36.00±0.00	812.53±0.11	35.00	1.15	36.00±0.00	812.77±0.10	35.00	1.14	$1.14_5 \pm 0.00_5$
36.00±0.00	812.49±0.05			36.00±0.01	812.54±0.08			
38.00±0.00	793.84±0.10	37.00	1.12	38.00±0.00	793.89±0.12	37.00	1.12	1.12±0.00
40.00±0.00	775.82±0.12	39.00	1.12	40.00±0.00	775.40±0.06	39.00	1.16	1.14±0.02
40.00±0.01	774.92±0.08			40.00±0.00	774.94±0.05			
42.00±0.01	758.42±0.05	41.00	1.07	42.00±0.00	758.44±0.11	41.00	1.07	1.07±0.00
44.00±0.00	741.79±0.10	43.00	1.11	44.00±0.01	741.72±0.10	43.00	1.12	$1.11_5 \pm 0.00_5$
46.00±0.00	725.60±0.10	45.00	1.12	46.00±0.00	725.10±0.10	45.00	1.15	$1.13_5 \pm 0.01_5$
46.00±0.00	725.02±0.10			46.00±0.01	725.01±0.08			
48.00±0.00	709.18±0.20	47.00	1.13	48.00±0.00	709.50±0.12	47.00	1.11	1.12±0.01
50.00±0.00	694.69±0.10	49.00	1.07	50.00±0.01	694.90±0.10	49.00	1.08	$1.07_5 \pm 0.00_5$

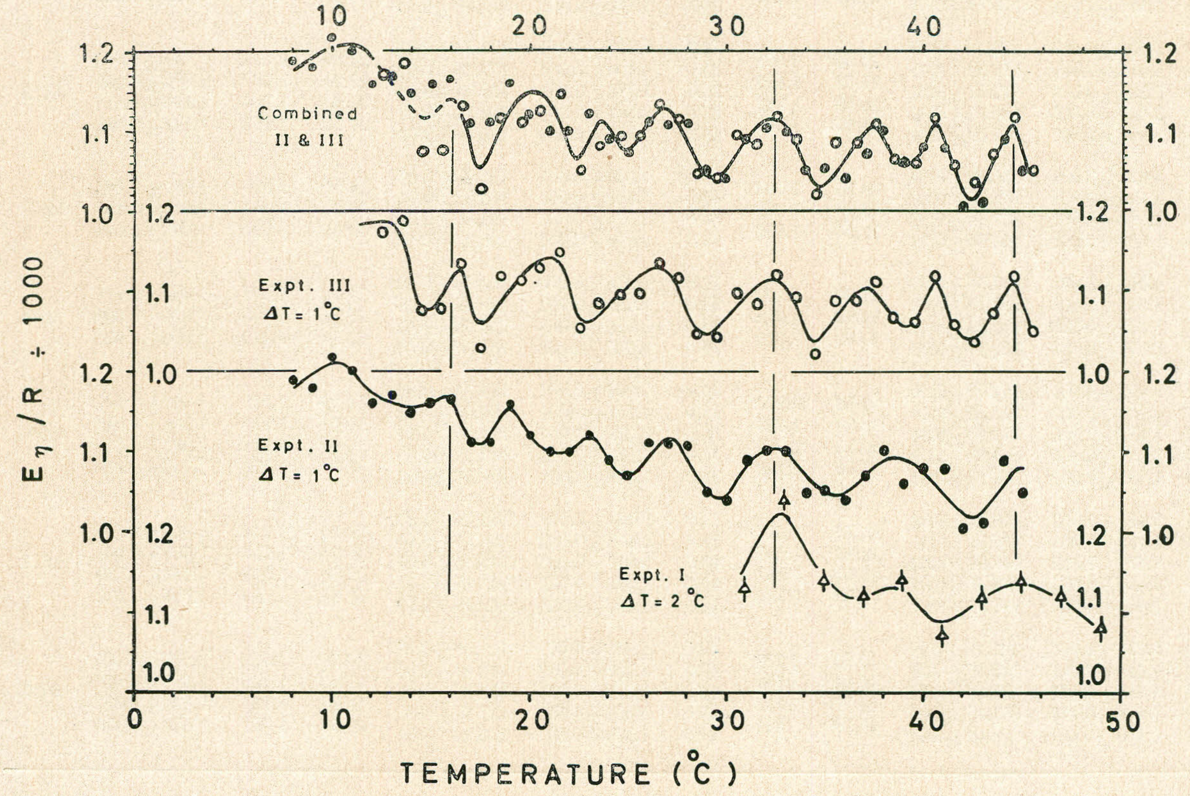

Fig. 1.—Series of graphs showing the results of repeated experiments on benzene to determine the values of $E/R = -T^2 \Delta \ln \nu/\Delta T$ at various temperatures:

(i) Lowest curve (triangles) is a plot of the measurements made at intervals of 2°C. with a fifth-degree thermometer, showing two clear maxima at 33°C. and 45°C.

(ii) Second curve (solid circles) marked "Expt. II" gives the results of the next experiment, which was carried out from 8°C. to 46°C. with a measuring interval $\Delta T = 1°C.$, and using a Beckmann differential thermometer. The peaks at 33°C. and 45°C. are again seen, and in addition several more at intervals of 4° to 5°C.

(iii) Curve marked "Expt. III" (hollow circles) shows a repetition of the previous experiment, but at temperatures displaced by 0.5°C. There is general agreement with "Expt. II."

(iv) Uppermost curve (solid and hollow circles) is a combined plot of Expt. II and III, and good concordance is obtained down to 16°C., below which there are a few substantial discrepancies. The mean graph above 16°C. has nicely regular appearance.

TABLE 3.—BECKMANN READING, FLOW TIMES AND CALCULATED VALUES OF E/R FOR PURE BENZENE (ANALAR GRADE), USING $\Delta T = 1\,^{\circ}C$. (EXPT. III).

Heating sequence					Cooling sequence					Overall mean	
Temp. (°C.)	Beckmann reading	Time of flow (sec.) corrected for level	Mean temp. (°C.)	E′/R ÷1000	Temp. (°C.)	Beckmann reading	Time of flow (sec.) corrected for level	Mean temp. (°C.)	E′/R ÷1000	Mean (E/R)/1000	Standard deviation for group
12.0	5.635±0.001	207.33±0.01	12.50	1.213	12.0	5.637±0.001	207.23±0.06	12.50	1.133	1.173±0.040	
13.0	4.612±0.001	204.20±0.02	13.50	1.195	13.0	4.615±0.001	204.33±0.05	13.50	1.178	1.186±0.008	
14.0	3.598±0.000	201.21±0.04	14.50	1.137	14.0	3.587±0.000	201.34±0.03	14.50	1.013	1.075±0.062	0.032
15.0	2.556±0.000	198.35±0.01	15.50	1.079	15.0	2.546±0.000	198.79±0.09	15.50	1.072	1.076±0.004	
16.0	1.561±0.001	195.81±0.03			16.0	1.578±0.001	196.33±0.05				
16.0	5.565±0.000	195.18±0.02	16.50	1.176	16.0	5.561±0.001	195.15±0.04	16.50	1.092	1.134±0.042	
17.0	4.549±0.000	192.42±0.03	17.50	1.014	17.0	4.546±0.001	192.59±0.10	17.50	1.042	1.028±0.014	
18.0	3.516±0.001	190.05±0.03	18.50	1.126	18.0	3.517±0.001	190.16±0.04	18.50	1.110	1.118±0.008	0.024
19.0	2.512±0.001	187.54±0.05	19.50	1.096	19.0	2.511±0.000	187.68±0.05	19.50	1.130	1.113±0.017	
20.0	1.514±0.001	185.16±0.02			20.0	1.511±0.001	185.22±0.08				
20.0	5.226±0.000	184.96±0.03	20.50	1.136	20.0	5.237±0.001	184.66±0.03	20.50	1.120	1.128±0.008	
21.0	4.231±0.000	182.55±0.03	21.50	1.142	21.0	4.234±0.001	182.27±0.03	21.50	1.149	1.149±0.004	
22.0	3.208±0.001	180.11±0.04	22.50	1.030	22.0	3.195±0.000	179.78±0.03	22.50	1.078	1.054±0.024	0.016
23.0	2.188±0.000	177.96±0.02	23.50	1.106	23.0	2.197±0.001	177.58±0.05	23.50	1.061	1.083±0.022	
24.0	1.191±0.001	175.74±0.01			24.0	1.196±0.001	175.45±0.03				
24.0	5.404±0.001	175.14±0.03	24.50	1.098	24.0	5.419±0.001	175.32±0.02	24.50	1.093	1.095±0.002	
25.0	4.412±0.001	173.00±0.03	25.50	1.105	25.0	4.404±0.001	173,15±0.02	25.50	1.087	1.096±0.009	
26.0	3.384±0.001	170.81±0.04	26.50	1.122	26.0	3.378±0.001	170.98±0.00	26.50	1.148	1.135±0.013	0.018
27.0	2.380±0.000	168.68±0.02	27.50	1.079	27.0	2.384±0.001	168.82±0.04	27.50	1.152	1.116±0.036	
28.0	1.386±0.001	166.69±0.04			28.0	1.383±0.000	166.68±0.04				
28.0	4.621±0.001	166.52±0.04	28.50	1.092	28.0	4.628±0.001	165.70±0.05	28.50	1.000	1.046±0.046	
29.0	3.614±0.001	164.52±0.02	29.50	1.080	29.0	3.618±0.001	163.87±0.02	29.50	1.008	1.044±0.036	0.048
30.0	2.592±0.001	162.55±0.02	30.50	1.138	30.0	2.575±0.001	162.00±0.04	30.50	1.056	1.097±0.041	
31.0	1.609±0.001	160.59±0.01			31.0	1.616±0.001	160.23±0.03				
31.0	4.065±0.002	160.70±0.02	31.50	1.102	31.0	4.076±0.000	160.76±0.02	31.50	1.065	1.084±0.019	
32.0	3.037±0.000	158.75±0.02	32.50	1.092	32.0	3.035±0.002	158.85±0.00	32.50	1.148	1.120±0.028	0.028
33.0	2.023±0.000	156.88±0.02	33.50	1.068	33.0	2.056±0.001	156.95±0.01	33.50	1.115	1.092±0.023	
34.0	1.041±0.002	155.14±0.03			34.0	1.040±0.001	155.07±0.02				
34.0	5.137±0.001	154.79±0.00	34.50	0.978	34.0	5.162±0.001	155.34±0.02	34.50	1.065	1.022±0.042	
35.0	4.150±0.001	153.23±0.01	35.50	1.043	35.0	4.161±0.001	153.60±0.02	35.50	1.129	1.086±0.043	
36.0	3.137±0.000	151.53±0.01	36.50	1.058	36.0	3.128±0.001	151.73±0.02	36.50	1.116	1.087±0.019	0.040
37.0	2.127±0.000	149.85±0.02	37.50	1.144	37.0	2.126±0.001	149.97±0.03	37.50	1.076	1.110±0.034	
38.0	1.132±0.002	148.12±0.03			38.0	1.128±0.001	148.31±0.01				
38.0	5.463±0.002	148.20±0.02	38.50	1.017	38.0	5.464±0.002	148.45±0.02	38.50	1.116	1.066±0.050	
39.0	4.465±0.001	146.66±0.01	39.50	1.057	39.0	4.462±0.002	146.75±0.00	39.50	1.068	1.062±0.006	
40.0	3.470±0.002	145.09±0.00	40.50	1.087	40.0	3.459±0.002	145.15±0.02	40.50	1.148	1.118±0.030	0.032
41.0	2.460±0.001	143.48±0.02	41.50	1.080	41.0	2.450±0.002	143.45±0.02	41.50	1.036	1.058±0.022	
42.0	1.465±0.002	141.93±0.01			42.0	1.466±0.002	141.98±0.02				
42.0	5.429±0.002	141.96±0.01	42.50	1.038	42.0	5.410±0.001	141.88±0.01	42.50	1.036	1.037±0.001	
43.0	4.416±0.002	140.47±0.01	43.50	1.046	43.0	4.408±0.002	140.41±0.02	43.50	1.106	1.073±0.027	
44.0	3.415±0.001	139.01±0.02	44.50	1.126	44.0	3.409±0.001	138.87±0.01	44.50	1.113	1.120±0.007	0.010
45.0	2.404±0.002	137.45±0.03	45.50	1.051	45.0	2.401±0.001	137.31±0.00	45.50	1.051	1.051±0.000	
46.0	1.408±0.001	136.04±0.02			46.0	1.404±0.002	135.90±0.01				

the heating and cooling sequences, together with the overall mean values. The final standard deviations are again estimated on the basis of the differences between the two sets of values.

TABLE 2.—CALCULATED VALUES OF $E'/R \div 1000 = -T^2 (\Delta \ln \nu/\Delta T)/1000$ FOR PURE BENZENE, $\Delta T = 1°C$.

Mean temp. (°C.)	(E'/R)/1000 Heating sequence	Cooling sequence	Mean	Standard deviation
8.00	1.154	1.234	1.194±0.040	
9.00	1.150	1.216	1.183±0.033	
10.00	1.240	1.199	1.220±0.020	±0.028
11.00	1.198	1.204	1.201±0.003	
12.00	1.141	1.195	1.163±0.027	
13.00	1.185	1.162	1.174±0.012	
14.00	1.148	1.152	1.150±0.002	
15.00	1.154	1.166	1.160±0.006	±0.012
16.00	1.180	1.160	1.170±0.010	
17.00	1.148	1.080	1.114±0.034	
18.00	1.184	1.040	1.112±0.072	
19.00	1.164	1.168	1.166±0.002	
20.00	1.066	1.181	1.123±0.058	±0.040
21.00	1.080	1.134	1.107±0.027	
22.00	1.085	1.113	1.099±0.014	
23.00	1.219	1.076	1.148±0.072	
24.00	1.100	1.081	1.090±0.010	
25.00	1.070	1.078	1.074±0.004	±0.026
26.00	1.113	1.106	1.109±0.003	
27.00	1.098	1.134	1.116±0.018	
28.00	1.100	1.116	1.108±0.008	
29.00	1.102	1.000	1.051±0.051	
30.00	1.108	0.976	1.042±0.066	±0.033
31.00	1.109	1.078	1.093±0.015	
32.00	1.096	1.106	1.101±0.005	
33.00	1.080	1.132	1.106±0.026	
34.00	1.023	1.090	1.056±0.034	
35.00	1.010	1.092	1.051±0.041	±0.030
36.00	1.032	1.049	1.040±0.009	
37.00	1.052	1.096	1.074±0.022	
38.00	1.113	1.096	1.104±0.008	
39.00	1.037	1.089	1.063±0.026	
40.00	1.072	1.108	1.090±0.018	±0.025
41.00	1.083	1.092	1.087±0.005	
42.00	1.059	0.948	1.004±0.055	
43.00	1.042	0.983	1.013±0.030	
44.00	1.086	1.109	1.098±0.011	±0.030
45.00	1.092	1.014	1.053±0.039	

Overall standard deviation = ± 0.030

These over-all mean values are plotted as hollow circles in the upper half of Fig. 1, the graph being labelled Expt. III.

4. Conclusions

The graphs for Expts. II and III show a satisfactory measure of correspondence in the positions of the maxima and minima, and therefore a combined plot is shown in the top-most graph of Fig. 1, the data from the two experiments being plotted with solid and hollow circles as before. This combined plot is a considerable improvement on the individual graphs and enables us to draw a nicely undulating regular graph down to a temperature of 16°C. or so, with the individual points showing an r.m.s. scatter about the graph of only ± 0.022, which compares with the estimated standard deviations ranging from 0.02 to 0.04 in Tables 2 and 3. It follows that the deviation for the mean of pairs of successive points (from Expts. II and III) 0.5° apart is ± 0.016, while the peak-to-peak amplitude of the undulations in this graph lies between 0.06 and 0.10, i.e. four to six times this standard deviation for the means of successive points. Below 16°C., there are some large discrepancies between the results for Expt. II and Expt. III, which could be due to the presence of traces of water in the benzene, which became slightly milky below 12°C., corresponding to about 0.03% water content.

Thus we may conclude the existence of a definite, more or less cyclic, variation in activation energy E_η for flow of benzene in the range of 16°C. to 46°C., the period being nearly 4.0° ± 0.9°C. and the amplitude about 8% of the mean value. Further experiments are being carried out on heptane, on benzene of various degrees of purity, and on light mineral oils, such as high-speed diesel oil.

References

1. M.M. Qurashi and A. K. M. Ahsanullah, British J. Appl. Phys., **12**, 65 (1961).
2. A. K. M. Ahsanullah and M. M. Qurashi, ibid., **13**, 334 (1962).
3. A. K. M. Ahsanullah, S. R. Ali and M. M. Qurashi, Pakistan J. Sci. Ind. Research, **5**, 133 (1962).
4. M. Tayyab Qureshi and M. M. Qurashi, ibid., **5**, 222 (1962).