STUDIES IN THE RELATIONSHIP BETWEEN VISCOSITY AND MOLECULAR STRUCTURE

Part I.—Temperature Dependence of the Viscosity of certain Typical Mineral Oils.

Mazhar Mahmood Qurashi

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

1. Introduction

For some time past, the behaviour of mixtures of mineral oils with various hydroxylic liquids has been the subject of investigation in this laboratory.[1] On examining the results obtained it was thought worth-while to undertake a detailed study of the temperature-dependence of the viscosities of mineral oils as well as hydroxylic compounds. Because these liquids have high viscosities and are usually considered to be more or less anomalous, it was expected that their study would give valuable information about the correlation between viscosity and molecular structure. In general terms, we may picture such a liquid as composed of molecular aggregates of varying size and orientation, each with exposed hydroxyl (or other polar) groups capable of forming some sort of "transitory bond" with any neighbouring aggregates. The viscosity would then be dependent both on the size of the aggregates and on the strengths of these "bonds" between them. One or both of these quantities may vary with temperature, and therefore a detailed study of the temperature variation of the viscosity should give quantitative information about these characteristics of the aggregates.

There is also a more practical aspect of the problem, namely that of predicting the viscosity of a given oil or other liquid at elevated temperatures or at very low temperatures. The establishment of a simple generalized formula for this could be of considerable utility in the field of lubricants, anti-freeze compounds, etc.

2. Preliminary Experiments

The earliest results were obtained with a commercial straight mineral oil cut, B.O.C. "450," which has a viscosity of 400 centistokes at a temperature of 40 °C., and corresponds to a fairly heavy lubricating oil. The kinematic viscosities were measured at different temperatures with a U-tube viscometer of the British Standard pattern mounted vertically in an electrically controlled thermostatic bath, the measurements being carried out in accordance with the Standard Specifications. The final accuracy of the determinations at each temperature was of the order of 0.2%. The results are given in Table 1(a) at intervals of 5 °C. to 10 °C., over the temperature range 20°—85 °C. An attempt was first made to obtain a linear plot against temperature by means of a power-law, as has been done for several non-associated liquids cf. for example Mitra.[2] It was found that $1/v^{\frac{1}{4}}$ gave good results, as shown by the straight line through the observed data in Fig. 1(a). The fit is remarkably good, except for the two initial points, both of which lie above the line, suggesting a systematic divergence at low temperatures.

In order to follow up this phenomenon by working at lower temperatures, a small 2-litre thermostat was built incorporating a copper cooling coil, through which ice-cold water could be circulated at a regulated speed. In this way, it was possible to work at temperatures down to 4 °C., the degree of constancy attained during each reading was however poorer than with the electrically controlled apparatus, being now only of the order of $\pm$ 0.2 °C. The additional observations obtained in this way are shown in Table 1(b), and are plotted in Fig. 1(b) as hollow circles. It is seen that the complete data can be fitted almost exactly by means of two straight lines intersecting at a temperature of about 30 °C., the slopes of the two lines are 0.112/°C. and 0.135/°C., respectively. The experimental point at 30 °C. lies a little above both lines, but can be made to fit over the temperature range 25 °C. to 35 °C., if a gradual transition from one line to the other is assumed, cf. the broken line in Fig. 1(b). At all events, these graphs show evidence of some sort of transition in the viscous behaviour of the oil at a temperature of about 28 °C. and a viscosity of nearly 1,000 centistokes.

The investigation was next carried over to the light lubricating oils by working with another straight mineral oil cut, B.O.C. "60," which has a viscosity of 38 centistokes at 40 °C. The experimental values are given in Table 1(c), while the upper graph of Fig. 1(b) shows that these values can again be represented quite well by two straight lines with a fairly sharp change-over in the region of 55 °C. The slopes of the two lines are 0.157/°C. and 0.133/°C. in this case, the direction of the knee being opposite to that in the first case. It
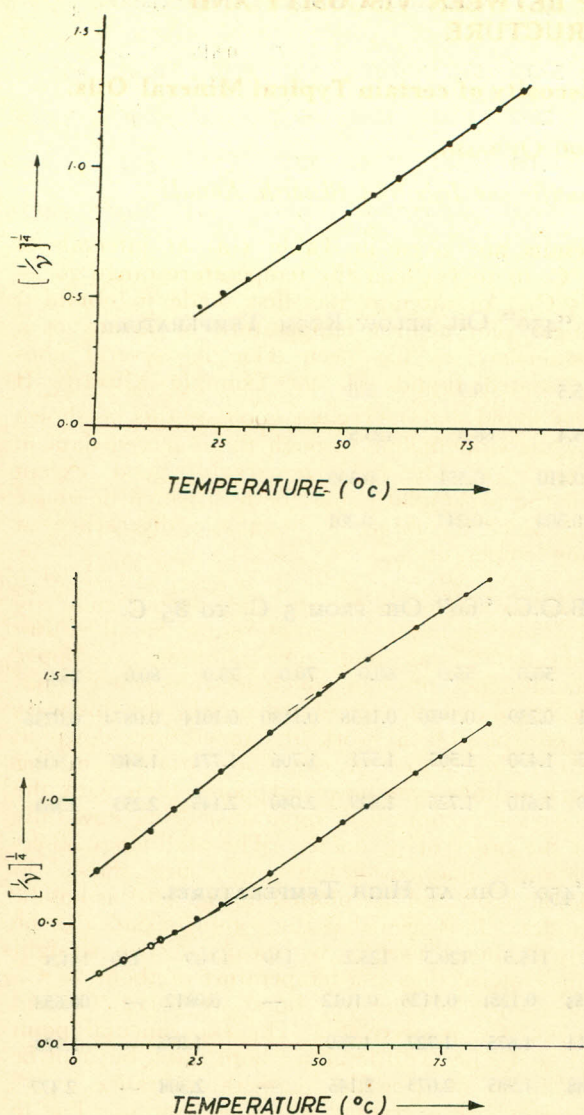
Fig. 1.—Preliminary graphs of $(1/\nu)^{\frac{1}{4}}$ against temperature for mineral oils: (a) top: B.O.C. "450" oil from 20°C. to 85°C. (b) bottom: B.O.C. "450" oil and "60" oil from 5°C. to 85°C.

is known (Chemical Engineers Handbook, 1950) that the viscosity versus temperature graphs for many liquids can be fitted to each other and to a "generalized" graph by an appropriate shift parallel to the temperature axis. This is seen to be roughly true in the present case, because a translation of the upper graph of Fig. 1(b) through about 40°C. parallel to the temperature axis will bring it into near-coincidence with the corresponding portion of the lower graph. Carrying the comparison between the two graphs a little further, we should expect another change of slope in the lower graph in the neighbourhood

of $1/\nu^{\frac{1}{4}} = 1.45$, *i.e.*, around a temperature of 95°C. To test this point, the viscosity measurements were extended to temperatures well above 100°C.

3. Measurements above 85°C.

For this purpose, a high-temperature thermostatic glycerol bath was designed and built in the laboratory. A diagrammatic sketch of the apparatus is shown in Fig. 2(a) and the electrical circuit for controlling the heater current is shown in Fig. 2(b). Essentially, the thermostat consists of a cylindrical glass vessel about 20 cm. diameter and 25 cm. high, contained in a rectangular wooden box for added insulation. The wooden box is provided with small plate-glass windows on opposite sides, one for providing illumination, and the other for observing the liquid levels in the viscometers. The top of the box is closed with a wooden lid that has suitably placed openings for the electrical heater, the stirrer, the control thermometer, and the viscometer holder. Two small openings are also provided for inserting two thermometers in such a way that their bulbs shall be as close as possible to the middle portion of the U-tube viscometer.

This thermostat was tested extensively from 70°C. upto 200°C., and it was found possible to maintain the temperature constant to within one or two hundredths of a degree, provided a certain amount of care was exercised in the setting of the electrical controls. This was considered to be quite satisfactory for the work in hand.

In the first instance, the viscosity of the heavy B.O.C. "450" oil was measured at various temperatures in the range of 80°C. to 145°C. The results of the measurements are given in Table 2 and the complete data from 5°C. to 145°C. are plotted in Fig. 3 as $1/\nu^{\frac{1}{4}}$ against temperature.

It is evident that the predicted change of slope at the higher temperatures does indeed occur, but the actual temperature of the transition is considerably lower than expected, being about 85°C. instead of 95°C. The direction of the bend in the graph is also as expected from analogy with the case of the lighter oil. Furthermore, the points for temperatures above 120°C. distinctly show the presence of another such bend at about 120°C. The obvious suggestion is that the viscous behaviour of the two oils studied changes fairly sharply after very definite temperature intervals, whose extent varies, but which may be estimated to be of the order of 40°C. Further elucidation of this point is reserved for the later part of the paper (section 7), in which additional and more accurate data are introduced and discussed.

TABLE 1(A).—KINEMATIC VISCOSITIES OF B.O.C. "450" OIL ABOVE ROOM TEMPERATURE.

Temperature (°C.)		20.3	25.0	30.0	40.0	50.0	55.0	60.0	70.0	75.0	80.0	85.0
v (Stokes)		21.35	13.53	8.84	3.97	1.958	1.437	1.095	0.657	0.515	0.415	0.335
$[1/v]^{\frac{1}{4}}$		0.465	0.521	0.580	0.708	0.845	0.913	0.930	1.111	1.180	1.246	1.313
$[1/v]^{\frac{1}{3}}$		0.360	0.419	0.484	0.632	0.800	0.886	0.971	1.150	1.247	1.341	1.439

TABLE 1(B).—KINEMATIC VISCOSITIES OF B.O.C. "450" OIL BELOW ROOM TEMPERATURE.

Temperature (°C.)		15.5	9.9	5.0
v (Stokes)		35.4	66.5	123.5
$[1/v]^{\frac{1}{4}}$		0.410	0.351	0.300
$[1/v]^{\frac{1}{3}}$		0.304	0.247	0.201

TABLE 1(C). KINEMATIC VISCOSITIES OF B.O.C. "60" OIL FROM 5 C. TO 85 C.

Temp. (°C.)	4.4	10.7	15.5	20.3	25.0	30.0	40.0	50.0	55.0	60.0	70.0	75.0	80.0	85.0
v (Stokes) ..	3.925	2.290	1.702	1.163	0.867	0.647	0.381	0.239	0.1950	0.1638	0.1180	0.1014	0.0874	0.0756
$[1/v]^{\frac{1}{4}}$ ..	0.711	0.813	0.876	0.963	1.036	1.115	1.273	1.430	1.505	1.571	1.706	1.771	1.840	1.908
$[1/v]^{\frac{1}{3}}$ ..	0.634	0.759	0.838	0.951	1.050	1.156	1.380	1.610	1.726	1.829	2.040	2.145	2.253	2.364

TABLE 2.—KINEMATIC VISCOSITY OF B.O.C. "450" OIL AT HIGH TEMPERATURES.

Temperature(°C.)	85	90.3	95.1	100.0	105.5	110.2	115.5	120.3	125.2	130	134.9	140	144.8
v (Stokes) ..	0.3435	0.2836	0.2388	0.2038	0.1723	0.1485	0.1281	0.1126	0.1012	—	0.0812	—	00.658
$[1/v]^{\frac{1}{4}}$ ..	1.309	1.372	1.431	1.490	1.552	1.614	1.675	1.727	1.769	—	1.876	—	1.978
$[1/v]^{\frac{1}{3}}$ ..	1.430	1.523	1'611	1.701	1.798	1.888	1.985	2.073	2.146	—	2.308	—	2.477

TABLE 4.—"SMOOTHED" VALUES OF ε/k × 10⁻³ FOR B.O.C. "450" OIL.

Temperature (°C.)		20	40	60	80	100	120	140	160	180	200	220	240
$\left(\dfrac{\varepsilon/k}{1000}\right)$smoothed		8.66	7.32	6.21	5.32	4.62	4.08	3.68	3.38	3.12	2.95	2.86	2.82

TABLE 5

Temperature (°C.)		30	35	40	45	50	55	60	65	70	75	80
$\dfrac{\varepsilon'/k}{1000}$		8.79	8.09	7.57	7.11	6.73	6.43	6.17	5.94	5.74	5.57	5.42
First differences			0.70	0.52	0.46	0.38	0.30	0.26	0.23	0.20	0.17	0.15
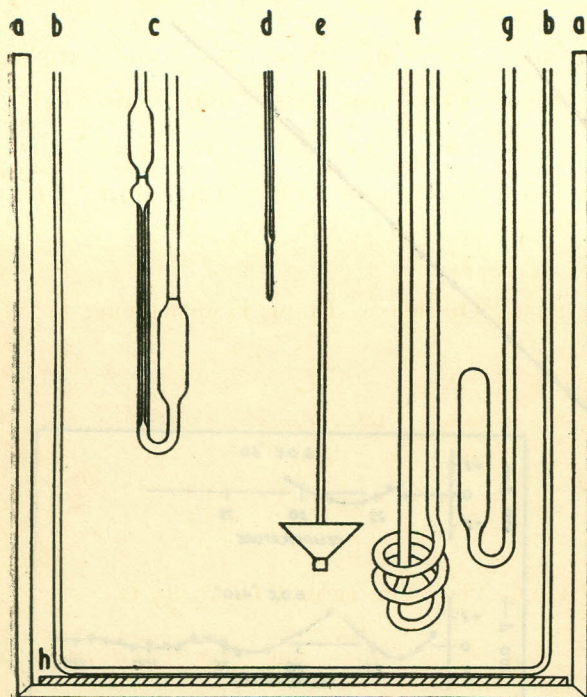
a, Wooden box; b, glass vessel; c, viscometer; d, centigrade thermometer; e, stirrer; f, heater; g, thermal control; h, asbestos sheet.
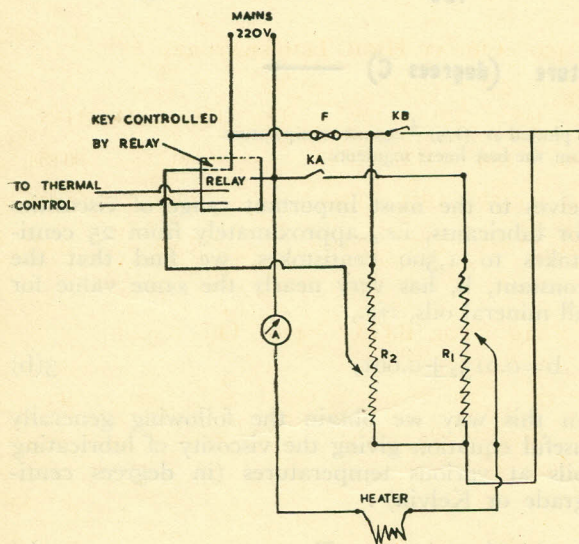
R1 & R2, Reheostats; KA & KB, keys; F, fuse; A, ammeter.

Fig. 2.—Sketch of high temperature glycerol thermostat and the associated temperature control circuit.

For the time being, we analyse the practically important portions of these graphs, which fall in the viscosity range 5,000 to 10 centistokes.
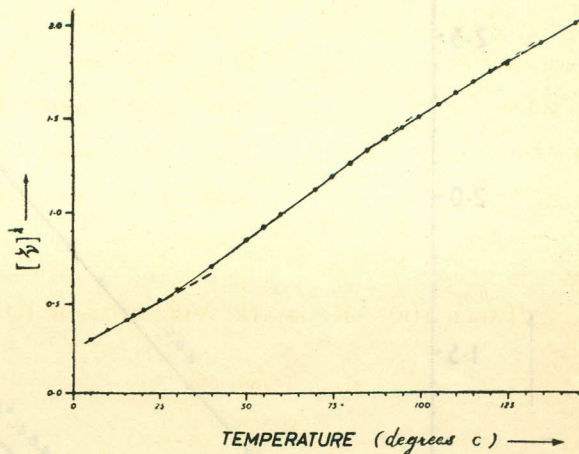

TEMPERATURE (degrees c) ⟶

Fig. 3.—Extended graphs of $(1/\nu)^{\frac{1}{4}}$ against temperature for B.O.C. "450" oil.

4. Discussion of the $[1/\nu]^{\frac{1}{4}}$ graphs

Within the above-mentioned range, the graphs for $[1/\nu]^{\frac{1}{4}}$ consists of three straight lines, whose intersections give two quite sharp bends in opposite directions, thus giving the whole graph a sort of chair-like shape. In Fig. 4, the previously obtained data for B.O.C. "450" oil are plotted in the form of $[1/\nu]^{\frac{1}{3}}$ against temperature. Comparison of Fig. 4 with Fig. 3 brings out the fact that, although the various segments of the curves obtained can still be approximately represented by straight lines, a systematic curvature is detectable in each of the segments in Fig. 4. This curvature is best seen by separately plotting the deviation, Δ, of the observed points from the best straight lines drawn through them. These deviation plots are given in the inset to Fig. 4, and it is seen that the plot corresponding to each segment of the original graphs shows a downward convexity, which indicates that the correct index to be used for $1/\nu$ to get linearity is lower than $1/3$. The exact value, n, of this index that will give linearity in any particular segment of the graph can be got by means of the following formula, which is developed in Appendix I :

$$\frac{1}{3}-n= \frac{\overline{y}}{3} \times \overline{\frac{d^2\Delta}{dT^2}} \bigg/ \left(\frac{dy}{dT}\right)^2 \qquad (1)$$

where $y=[1/\nu]^{\frac{1}{3}}$, $\overline{y}=$mean value of y in the range considered, $\Delta=$deviation of y from the best straight line through the points, T=temperature. With this formula, we get for the three segments of the graph for B.O.C. "450" oil, $1/3-n=0.054$, 0.097, 0.081, respectively, giving a mean value of $1/3-n=0.077\pm0.012$, whence $n=0.256\pm0.012$.
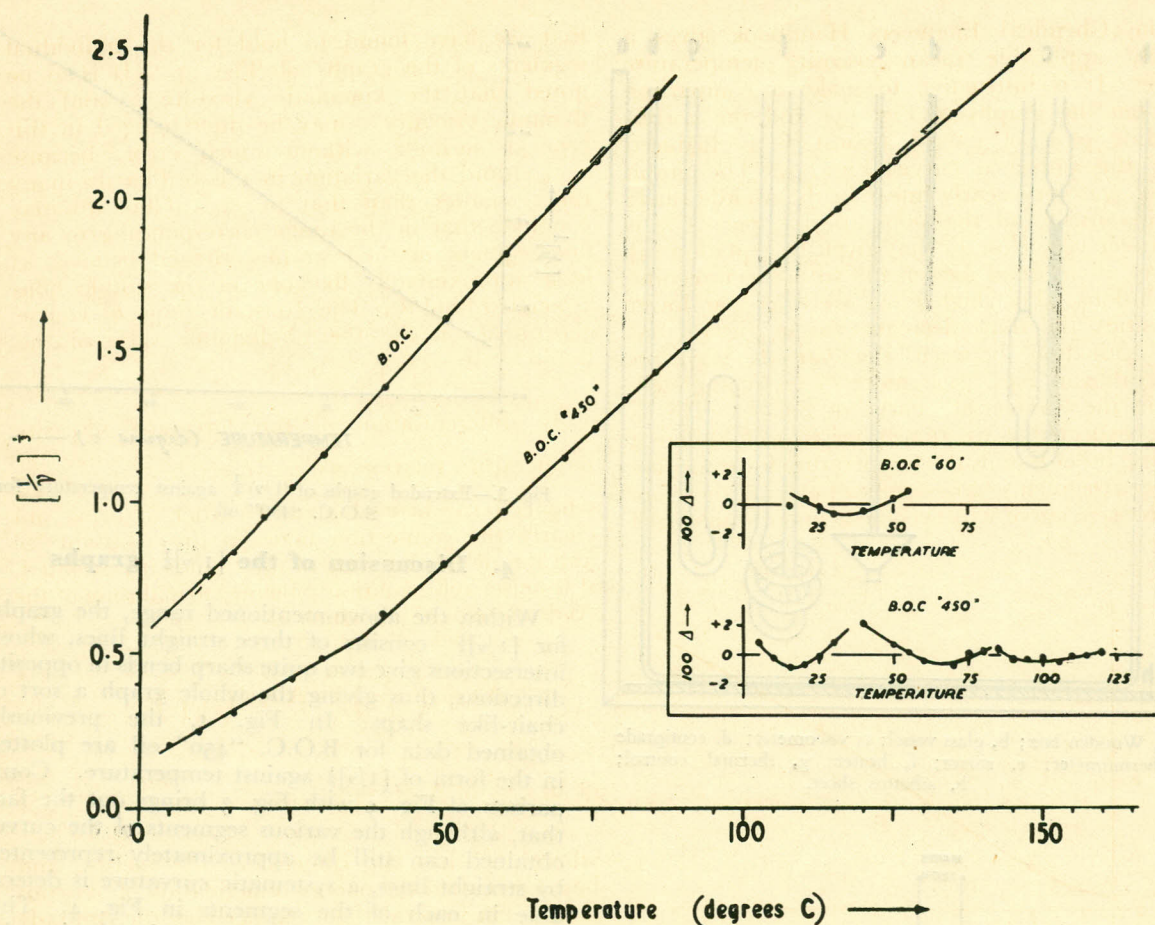
2(a)

Fig. 4.—Data on B.O.C. "450" and "60" oils plotted as $(1/v)^{\frac{1}{3}}$ against temperature.
The inset shows the deviations from the best linear segments.

The corresponding plot for the B.O.C. "60" oil gives

$$n = 0.258 \qquad\qquad 2(b)$$

(No internal estimate of the standard deviation could be got in this case because the experimental points on the two other segments are too few to give reliable estimates for $1/3 - n$.) From the results 2(a) and 2(b), it follows that for both these oils the index, n, may be taken to lie definitely between 0.25 and 0.27 over the entire range of temperatures studied, i.e., from 5 °C. to over 100 °C.

We may now represent the viscosity of a mineral oil by means of the formula

$$[v]^{-0.26} = a + bT, \qquad\qquad 3(a)$$

where a, b, will be constant in any given segment of the graphs of Fig. 3. If we further limit ourselves to the most important range of viscosities for lubricants, i.e., approximately from 25 centistokes to 1,500 centistokes, we find that the constant, b, has very nearly the same value for all mineral oils, viz.,

$$b = 0.015_2 \pm 0.001, \qquad\qquad 3(b)$$

In this way we obtain the following generally useful equation giving the viscosity of lubricating oils at various temperatures (in degrees centigrade or Kelvin) :

$$1/v^{0.26} = a + 0.0152\,T, \qquad\qquad (4)$$

where the quantity, a, varies with the grade of the oil, and can be determined from equation (4) provided we measure the viscosity of the oil at any one convenient temperature. ('a' is of course to be inversely correlated with the boiling range of the oil).

The Chemical Engineers Handbook gives a widely applicable mean viscosity temperature curve. It is instructive to make a comparison between the graphs of Fig. (3) and the corresponding plots of $1/v^{0.26}$ against T as deduced from this universal curve (Fig. 5). The graph of Fig. 5 is very nearly linear in the middle range of viscosities, and the slope (0.0165 per °C.) is moreover very close to that given by equation (4) above, all in good agreement with the foregoing conclusions. For higher as well as for lower viscosities, the slope decreases (as in Fig. 3), but the distinction between the various segments observable in Fig. 3 is more or less completely lost in the "universal" curve of Fig. 5. This is to be expected if we remember that in different oils and other liquids the temperature for transition between segments varies somewhat and therefore the average curve will become a smooth unbroken one.
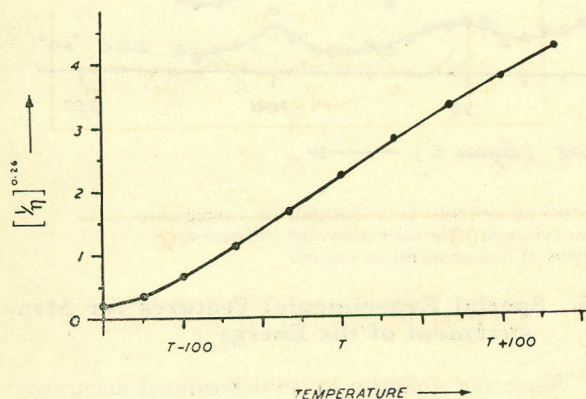

Fig. 5.—$(1/\eta)^{0.26}$ plot calculated from the generalized viscosity curve for liquids.

5. Correlation with Inter-molecular Energy

Besides their application to practical problems, the above results are interesting in themselves, and it is worthwhile to discover their fundamental connection with the phenomena occurring inside the liquids. Mitra[2] has developed the theory for a $1/T^3$ law for the variation of viscosity, based on the free-volume theory of liquids. The $1/T^3$ law was first given empirically by Batschinsky,[3] and is in fair agreement with the data on several simple liquids. On this basis, the reciprocal of the cube-root of the viscosity may be expected to vary linearly with temperature for such simple liquids ; this is very close to the law,

$$\frac{1}{v^{0.26}} = a + b\,T,$$

that we have found to hold for the individual segments of the graphs of Fig. 3. (It is to be noted that the kinematic viscosity v and the dynamic viscosity η may be interchanged in this type of formula without much error, because $v = \eta/\rho$, and the variation in ρ is ordinarily many times smaller than that in η). Thus we may conclude that in the range corresponding to any one segment of these graphs, the oil behaves at least approximately like one of the simple non-associated liquids. The constant b, is of course dependent on the thermo-dynamic state of the liquid.

By differentiation of the foregoing viscosity temperature relation, we easily get $b = \dfrac{-1}{v^{1.26}}\dfrac{\partial v}{\partial T}$ whence b can be evaluated. In order to bring out clearly the connection between this constant 'b' and the molecular state of the liquids investigated, it is better (cf. equation 7 below) to make use of the Andrade equation, which is

$$\eta = A\exp\left(\frac{c}{T}\right) = A\exp\left(\frac{\varepsilon}{kT}\right),$$

$$\text{or } \ln \eta = \ln A + \frac{\varepsilon}{kt}, \tag{5}$$

where "ε" has the dimensions of energy, and has been called the energy of activation of viscous flow. The general theory underlying the Andrade equation shows that the quantity ε is a measure of the mutual potential energy of the molecules or molecular aggregates in the liquid, while A can be considered as a measure of the concentration of these aggregates. For simple monatomic liquids, ε is practically constant, while for the majority of liquids it is found to vary with temperature possibly tending to a minimum near the boiling point. To a first approximation, both ε and A can be taken as constant over a small temperature range. Then by differentiation of equation (5), we get

$$\frac{\partial \ln \eta}{\partial T} = \frac{1}{\eta}\frac{\partial \eta}{\partial T} = -\frac{\varepsilon}{kT^2},$$

$$\text{whence } \frac{\varepsilon}{k} = -\frac{T^2}{\eta}\frac{\partial \eta}{\partial T} = -\frac{T^2 \Delta \ln \eta}{\Delta T}, \tag{6a}$$

If we neglect the small difference between $\Delta \ln \eta$ and $\Delta \ln v$, then this equation leads to the following connection between ε and b,

$$b = -\frac{1}{v^{1.26}}\frac{\partial v}{\partial T} = \frac{-1}{v^{0.26}}\frac{\partial \ln v}{\partial T} \sim \frac{\varepsilon/k}{T^2 \times v^{0.26}} \tag{7}$$
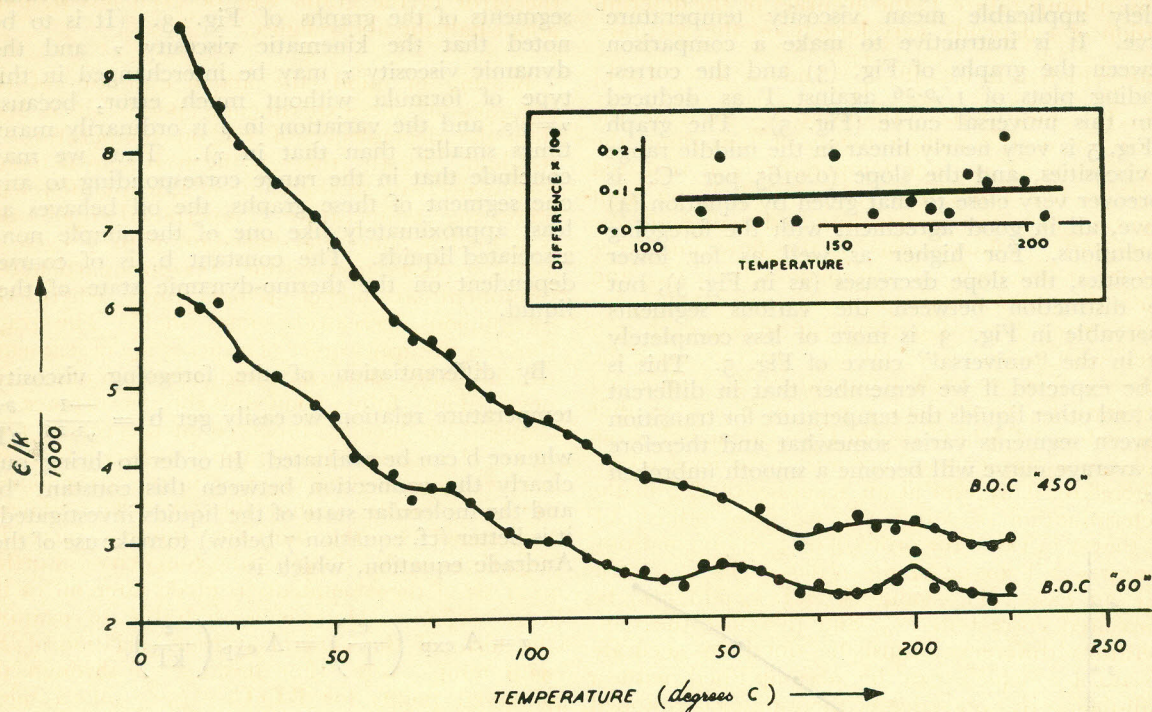
Fig. 6.—Graphs for the activation energy, ε, of the two mineral oils as a function of temperature upto 225°C. The regularly recurring segments are in evidence. The inset shows the differences between the values of $\Delta \ln t / \Delta \eta$ for two sets of measurements on one oil.

For $\nu < 100$ centistokes, $(T^2 \times \nu^{0.26})$ varies rather slowly, so that b is approximately proportional to ε.

When ε is constant over an appreciable range of temperatures, equation (6a) is exact, and when ε varies with temperature, this equation can be taken to give the mean value of ε/k in the temperature-range for which $\Delta \ln \eta$ and ΔT are measured. The value of A is then obtained by substitution for ε in equation (5). This gives

$$\ln A = \ln \eta - \frac{\varepsilon}{kT} = \ln \eta + T \frac{\Delta \ln \eta}{\Delta T} \qquad (6b)$$

Thus if the viscosity is measured at a number of closely spaced temperatures, it is possible to obtain from equations (6a) and (6b) values of ε and ln A over the whole experimental range of temperatures. This procedure was accordingly applied to the data already obtained on the B.O.C. "450" and "60" oils. The results (Fig. 6) were so encouraging that it was decided to extend the observations on both oils up to temperatures above 200°C. Some points in the experimental technique for these measurements deserve comment.

6. Special Experimental Features for Measurement of the Energy ε

Since the quantity to be determined accurately for equations (6a) and (6b) is $\frac{\Delta \ln \eta}{\Delta T}$ rather than η, absolute measurements of the viscosity η can now be advantageously replaced by relative measurements, so that the accuracy is not limited by the accuracy of calibration of the U-tube viscometer. Furthermore, it is not essential to adjust the level of the liquid in the viscometer for each temperature. It is much better to leave the experimental liquid entirely enclosed (and safe from contamination) for a complete set of observations extending over about 40°C., and to apply an appropriate correction for the changing level. This level correction is small, being of the order of 0.1% for one mm. rise in level, which corresponds to a rise in temperatures of about 3°C. The correction for changing kinematic energy of flow (through the capillary) is also small, and is readily applied. The calculations for these and other corrections are worked out in Appendix II.

Since $\frac{\Delta \ln \eta}{\Delta T} \simeq \frac{\Delta \ln t,}{\Delta T}$ where t is the time of

flow at temperature T, the accuracy of the determination of ε depends very largely on the accuracy with which $\Delta \ln t = \ln \dfrac{t_2}{t_1}$ and $\Delta T = T_2 - T_1$ can be measured. In order to increase the accuracy of the measurements of flow-time, the observation at any one temperature was repeated four to five times, the temperature being kept constant to within a few hundredth of a degree centigrade. Observations of the flow-time were made at intervals of approximately 5 °C., and the values for each temperature were taken twice first during the rising temperature sequence and then with temperature falling. In this way, the time of flow at each temperature was obtained accurate to better than 1 part in 2,000, so that the values of $\Delta \ln t$, i.e., $\ln t_2/t_1$ calculated from these measurements are accurate to at least 0.001. Therefore, if we aim at an accuracy of 2% in the determination of $\Delta \ln t/\Delta T$, we must adjust ΔT so that $\Delta \ln t$ is of the order of 0.1. This condition requires ΔT to be of the order of 10 °C. in the present case. The value of ΔT should also be measured correct to 1%, and therefore the temperature differences must be obtained accurate to 0.1 °C., which can be accomplished with a half-degree or even a degree thermometer equipped with a magnifying thermometer-reader. Because of the foregoing consideration, a 10 °C. interval was used for ΔT in the calculations, although most of the observations were taken every 5 °C. This procedure will of course mask some of the small-scale variations in ε that occur within a temperature range of 10 °C.

7. Discussion of the Graphs for ε against Temperature

The results obtained for B.O.C. "60" and "450" oils are given in Table 3, and the quantity $\dfrac{\varepsilon}{k} = -T^2 \Delta \ln \nu / \Delta T + T^2 \times \beta$ is plotted against temperature in Fig. 6. The inset to this figure shows a plot of typical differences between the values of $-\dfrac{\Delta \ln t}{\Delta T}$ for the sets of observations taken with rising and falling temperature sequences: it is seen that, the mean difference is of the order of 0.8×10^{-3} so that the standard deviation of the mean is nearly 0.5×10^{-3}, which corresponds to an error of 0.05 to 0.1 in the value of $\dfrac{\varepsilon/1000}{k}$. This is as expected from the foregoing analysis of the experimental technique. It is to be noted that since each small portion of the graph for $\dfrac{\varepsilon/k}{1000}$ against temperature is drawn as a sort of mean of the two or three nearest experimental points,

the error in the graph will be even less perhaps about half the above figure.

Bearing in mind the above estimates of the accuracy of the experimental points, it is seen that the dependence of ε/k on temperature is two-fold. Firstly, there is the well-known monotonous decrease in the value of this quantity with increasing temperature; superposed upon this is a further sinusoidal variation with a cycle of about 30 °C. to 40 °C., which becomes particularly prominent at higher temperatures where the monotonous decrease becomes small. The graph thus has the appearance of a succession of segments, which change somewhat gradually from one to the next. This fully confirms the occurrence of "knees" or "bends" observed in the earlier plots of $[1/\nu]^{1/4}$ against temperature, and points to the occurrence of certain changes in the arrangement of the molecules within the oil. (The "knees" correspond to the portions joining successive segments with downward convexity. Further analysis of these segments is given later on in the next section). Here it is desirable to examine the form of the general average variation of ε/k with temperature. For instance, if through the observed points for B.O.C. "450" oil, a mean curve is drawn ignoring the sinusoidal variation, this curve is found to be approximately parabolic. (The inclusion of small terms in T^3 and T^4 gives a virtually perfect fit). The ordinates for this "smoothed" curve are given in Table 4 at intervals of 20 °C. (cf. p. 118). A least-squares treatment gives the following best parabolic equation for this curve:—

$$\left(\frac{\varepsilon/k}{1000}\right)_{smoothed} = 2.80 + 1.4 \left(\frac{T-493}{100}\right)^2 \pm 3\%$$

(T in degrees Kelvin)

The differences between this equation and the values of Table 4 are small, and lie within the superposed sinusoidal variations in the experimental curves of Fig. 6. Similar results are got with B.O.C. "60" oil, so that we may take, as a working approximation for these oils, the general equation,

$$\frac{\varepsilon}{k} = -T^2 \frac{\Delta \ln \eta}{\Delta T} = c + b \ (T_0 - T)^2, \qquad (8)$$

i.e., $\quad \dfrac{\Delta \ln \eta}{\Delta T} = -\dfrac{c + b \, T_0^2}{T^2} + \dfrac{2b \, T_0}{T} - b,$

which can be integrated to give

$$\ln \eta = \frac{c + b T_0^2}{T} + 2b \, T_0 \ln \frac{T}{T_0} - bT + \ln A_0$$

TABLE 3.—VALUE OF $\dfrac{\varepsilon/k}{1000} = -\dfrac{T^2}{1000}\dfrac{\Delta \ln \nu}{\Delta T} + \dfrac{T^2\beta}{1000}$ FOR VARIOUS TEMPERATURES BETWEEN 10°C AND 225°C.

(β varies from 0.000,55 to 0.000,75) — B. O. C. "450" Oil — | (β varies from 0.000,60 to 0.000,95) — B. O. C. "60" Oil —

Mean Temp.	−Δlnt/ΔT Temp. rising	Temp. falling	Mean	$-\dfrac{T^2}{1000}\dfrac{\Delta\ln\nu}{\Delta T}$	Correction $=\dfrac{T^2\beta}{1000}$	Mean Temp.	−Δlnt/ΔT Temp. rising	Temp. falling	Mean	$\dfrac{T^2}{1000}\dfrac{\Delta\ln\nu}{\Delta T}$	Correction $=\dfrac{T^2\beta}{1000}$
10				9.64	0.04	10				5.91	0.05
15				8.99		15				5.96	
20				8.55		20				6.02	
25	Calculated from previous data			8.05	0.05	25	Calculated from previous data			5.32	0.06
30	of Table 1.			—		30	of Table 1.			—	
35				7.55		35				5.08	
40						40					
45				7.13		45				4.70	
50				6.76	0.06	50				4.56	0.07
55				6.36		55				4.04	
60				6.20		60				3.95	
65				5.76		65				3.80	
70				5.51		70				3.47	
75				5.50	0.08	75				3.61	0.09
80				5.33		80				3.65	
85	—	—	.03845	4.93		85	.0267	.0266	.02665	3.42	
90	—	—	.03615	4.76		90	.0251	.0241	.0246	3.24	
95	—	—	.0338	4.59		95	.0218	.0229	.02235	3.02	
100	—	—	.0320	4.45	0.09	100	.0204	.0209	.02065	2.87	0.11
105	—	—	.0312	4.46		105	.0210	.0195	.02025	2.89	
110	—	—	.02915	4.27		110	.0198	.0197	.01975	2.90	
115	.0272	.0276	.0274	4.13		115	.0171	.0184	.01775	2.67	
120	.0245	.0263	.0254	3.93		120	.0160	.0174	.0167	2.58	
125	—	—	—	—	0.11	125	—	.0156	.0156	2.47	0.13
130	0.227	.0226	.02265	3.68		130	.0158	.0148	.0153	2.48	
135						135	—	.0142	.0142	2.37	
140	.0212	.0211	.02115	3.60		140	.0132	.0133	.01325	2.26	
145						145	—	.0145	.0145	2.53	
150	.0200	.0181	.01905	3.41	0.13	150	.0142	.0142	.0142	2.54	0.15
155	—	—	—	—		155	—	.0136	.0136	2.48	
160	.0173	.0176	.01745	3.27		160	.0131	.0128	.01295	2.43	
165	—	—	—	—		165	—	.0120	.0120	2.31	
170	.0143	.0137	.0140	2.76		170	.0106	.0111	.01085	2.13	
175	.0150	.0146	.0148	2.97	0.15	175	—	.0111	.0111	2.22	0.18
180	.0147	.0144	.01455	2.99		180	.0105	.0099	.0102	2.09	
185	.0155	.0142	.01485	3.12		185	—	.0100	.0100	2.09	
190	.0133	.0144	.01385	2.97		190	.0109	.0091	.0100	2.14	
195	.0145	.0122	.01335	2.93		195	—	.0103	.0103	2.25	
200	.0141	.0130	.01355	3.03	0.17	200	—	.0116	.0116	2.60	0.21
205	.0127	.0129	.0128	2.93		205	—	.0092	.0092	2.10	
210	.0120	—	.0120	2.80		210	—	.0092	.0092	2.14	
215	.0113	—	.0113	2.69		215	—	.0086	.0086	2.04	
220	.0110	—	.0110	2.67		220	—	.0079	.0079	1.92	
225	.0111	—	.0111	2.75	0.20	225	—	.0083	.0083	2.06	0.25

NOTE :—The oils gave evidence of some chemical changes on heating above 200°C. as shown by a deepening of the colour. Therefore, the last five sets of readings have only a limited significance.
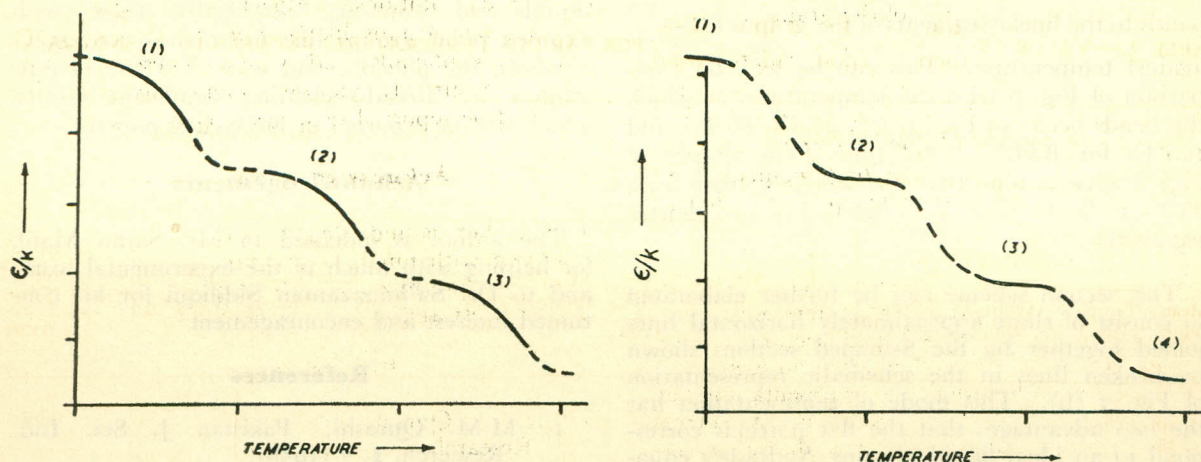
Fig. 7.—Schematic representation of two possible modes of visualization of the segments composing the curves for activation energy against temperature.

$(\ln A_0 = \text{constant of integration})$

$$= (c + b(T_0 - T)^2)/T + 2b \left(T_0 \ln \frac{T}{T_0} - T + T_0 \right) + \ln A_0$$

$$= \frac{\varepsilon}{kT} + 2b \left[T_0 \left(\frac{T - T_0}{T_0} - \frac{1}{2} \left(\frac{T - T_0}{T_0} \right)^2 + \frac{1}{3} \left(\frac{T - T_0}{T_0} \right)^3 \cdots \cdots \right) + (T_0 - T) \right] + \ln A_0$$

$$= \frac{\varepsilon}{kT} + \ln A_0 - \frac{b}{T_0} (T_0 - T)^2 \left(1 + \frac{2}{3} \frac{T_0 - T}{T_0} + \cdots \right) \quad (9)$$

Comparison of this result with the logarithm of the Andrade equation

$$\ln \eta = \ln A + \frac{\varepsilon}{kT}$$

gives us

$$\ln \frac{1}{A} = - \ln A \simeq - \ln A_0 + \frac{b}{T_0} (T_0 - T)^2 \quad (10)$$

thus showing that the variation of $\ln 1/A$ runs more or less parallel to that of $\dfrac{\varepsilon/k}{T_0}$.

This result is illuminating, because it shows how the variation of the viscosity with temperature can at least in theory be decomposed into its two elements of

(1) a nearly parabolic decrease of the potential energy, ε, with increase of temperature, and

(2) a corresponding increase in $\ln A$, where A may be taken to indicate the number of molecular aggregates taking part in the viscous interaction.

Since A increases, it follows that the aggregates become smaller at higher temperatures, which is surely reasonable, because the degree of association is then known to decrease. It is also reasonable to expect that as the size of the aggregates become smaller, so will the mutual potential energy tend to decrease. This decreasing mutual potential energy (at contact) is of course to be correlated with two factors (a) the decrease in the strength or number *per aggregate* of the *exposed* polar (or other type of bonding) groups present in the molecules, and (b) the increase in vibration and rotations of the atomic groups forming the molecular aggregates. These two factors may to some extent be interdependent.

8. Conclusions

Bearing these points in mind, we now examine the approximately sinusoidal fluctuation present in the curves for the potential energy, ε. The curves can be split up into segments, each of which consists of a steep portion and a comparatively flat portion, so that we may visualize the whole curve as being built up in one of two possible ways :—

(a) A series of parabolic segments, convex upwards, as shown schematically in Fig. 7 (a), with a more or less smooth transition from one to the next.

(b) The other alternative is to consider the curve ε against temperature to be made up of parabolic segments, concave upwards, again with a smooth transition between successive segments.

It is shown in Appendix III that each one of these particular parabolic segments now corres-

ponds to the linear segments of the graphs for $\frac{1}{v^{2.26}}$ against temperature. This can be seen by comparison of Fig. 6 with the temperatures at which the bends occur in Fig. 3, *viz.* 28°C., 86°C., and 120°C. for B.O.C. "450" oil. (The graphs of Fig. 6 give a hint that the long segment from 28°C. to 80°C. is in fact made up of two shorter segments).

This second scheme can be further elaborated to consist of short approximately horizontal lines joined together by the S-shaped sections shown by broken lines in the schematic representation of Fig. 7 (b). This mode of representation has the two advantages that the flat portions correspond to an ideal liquid obeying Andrade's equation (with constant A and ε), and the transition from one such state to the next (as shown by the broken lines) would correspond to a change of the second-order, somewhat along the lines of order $\underset{\longrightarrow}{\overset{\longleftarrow}{}}$ disorder transitions in alloys.

Thus, on fundamental grounds, and because of the linear v-0.26 plots, the second mode of visualization is to be preferred. We shall accordingly adopt this as an aid to further study, without in any way prejudicing the question of the precise mechanism responsible for the phenomena being investigated. Viewed in this light, the curves of Fig. 6 and 7(b) raise the following important points :—

(1) What is the significance of the energy differences between the various "steps" or segments in Fig. 7(b) ?

(2) In what way does this energy difference depend on the temperature ?

(3) What precise meaning is to be attached to the quantity A, which we provisionally label as the "Concentration factor?"

(4) What simple postulates can give a comprehensive theory describing the temperature dependence of viscosity *in full detail* ?

Since it is known that mineral oils are not pure liquids with a unique chemical formula, but are mixtures of several related hydrocarbons, the data on these oils can at this stage only point the way for further work. They also indicate the need for measurements of considerably greater precision than has been attained in the foregoing set of experiments. In order to get definite answers to the questions just raised, we have undertaken a series of investigations on several pure

liquids and solutions, especially those with exposed polar groups like the mono-, and poly-alcohols, the phenols, and water. These investigations are already yielding significant results, which will be reported in succeeding papers.

Acknowledgements

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Appendix I

Estimation of Index n

Suppose that $1/v^n = a + bT$, where n is the correct value of the index, and that
$$y = 1/v^{n'} = a' + b'T + \Delta$$
where n' is an approximate trial value of the index, and a', b' are the constants in the linear equation that gives the best fit in this case. Differentiation of these two equations then gives

$$\frac{d}{dT}(v^{-n}) = -nv^{-n-1}\frac{\partial v}{\partial T} = b, \; i.e., \; \frac{\partial v}{\partial T} = -\frac{b}{n}v^{n+1},$$

and

$$\frac{dy}{dT} = \frac{d}{dT}(v^{-n'}) = -n'v^{-n'-1}\frac{dv}{dT} = -n'v^{-n'-1}$$

$$\times -\frac{b}{n}v^{n+1} = b\frac{n'}{n}v^{n-n'}.$$

Further differentiation gives

$$\frac{d^2y}{dT^2} = b\frac{n'}{n}(n-n')v^{n-n'-1}\frac{\partial v}{\partial T} = b\frac{n'}{n}(n-n')v^{n-n'-1}$$

$$\times \left(-\frac{b}{n}\right)v^{n+1}$$

$$= b^2\frac{n'-n}{n}\times\frac{n'}{n}\times v^{2n-n'}$$

$$= \frac{n'-n}{n'}\times b^2\times\left(\frac{n'}{n}\right)^2\times(v^{n-n'})^2 v^{n'}$$

$$= \frac{n'-n}{n'}v^{n'}\left(-\frac{dy}{dT}\right)^2.$$

Thus $n'-n = n' \times \nu^{-n'} \times \dfrac{d^2y}{dT^2} \Big/ \left(\dfrac{d\nu^2}{d\imath}\right)$

$= n' \times y \times \dfrac{d^2\Delta}{dT^2} \Big/ \left(\dfrac{dy}{dT}\right)^2$

$= n' \times \left(y\ \dfrac{dT}{dy}\right)\left(\dfrac{d^2\Delta}{dT^2}\Big/\dfrac{dy}{dT}\right)$ (11)

since $y = 1/\nu^{n'}$

and $\dfrac{d^2y}{dT^2} = \dfrac{d}{dT^2}(a'+b'T+\Delta) = \dfrac{d^2\Delta}{dT^2}.$

Now, the mean value of $d^2\Delta/dT^2$ for any one segment can readily be obtained from the curvature of the corresponding deviation plot for Δ against T ; the corresponding value of y to be used is the mean for that segment.

Appendix II

Viscometer Corrections

At temperature T_1 the level is x_1 mm. above the mark, the mean time of flow being t_1 seconds, and at temperature T_2 the level is x_2 mm. above the mark, the mean time of flow being t_2 seconds. If the flow-time is increased by $\alpha\%$ for every 1 mm. rise in level ($\alpha \sim 0.1$), then the corrected times of flow at the two temperatures are

$(t_1)_{\text{corr}} = t_1\left(1 - \dfrac{\alpha x_1}{100}\right)$

and $(t_2)_{\text{corr}} = t_2\left(1 - \dfrac{\alpha x_2}{100}\right).$

The standard formula for the U-tube viscometers is

$\nu = A\,t - B/t = A\,t\left(1 - \dfrac{B/A}{t^2}\right)$

whence $\ln \nu = \ln (A\,t) + \ln\left(1 - \dfrac{B/A}{t^2}\right)$

$= \ln (A\,t) - \dfrac{B/A,}{t^2}$

to the first order of small quantities. Using this equation, we get to a sufficient accuracy,

$\ln \nu_1 = \ln\left[A\,t_1\left(1 - \dfrac{\alpha x_1}{100}\right)\right] - \dfrac{B/A}{t_1^2}$

$= \ln(A t_1) - \dfrac{\alpha x_1}{100} - \dfrac{B/A,}{t_1^2}$

and $\ln \nu_2 = \ln\left[A t_2\left(1 - \dfrac{\alpha x_2}{100}\right)\right] - \dfrac{B/A}{t_2^2}$

$= \ln(A t_2) - \dfrac{\alpha x_2}{100} - \dfrac{B/A,}{t_2^2}$

whence $\Delta\ln\nu = \ln\nu_2 - \ln\nu_1 = \ln\dfrac{t_2}{t_1}$

$- \dfrac{\alpha}{100}(x_2-x_1) - \dfrac{B}{A}\left(\dfrac{t_1^2-t_2^2}{t_1^2\times t_2^2}\right)$

$= \ln\dfrac{t_2}{t_1} - \dfrac{\alpha}{100}(x_2-x_1) + 2\,\dfrac{B/A}{\bar{t}^2}\,\dfrac{t_2-t_1}{\bar{t}}$

where $\bar{t} = \frac{1}{2}(t_1+t_2)$. It follows that

$\dfrac{\Delta\ln\nu}{\Delta T} = \dfrac{\ln t_2/t_1}{T_2-T_1} - \dfrac{\alpha}{100}\,\dfrac{x_2-x_1}{T_2-T_1}$

$+ 2\,\dfrac{B/A}{\bar{t}^2}\left\{\dfrac{(t_2-t_1)/\bar{t}}{T_2-T_1}\right\}$

$= \dfrac{\ln t_2/t_1}{T_2-T_1}\left(1 + 2\,\dfrac{B/A}{\bar{t}^2}\right) - \dfrac{\alpha}{100}\,\dfrac{x_2-x_1}{T_2-T_1},$ (12)

because the term in curly brackets is very nearly equal to $\left(\dfrac{\ln t_2}{t_1}\right)\Big/(T_2-T_1)$. In a typical case, $B/A \sim 40$, $\bar{t}$ is of the order of 200 secs., so that the kinetic energy correction term amounts to about $80/(200)^2$, i.e., 0.2%. When (T_2-T_1) is $5\,^\circ$C., $\ln\dfrac{t_2}{t_1}$ is of the order of 0.1 and x_2-x_1 is of the order of 2 mm., so that both the corrections together amount to about 1% of the measured quantity, $\Delta\ln\nu/\Delta T$. Another correction should be applied for the change in viscometer constant due to its thermal expansion, but this can be shown to be negligibly small, because the coefficient of cubical expansion of the glass is of the order of 0.000,02. Finally we must note that, for equations (6a) and (6b), we require $\Delta\ln\eta/\Delta T$, whereas experimentally we obtain $\Delta\ln\nu/\Delta T$ from equation (12) above. The difference between these quantities is given by

$\dfrac{\Delta\ln\eta}{\Delta T} = \dfrac{\Delta\ln(\nu\times\rho)}{\Delta T} = \dfrac{\Delta\ln\nu}{\Delta T} + \dfrac{1}{\rho}\,\dfrac{\partial\rho}{\partial T}$

$= \dfrac{\Delta\ln\nu}{\Delta T} - \beta,$ (13)

where β is the coefficient of cubical expansion of the liquid being investigated. Since the present investigation is confined to temperatures below the boiling point, β is more or less constant, and

will be of the order of 0.000,5. Since $\Delta \ln \nu / \Delta T$ is of the order of 0.02, the error introduced by neglecting β in the above equation would be more than 1%, and cannot therefore be ignored. However, this correction has only a slow variation with temperature, and is readily applied by means of equation (13).

Appendix III

Correlation between the Activation Energy Graph and the $1/\nu^{0.26}$ linear Plots

Essentially, the problem is to find the variation of ε'/k corresponding to a linear plot of $1/\nu^{0.26}$ against temperature. Consider, for instance, the long second segment of the graph for B.O.C. "450" oil in Fig. 3. Its equation is

$$1/\nu^{0.25} = 0.16 + 0.0136 \,(T - To),$$
differentiation of which gives

$$-0.25 \, \nu^{-1.25} \frac{\partial \nu}{\partial T} = 0.0136,$$

whence
$$\frac{\varepsilon}{k} \simeq -\frac{T^2}{\nu} \frac{\partial \nu}{\partial T} = T^2 \times \frac{0.0136/0.25}{\nu^{-0.25}}$$

$$= T^2 \times \frac{0.0544}{0.16 + 0.0136(T-To)}$$

Table 5 on page 118 gives the values of $\dfrac{\varepsilon/k}{1000}$ calculated from this relation over the range 30 °C. to 80 °C., together with the first differences. It is evident that the corresponding graph of $\dfrac{\varepsilon/k}{1000}$ against temperature will have a pronounced downward convexity, which is in agreement with the second mode of analysis of the ε/k curves into segments.

PRELIMINARY STRUCTURAL STUDY OF THE MAGNETIC FRACTION OF STEAM-TREATED MAKERWAL COAL

S. JAMAL QUADIR AND SADRUL HASAN RIZVI

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

Introduction

In the course of their studies in the de-sulphurization of Makerwal and other sulphuraceous coals of West Pakistan by treatment with super-heated steam, Siddiqui et al.[1] noted that the beneficiated coal residue contains 5 to 10% of a strongly magnetic component. This component could be removed by simple magnetic separation, and it was found that it carried away a considerable fraction of the residual sulphur, thus providing a basis for additional beneficiation of the coal. The present communication deals with an account of a preliminary investigation in the composition and structure of this magnetic fraction.

Two Possible Paramagnetic Compounds

Since it was known that the original coal contained both sulphur and iron, all the iron being in the form of pyrites, it was at first thought that the magnetic property was due to the formation of compounds of the series Fe_nS_{n+1}, which are known to be strongly paramagnetic. Non-stoichiometric compounds of iron and sulphur, both ferromagnetic and paramagnetic, are known to occur naturally and have even been prepared synthetically; but they form a somewhat peculiar class of compounds and their structure and magnetic behaviour are not fully understood. FeS and FeS_2 are the two well-established compounds of iron with sulphur, but they are both non-magnetic and have structures of the nickel-arsenide and pyritic types, respectively. The compounds, $Fe_{0.48}S_{0.52}$ to $Fe_{0.466}S_{0.534}$ (corresponding to $Fe_{12}S_{13}$ to Fe_7S_8 approximately), have been reported as being ferromagnetic in character, with a nickel-arsenide structure, whereas the compounds in the composition range between $Fe_{0.50}S_{0.50}$ and $Fe_{0.48}S_{0.52}$ (corresponding to FeS to $Fe_{12}S_{13}$ approx.) are reported to be