STUDIES IN THE INFLUENCE OF LONG-CHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part 1—Mixture of Mineral Oil with Bhilawanol and its Derivatives

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In the course of studies in the industrial applications of Bhilawan and Cashew shell liquids, Siddiqui and co-workers have reported the action of the former as an anti-oxidant,[1] and also the marked depression they both exercise on the viscosities of mineral oils.[2] Insofar as some of the problems in the compounding of lubricants for modern engines relate to (a) prevention of oxidation at higher temperatures and (b) control of viscosity over a wide range of working and storage temperatures, it was considered of interest to study the influence of the principal constituents of these shell liquids (namely Bhilawanol, 1,2,3$C_6H_3(OH)_2C_{15}H_{27}$, and Anacardol, $C_6H_4(OH)C_{15}H_{27}$) as well as of their derivatives on the viscosity of mineral oils.

Because of the remarkable stability conferred upon suspensions of carbon black in mineral oil by the addition of a small percentage of Bhilawan and Cashew shell liquids, Mathur et al.[2] had investigated the viscous behaviour of mixtures of Bhilawan shell liquid and of Cashew shell liquid with mineral and vegetable oils.[2] They found that in such mixtures the viscosity was not a linear function of the concentration of the shell liquid, but exhibited very definite maxima and minima. These effects were tentatively attributed to the interaction between the polar OH groups of the constituents of the mixtures. Their curves for mixtures of Bhilawan shell liquid with mineral oils of nearly the same viscosity are shown in Figure 1, an especially remarkable feature of which is the steep drop in the curves for the first few per cent of added Bhilawan shell liquid.

Since this phenomenon of viscosity depression can be expected to throw light on the structure of the molecules in the liquid state, it was considered of interest to continue this work with pure liquids rather than indefinite mixtures of products constituting the shell liquids. The present paper deals with results obtained with pure Bhilawanol (which is a catechol derivative with a $C_{15}H_{27}$ side chain in position 3, having an aggregate of two double bonds) and its mono-methyl ether.

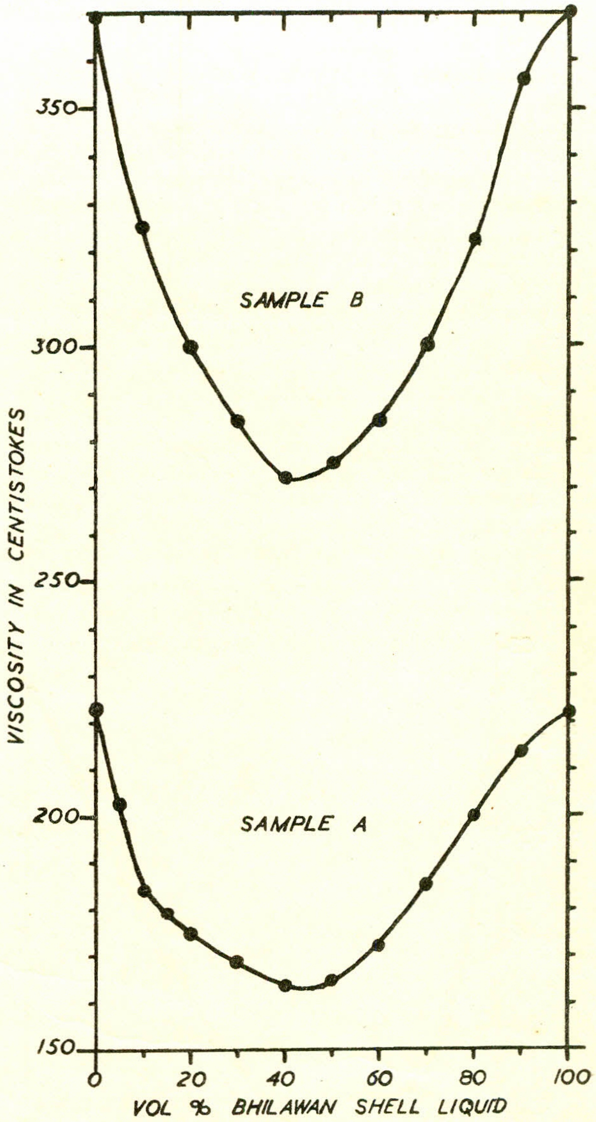

Fig. 1

Experimental

The viscosity of Bhilawanol prepared by the method recorded by Pillay and Siddiqui[3] and distilling at 230° to 235°C./3 mm. of Hg was found to be about 81 centistokes at 40°C. Bhilawanol was mixed in varying proportions with a 'straight' mineral oil blend having a viscosity of 81.1 centistokes at 40°C. The mixtures were prepared by weighing out the appropriate quantities of the constituents in a tall covered weighing bottle and then shaking well to ensure thorough mixing.

After allowing time for any air bubbles to clear, the kinematic viscosity was measured in a U-tube viscometer No. 2 (British standard specifications) supported vertically in a water-bath, whose temperature was maintained at 40.0° C. ± 0.05° C. (The viscometer had previously been calibrated with sugar solution as recommended in the specifications.) Several readings were taken for each viscosity measurement, the estimated standard deviation of the experimental values being about 0.15 centistoke *i.e.*, about 0.2%. No correction for kinetic energy of flow was made because the times of flow were of the order of 20 minutes, for which this correction produces a change of less than 0.01 centistoke in the measured viscosity. Measurements of the viscosity were made for mixtures with Bhilawanol concentrations differing in steps of about 10%, except for the initial steep part of the curve (for small percentages of Bhilawanol), where it was found necessary to space the readings closer together.

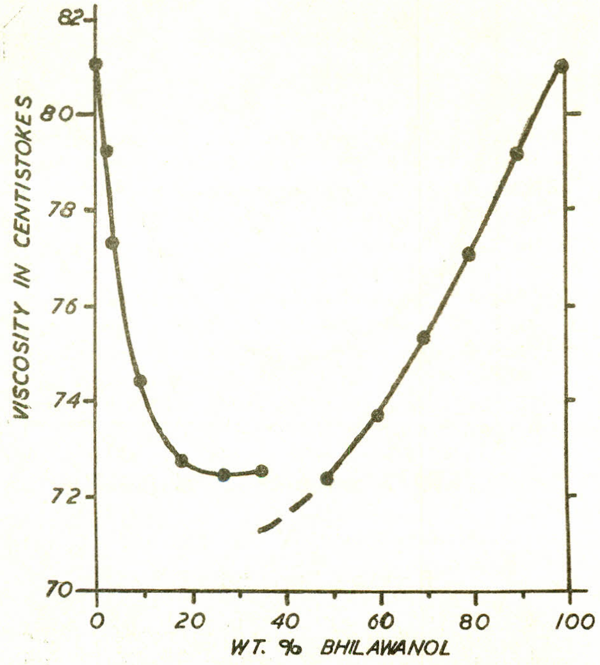

Fig. 2

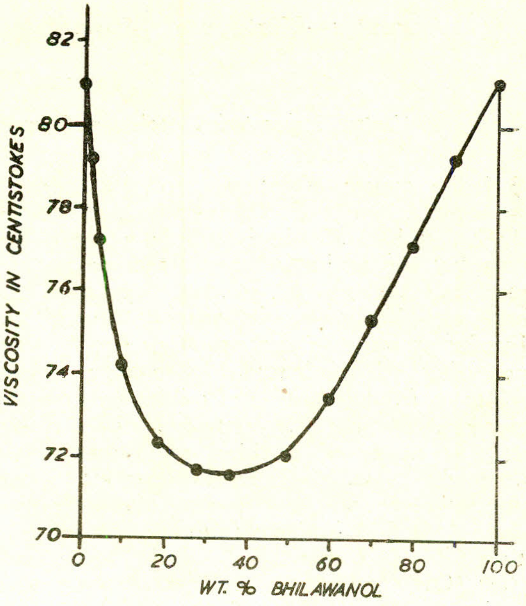

Fig. 3

Readings were taken with *decreasing* Bhilawanol concentrations from 100% to 50% and then with *increasing* Bhilawanol concentrations from 0 % upto 50%.

Results with Bhilawanol

The results are shown graphically in fig. (2). It appears as though *two separate* curves can be drawn, one beginning with pure mineral oil and the other with pure Bhilawanol ; the two curves do not meet in the middle of the diagram. Further examination showed that, near the minimum, the left hand half of the curve will lie above the right hand half of the curve, suggesting that there has been a gradual increase in the viscosity of the Bhilawanol in the course of the observations, which were spread over a period of six days. This was confirmed by a redetermination of the viscosity of the Bhilawanol, when a value of 82.89 centistokes was obtained. This corresponds to an increase of 1.8 centistokes in six days, *i.e.*, an average of 0.3 centistokes per day. A chemical basis for such a steady increase in viscosity is to be found in the gradual oxidation of phenolic compounds, usually accompanied by a deep coloration. The phenomenon is interesting in itself and is being studied separately. The simplest way to reduce observations for comparison with the initial state of the Bhilawanol is to apply to each

TABLE 1

Wt. % Bhilawanol (=100 xx)	Measured viscosity in centistokes	Correction (centistokes)	ν=corrected viscosity centistokes	Slope =Δν/Δx
100	81.09	-.00	81.09	
				+ 19 Extra-polates to 19±1
90.03	79.23	-.02	79.21	
				+ 21
79.99	77.13	-.03	77.10	
				+ 18
69.90	75.36	-.10	75.26	
				+ 18
59.93	73.73	-.29	73.44	
				+ 13
49.15	72.40	-.39	72.01	
				+ 3
35.93	72.57	-.92	71.65	
27.74	72.49	-.75	71.74	
				− 6
18.72	72.73	-.36	72.37	
				− 21
9.63	74.45	-.20	74.25	
				− 46 Extra-polates to 110± 15.
3.89	77.33	-.08	77.25	
				−104
2.01	79.25	-.04	79.21	
				− 94
0	81.10	-.00	81.10	

reading a correction proportional to the Bhilawanol concentration and to 0.3×(no. of days elapsed since the commencement of the experiment). The uncorrected and corrected readings are both tabulated in table (1), while the corrected results are shown graphically in fig. (3), which affords a perfectly smooth continuous curve.

The very sharp drop in viscosity resulting from a small addition of Bhilawanol to the mineral oil is clearly brought out by the left hand portion of the curve. To ascertain whether the initial part of the curve is linear or otherwise, values of the slope($=\Delta\nu/\Delta x$) have been calculated in column five of the table, and it is easily seen that these values do extrapolate to a finite value (-110 ± 15) at extremely small concentrations of Bhilawanol. This shows that the initial part of the viscosity graph is linear, *i.e.*, the viscosity depression is approximately proportional to the percentage of Bhilawanol added. The minimum viscosity of the series of mixtures occurs at about 35% by weight of Bhilawanol, which is to be compared with the corresponding recorded value of 40% for Bhilawan shell liquid, cf. Fig. 1. A detailed comparison of the curves of figures 1 and 3 shows that, apart from a shortening of the viscosity scale by a factor of about four, the effect in the pure Bhilawanol is on the whole very much the same as in the composite Bhilawan shell liquid.

Results with Monomethoxy Bhilawanol

It has been suggested by Mathur et al.[2] on the basis of their experiments that the viscosity depression observed in figure (1) is to be attributed to the influence of the polar OH groups of Bhilawanol and their interaction with the molecules of the mineral oil. In

TABLE 2

Wt. % monomethoxy Bhilawanol = 100x	ν=Measured viscosity (centistokes)	Slope = $\Delta\nu/\Delta x$
100.0	16.20	
70.0	14.9	
40.3	14.30	
23.3	14.59	−5.1
9.10	15.32	−8.3
5.00	15.66	−11.8
0.00	16.25	

order to examine this suggestion further, experiments were tried with the monomethyl derivative of Bhilawanol, $C_6H_3(OCH_3)(OH)C_{15}H_{27}$, prepared according to a procedure which will be described elsewhere. This product does not show any changes of colour, etc. due to oxidation, even on standing for many months. The kinematic viscosity of mono-methoxy Bhilawanol, measured at 40°C., is 16.2 centistokes, *i.e.*, about one fifth of the viscosity of Bhilawanol. This confirms that the high viscosity of Bhilawanol is largely due to the interaction of the polar OH groups ; the ratio of the viscosities of the two liquids, *viz.* 1 :5, is also consistent with this, cf. the fact that cashew shell liquid with one hydroxyl on the aromatic nucleus has a viscosity about one-third that of Bhilawan shell liquid with two hydroxyls on the nucleus.

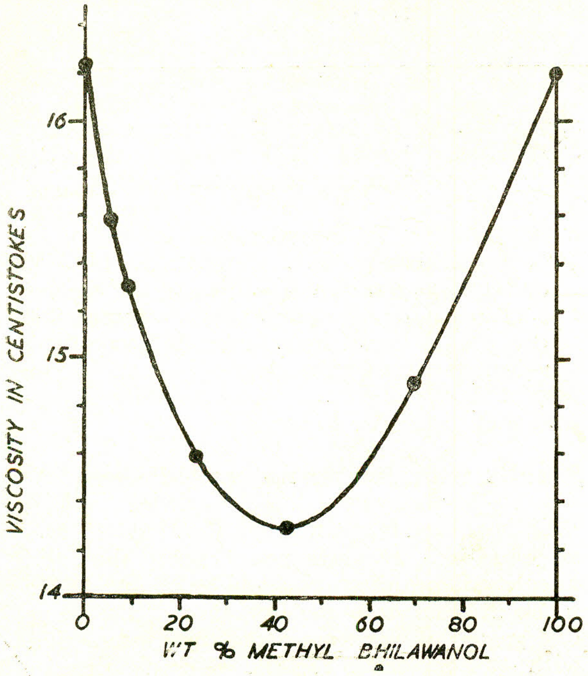

Fig. 4

Monomethoxy Bhilawanol was mixed in various proportions with a straight mineral oil of about the same viscosity, and the kinematic viscosity of the mixtures was measured at 40°C. following the same procedure as with Bhilawanol. (Viscometer No. 2 was still good enough, but the flow times were now of the order of four minutes, thus necessitating a small kinetic-energy correction, amounting to about 0.01 centistoke, in the measured values of the viscosity). The accuracy attained was again of the order of 0.2%. The results are tabulated in table (2), and are shown graphically in fig (4). Due to the small quantity of the monomethoxy Bhilawanol available, the observations could not be spaced very closely ; however, it is seen from fig. (4) that the portion of the curve corresponding to the lower concentrations of monomethyl Bhilawanol can be graphed accurately upto and beyond the minimum in the viscosity curve.

Contrary to expectation, a very marked minimum is present in the viscosity-composition curve. In other ways, too, this curve is very similar to those of fig. (1)and fig. (3)

TABLE 3

Substance		Kinematic viscosity	$I_1 = -\left(\frac{1}{\nu}\frac{\partial\nu}{\partial x}\right)_{x\to 0}$	$I_2 = \frac{1}{\nu}\frac{\nu_0 - \nu_{xm}}{x_m}$	$\left(\frac{\partial T}{\partial x}\right)_{x\to 0}$
Bhilawan shell liquid	(a)	370 c.s.	1.7 /part	0.70 per part	23 °C/part. (mean)
	(b)	222 c.s.	1.9 /part	0.66	
Bhilawanol		80.1 c.s.	1.35/part	0.36/part	25 °C/part
Monomethoxy Bhilawanol		16.2 c.s.	0.86/part	0.28/part	27 °C/part

(for bhilawan-shell liquid and Bhilawanol respectively), the main difference being a further shortening of the viscosity scale.

Discussion

Since the viscosity depression is present in all the three cases, it becomes necessary to make a quantitative comparison. For this purpose, two "indices" of the viscosity-depression may be defined as

$$I_1 = -\left(\frac{1}{\nu}\frac{\partial\nu}{\partial x}\right)_{x\to 0}, \text{ and } I_2 = \left(\frac{1}{\nu}\frac{\nu_0 - \nu_{xm}}{x_m}\right)$$

where x are the parts by wt. of the three respective products per part of mixture, and x_m is the value of x for the minimum viscosity. I_1 gives a measure of the fractional depression produced per part of the additive for small concentrations of it, while I_2 measures the corresponding quantity for maximum depression. It is readily shown that, if the curve is parabolic to a first approximation, then I_2 will be one-half of I_1. Table (3) shows the calculated values of these indices for Bhilawan shell liquid, Bhilawanol, and monomethoxy Bhilawanol.

It is remarkable that on the whole the two indices of depression show a gradual decrease with the decreasing viscosity of the substance investigated but *not* a sudden drop to a very small value on methylation. The total change in each index is covered by a factor of two. This comparatively small change suggests that the minimum in the viscosity-composition curves is perhaps a secondary phenomenon not *directly* associated with the presence of the active hydroxyl groups. Further indication in this direction is obtained when we calculate the rise in temperature of the mixtures that will produce an equivalent drop in viscosity : this can be calculated as

$$\left(\frac{\partial T}{\partial x}\right)_{x\to 0} = \left(\frac{\partial\nu}{\partial x}\right)_{x\to 0} \Big\backslash \frac{\partial\upsilon}{\partial T} = \left(\frac{1}{\nu}\frac{\partial\nu}{\partial x}\right)_{x\to 0} \Big/ \left(\frac{1}{\nu}\frac{\partial\nu}{\partial T}\right)$$

It is seen from the last column of table (3) that a value close to 25 °C./part is obtained in each case, the figure for the mono-methoxy Bhilawanol being in fact the highest of the three. The phenomenon of the viscosity depression thus appears to be rather more complex than was suggested by the earlier workers. It is expected that further elucidation of this phenomenon will be provided by studies that are being undertaken with simpler phenolic compounds.

Acknowledgement

Grateful acknowledgement is made to Dr. S. Siddiqui for suggesting the problem, to Mr. Salim Malik for helping in much of the experimental work, and to Mr. Rafiq Ahmad Siddiqui for preparing the Bhilawanol and its monomethoxy derivative.

References

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