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

Part II.—Derivation of a Generalized Law for the Viscosity Depression in the Bhilawanol Series

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Introduction

In Part I of this paper,[1] some results were presented on the depression of viscosity produced in straight mineral oils by the addition of various proportions of bhilawanol and its monomethyl ether. A preliminary analysis of the curves for viscosity against concentration in these two cases, taken in conjunction with the results of earlier work by Mathur et al.,[2] indicated that the viscosity depression does not fall abruptly on methylation but appears to be a uniform function of the viscosity of the products. Further data in this field have now been obtained on dimethoxy-bhilawanol (in which both hydroxyls are converted into inactive OCH_3 groups), and, on the basis of all the data obtained so far, it is shown that the viscosity depression is correlated with the viscosity of the resinol (or its derivative) rather than with the number of OH groups. An attempt is made to derive the form of the function describing the dependence on viscosity, and further analysis leads to the setting up of a function, ψ, of the viscosity such that $\Delta \psi = (\psi_{expt} - \psi_{ideal})$ defines a function of concentration that is identical for all the compounds of the bhilawan series as well as for cashew-shell liquid.

Experiments with Dimethoxybhilawanol

Dimethoxybhilawanol was prepared according to the method described in the literature and a pale yellow product, whose colour does not unlike bhilawanol deepen on standing, was obtained. Its viscosity was measured with a U-tube viscometer of the British Standard pattern, held vertically in a water-bath kept at a temperature of $40.0° \pm 0.05 °C.$, and was found to be $5.05_2 \pm 0.01$ centistokes. A mineral oil of nearly the same viscosity was prepared by blending two oils of viscosities 3.1 centistokes and 15 centistokes respectively (at $40°C.$) in the ratio of 7 to 3. The viscosity of the blended oil at $40.0 °C.$ was measured in the same viscometer, and was found to be $4.90_2 \pm 0.01$ centistokes. This was considered close enough to the dimethyl product for the present experiment, since a correction can be applied for the difference, as discussed later in this paper.

Dimethylbhilawanol was mixed in various proportions with the blended mineral oil by weighing out appropriate quantities in a tall, covered weighing bottle. The two constituents were mixed by thorough shaking and then sufficient time was allowed for all the air bubbles to clear. The mixture was transferred into the viscometer by means of a pipette and a drawn-out filling tube so as to keep the upper portion of the viscometer tube dry. In view of the small quantities of the sample available, a semimicro-viscometer made in this laboratory was used in these experiments. The viscometer was supported vertically in a controlled temperature bath and had drying tubes connected to its ends to prevent the entry of moisture. Four to five readings of the time of flow concordant to $\frac{1}{2}\%$ were taken and their mean was used to calculate the viscosity by means of the formula

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

where the values of the constants A and B had previously been determined by measuring the flow times of 40% sugar solution and distilled water at temperatures of $30 °C.$ to $50 °C.$ (cf. the graph of Fig. 1, which gives $A = 0.191 \pm 0.001$, and $B = 0.35 \pm 0.02$). The final accuracy of the times of flow was estimated to be of the order of
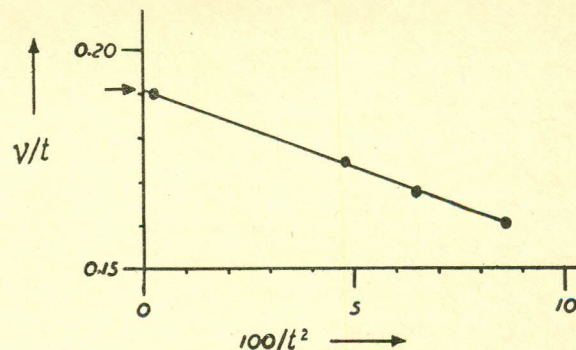

Fig. 1.—Calibration of semi-micro viscometer : linear graph for apparent viscometer constant, ν/t, against $100/t^2$.

0.2% or better, so that the relative accuracy of the various measurements of viscosity with this instrument will also be the same, which corresponds to 0.01 centistokes in the case of dimethoxybhilawanol and its mixtures with mineral oil. Viscosity measurements were made with mixtures, whose composition was selected so as to cover the curve in a uniform manner. The experimental results are collected in Table 1, and the graph for viscosity against wt% dimethoxybhilawanol is drawn in Fig. 2, lower curve, which clearly
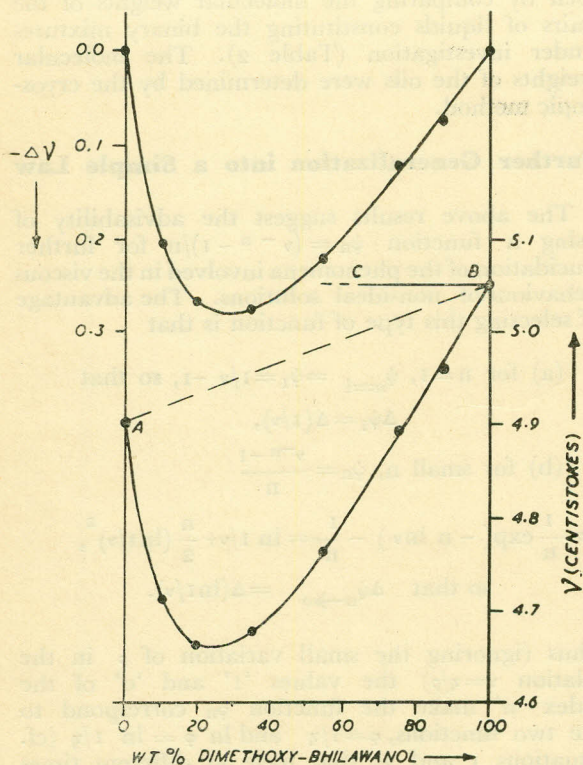

Fig. 2.—Graphs for viscosity of mixtures of dimethoxybhilawanol with mineral oil; bottom, uncorrected curve, and top, corrected depression, —$\Delta \nu$.

shows the dip in the middle of the curve. It is, however, necessary at this stage to apply a correction for the small difference in viscosity between the oil and the dimethoxybhilawanol. On the assumption of "ideal" behaviour, two theoretical relations for the viscosity of a solution of constituents 'A' and 'B' in molar proportions x_A and x_B have been proposed[3] viz.

$$\varphi \text{ ideal} = x_A \varphi_A + x_B \varphi_B \qquad (1)$$

and $$\ln \varphi \text{ ideal} = x_A \ln \varphi_A + x_B \ln \varphi_B \qquad (2)$$

where the fluidity, φ, is the reciprocal of the dynamic viscosity, η. It can be shown that

when φ_A and φ_B differ by only a few percent,* both these relations are approximated to by

$$\eta \text{ ideal} = x_A \eta_A + x_B \eta_B, \qquad (3)$$

which can be replaced by ν ideal $= y_A \nu_A + y_B \nu_B$, where y_A and y_B are the proportions by volume or weight of A and B, provided the molecular weights and densities of A and B are not very different. Thus the viscosity of the ideal solution of the mineral oil and dimethoxybhilawanol would be given by the straight line AB joining the points for the two pure constituents in Fig. 2. (The required corrections would then be given by the departure of this line from the horizontal line BC). These ideal calculated values are given in column 3 of Table 1, and the corrected viscosity depressions, $\Delta \nu$, are given in column 4 while the corrected graph is drawn in the upper half of Fig. 2. This graph has a minimum at 30% of dimethoxybhilawanol, and is seen to possess the essential characteristics of the previously obtained graphs for bhilawan shell liquid, bhilawanol, and monomethoxybhilawanol. It is necessary to note here that, because there are no hydroxyl groups left in dimethoxybhilawanol, the observed viscosity depression is to be attributed to the residual polar character of the molecule.

Discussion of the Data on the Bhilawanol Series at 40 °C.

At this stage, we have available the data on the viscosity depression produced by five bhilawan products and derivatives with viscosities ranging from 370 centistokes down to 5 centistokes. The important quantities derived from the graphs for these compounds are collected together for analysis in Table 2. As noted in Part I of this paper, the two indices I_1, I_2, which were used as measures of the viscosity depression, are neither constant nor do they show a precipitous drop on methylation, whether partial or complete. Simple correlation with the number of hydroxyl groups is further upset by the fact that bhilawan shell liquid (with only two OH groups) has considerably higher values of the indices than bhilawanol. Rather, the indices appear to vary uniformly with the viscosity of the product investigated and it is desirable to determine the precise law of this variation. Since inspection shows the possibility of a proportionality with some power of the viscosity, ν, a logarithmic plot is indicated. Accordingly the logarithms of ν, $- (\partial \nu / \partial x)_{x = 0}$, $- (\Delta \nu_m / x_m)$, $- \Delta \nu_m$, and $\bar{\nu}$ have been calculated in Table 3, $\bar{\nu}$ being the mean of the original and the lowered values of the viscosity. Fig. 3

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*In fact it can be shown (see Appendix to present paper) that for mineral oils (known to obey equation 2 fairly well) with viscosities differing by 3% as in the present case, the maximum difference between equations 2 and 3 is nearly 0.01% of the viscosity.
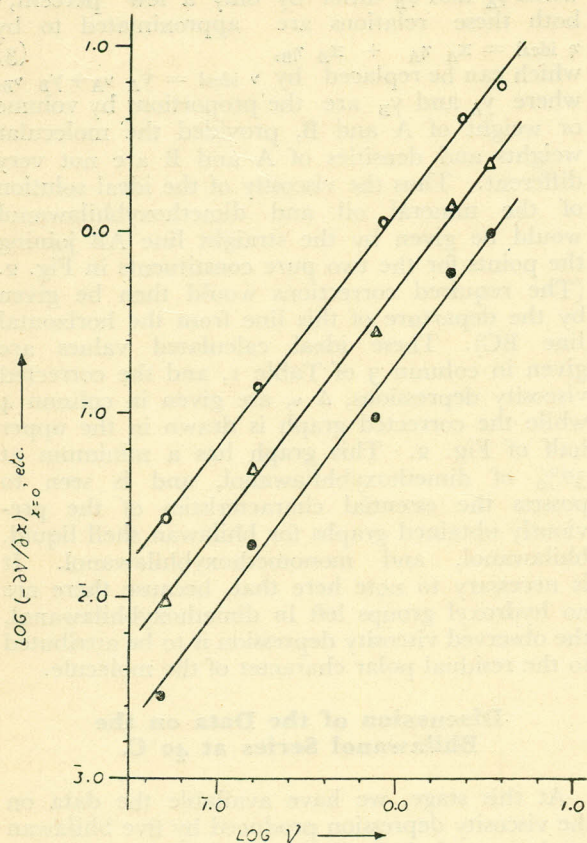
Fig. 3.—Linear logarithmic graphs showing the dependence of the viscosity depression on the viscosity of the compounds. Hollow circles, $\log -(dv/dx)_{x=0}$ against $\log v$; triangles, $\log (-\Delta v /x_m)$ against $\log \bar{v}$; solid circles, $\log (-\Delta v_m)$ against $\log \bar{v}$.

shows plots of $\log (-\partial v/\partial x)_{x=0}$ against $\log v$ (hollow circles) and $\log (-\Delta v_m/x_m)$ against $\log \bar{v}$ (triangles). There result two acceptable straight lines that are sensibly parallel to each other, the slopes being 1.29_5 and 1.30_5, respectively. The mean is $1.30_0 \pm 0.005$, which shows that both $(-\partial v/\partial x)_{x=0}$ and $(-\Delta v_m/x_m)$ are very nearly proportional to $v^{1.30}$. However, the corresponding plot of $\log (-\Delta v_m)$ against $\log v$ (solid circles) has a slope of $1.33_8 \pm 0.02$, indicating that $\Delta v_m \propto (\bar{v})^{1.34}$. Since this last value does not depend on the composition for maximum depression, it is given greater weight, and the best value of the index for the curve as a whole may be taken as 1.33 ± 0.01. We can now write

$$-(\partial v/\partial x)_{x=0} = \text{Constant} \times v^{1.33}, \qquad (4)$$

from which it follows that

$$\frac{\partial}{\partial x}(v^{-0.33}/0.33) = -v^{-1.33} \partial v/\partial x = \text{Constant}, \quad (5)$$

with the value 1.40 for the bhilawanol series. Similarly we get

$$\Delta (v^{-0.33}/0.33)_{max} = \text{Constant} \qquad (6)$$

with the value 0.20 for the bhilawanol series.

It is well to note here that, although the concentration, x, has been expressed as parts by weight in our measurements, it is in fact very close to the corresponding mole fraction, as can be seen by comparing the molecular weights of the pairs of liquids constituting the binary mixtures under investigation (Table 2). The molecular weights of the oils were determined by the cryoscopic method.

Further Generalization into a Simple Law

The above results suggest the advisability of using a function $\psi_n = (v^{-n} - 1)/n$ for further elucidation of the phenomena involved in the viscous behaviour of non-ideal solutions. The advantage of selecting this type of function is that

(a) for $n=1$, $\psi_{n=1} = \psi_1 = 1/v - 1$, so that

$$\Delta \psi_1 = \Delta (1/v),$$

(b) for small n, $\psi_n = \dfrac{v^{-n}-1}{n}$

$$= \frac{1}{n} \exp(-n \ln v) - \frac{1}{n} = \ln 1/v + \frac{n}{2}(\ln 1/v)^2,$$

so that $\Delta \psi_{n \to 0} = \Delta (\ln 1/v).$

Thus (ignoring the small variation of ρ in the relation $v = \eta/\rho$) the values '1' and 'o' of the index 'n' make the function ψ_n correspond to the two functions, $\varphi = 1/\eta$ and $\ln \varphi = \ln 1/\eta$ (cf. equations 1 and 2) that have at different times been supposed to vary linearly with the concentrations of the two components of an ideal solution[3]. It is therefore significant that the above analysis of the viscosity depression, i.e., the departure from ideal behaviour, leads to the conclusion (equations 5 and 6) that $(\partial \psi_{0.33}/\partial x)_{x=0}$ and $(\Delta \psi_{0.33})_{max}$ are constant. This means that the curves for $\Delta \psi_{0.33}$ against concentration, x, should be identical for all the substances of the one series listed in Table 2, from which it can be inferred that, for an analysis of the viscosities of solutions, the function $\Delta \psi_{0.33}$ is of considerable importance.* The values of

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* It is worth noting here that if the correction in Table 1 is entirely neglected, the maximum error in Δv_{max} is 0.075, which would correspond to an alteration of only 0.01 in the mean slope of the straight line graphs of Figure 3, and therefore in the index 0.33 found for the function ψ_n.

TABLE 1.—VISCOSITY OF MIXTURES OF DIMETHOXYBHILAWANOL WITH MINERAL OIL.

wt% Dimethoxybhilawanol	Measured viscosity (centistokes)	Calculated viscosity for "Ideal" solution (centistokes)	Corrected depression $= \Delta \nu$ (centistokes)
0.0	4.902	4.90$_2$	—0.000
10.2	4.71$_2$	4.917	—0.205
19.7	4.66$_2$	4.93$_2$	—0.270
35.0	4.67$_7$	4.95$_4$	—0.277
54.6	4.76$_3$	4.984	—0.221
75.1	4.89$_3$	5.015	—0.122
87.2	4.95$_9$	5.03$_2$	—0.073
100.0	5.05$_2$	5.05$_2$	—0.000

TABLE 2.—SYNOPSIS OF DATA ON DEPRESSION OF VISCOSITY FOR THE BHILAWAN SERIES (x=PARTS OF SUBSTANCE BY WEIGHT).

Workers	Substance	Viscosity at 40% C. (stokes)	Density (g./ml.) Substance	Density (g./ml.) Mineral oil	Molecular wt. Substance	Molecular wt. Mineral oil	$I_1 = -\frac{1}{\nu}\left(\frac{\delta \nu}{\delta x}\right)_{x=0}$	$I_2 = -\frac{1}{\nu}\frac{\Delta \nu_m}{x_m}$	Ratio I_2/I_1
Mathur et al.	Bhilawan (a)	3.70	0.975	0.940	—	—	1.65/part	0.70/part	0.41
	Shell liquid (b)	2.22	—	—	—	—	1.9/ ,,	0.66/ ,,	0.36
Qurashi	Bhilawanol	0.801	0.954	0.905	316	360	1.35/ ,,	0.36/ ,,	0.48
Qurashi	Monomethoxybhilawanol	0.162	0.90	0.875	330	320	0.86/ ,,	0.28/ ,,	0.33
This paper	Dimethoxybhilawanol	0.0505	0.91	0.850	344	280	0.55/ ,,	0.19/ ,,	0.36

Mean $= 0.39 \pm 0.02$

TABLE 3.—VALUES OF LOG $\left(-\frac{\partial \nu}{\partial x}\right)_{x=0}$ ETC., FOR COMPOUNDS OF THE BHILAWAN SERIES (ν TAKEN IN STOKES).

Substance	$\left(-\frac{\partial \nu}{\partial x}\right)_{x=0}$	$\log\left(-\frac{\partial \nu}{\partial x}\right)_{x=0}$	$\log \nu$	$-\frac{\Delta \nu_m}{x_m}$	$\log\left(-\frac{\Delta \nu_m}{x_m}\right)$	$\log \nu$	$\log(-\Delta \nu_m)$
Bhilawan (a)	6.10	0.78$_6$	0.657	2.25	0.353	0.507	$\overline{1}$.987
Shell liquid (b)	4.10	0.61$_3$	0.347	1.34	0.128	0.284	$\overline{1}$.771
Bhilawanol	1.10	0.042	$\overline{1}$.904	0.27$_5$	$\overline{1}$.440	$\overline{1}$.878	$\overline{2}$.974
Monomethoxy-bhilawanol	0.13$_9$	$\overline{1}$.144	$\overline{1}$.210	0.048	$\overline{2}$.682	$\overline{1}$.184	$\overline{2}$.282
Dimethoxy-bhilawanol	0.027$_5$	$\overline{2}$.439	$\overline{2}$.703	0.0094	$\overline{3}$.974	$\overline{2}$.690	$\overline{3}$.451
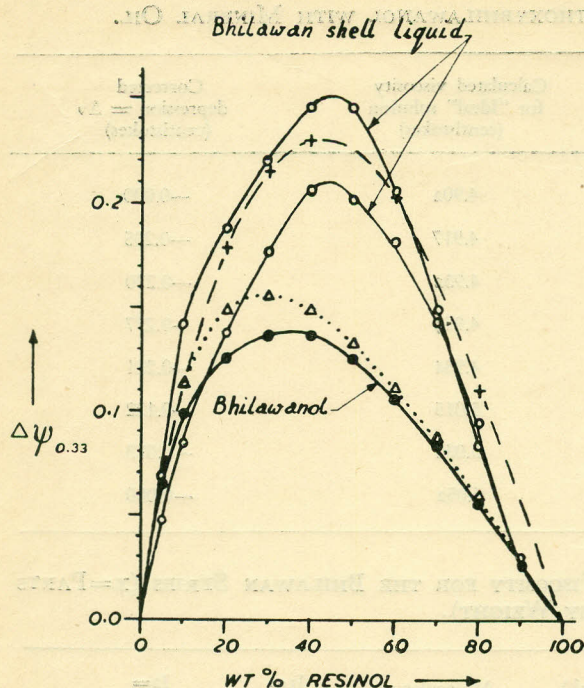
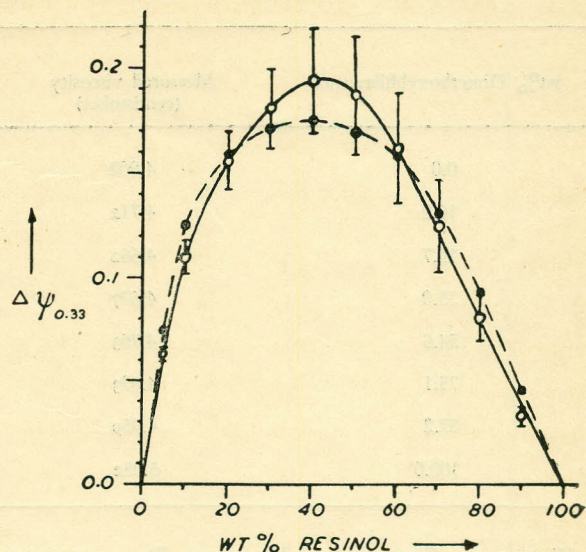Fig. 4 (a).—Graphs of $\Delta\psi_{0.33}$ against concentration for the five bhilawanol products.

Fig. 4 (b).—Plot of mean values of $\Delta\psi_{0.33}$ for the five bhilawanol products (full line) compared with the corresponding curve for cashewshell liquid (broken line).

$\Delta\psi_{0.33}$ for the five products in Table 2 are calculated below for $x = 0.05$, 0.1, 0.2, 0.3, ... etc. in Table 4(a), and the corresponding graphs are drawn in Fig. 4(a). All these graphs are seen to agree closely with each other in the region of small concentration of the resinol (or its derivative), almost upto the point of maximum viscosity depression. The last rows of Table 4(a) give the mean values of $\Delta\psi_{0.33}$ for the bhilawanol series, together with the standard deviations of the means. These mean values are plotted in Fig. 4(b), where the deviations are shown by short vertical lines through the points.

Applications and Discussion

As an application of the above generalization, we consider the data obtained by Mathur at al.[2] on cashew shell liquid, whose principal constituent, anacardol [$C_6H_4(OH)C_{15}H_{27}$] is similar to bhilawanol, except that it contains only one hydroxyl group, instead of the two in bhilawanol, and therefore corresponds in a sense to monomethoxybhilawanol although its viscosity (150 centistokes) is nine times greater. Table 4(b) gives the values of viscosity taken from the data of Mathur et al. on mixtures of cashew shell ilquid with three different mineral oil blends at

$40\,^{\circ}\mathrm{C}$. The mean values of viscosity and $\Delta\psi_{0.33}$ are given in the last two rows of the table, and the corresponding curve is drawn in Fig. 4(b) with a broken line. It is evident that the $\Delta\psi_{0.33}$ curve for cashew shell liquid agrees within the limits of experimental error with the mean curve for the bhilawanol series. This agreement confirms the earlier conclusion that the viscosity depression is correlated with the viscosity of the compounds rather than with the number of active OH groups, because the actual viscosity depression for cashew shell liquid is ten times that obtained with the similar (monohydroxylic) compound mono-methoxybhilawanol.

Finally, in Table 4(c) a comparison of the standard deviation of any one curve from the means is given for the bhilawanol series and for cashew shell liquid. On the whole, these deviations are proportional to $\Delta\psi_{0.33}$, so that the overall mean of these standard deviations, when expressed as a percentage of $\Delta\psi_{0.33}$, in the last row of Table 4(c) is nearly constant at 22%. It follows that the measurement of either $(\partial\psi_{033}/\partial x)_{x=0}$ or $(\Delta\psi_{0.33})_m/x_m$ is equally representative in any given case. Now the determination of the first of these two quantities involves uncertainties inherent in drawing a tangent to a curve at the origin ($x=0$), while the second is uncertain due to the usual indefiniteness in the value of x for the maximum. The determination of $(\Delta\psi_{0.33})_{max}$, on the

TABLE 4(A).—VALUES OF $\Delta\psi_{0.33}$ FOR BHILAWAN SHELL LIQUID, BHILAWANOL, AND ITS DERIVATIVES.

100x = wt % Substance		0	5	10	20	30	40	50	60	70	80	90	100
Bhilawan shell	(a) ..	.000	.048	.084	.13$_8$	.17$_7$	.20$_7$	.20$_2$	.18$_2$	.14$_4$	.09$_5$	.02$_7$	.000
liquid	(b) ..	.000	.06$_9$	.14$_2$	.188	.220	.24$_6$	.24$_6$	.20$_6$	.15$_0$	.08$_4$	.03$_0$	.000
Bhilawanol	..	.000	.06$_5$	.099	.12$_6$	.137	.137	.126	.10$_6$	.083	.05$_6$	.02$_0$	.000
Monomethylbhilawanol		.000	.06$_3$	.11$_1$	.179	.21$_6$	.23$_0$	(.22$_7$)	.204	(.163)	.11$_1$	(.055)	.000
Dimethylbhilawanol	..	.000	.07$_2$	.11$_3$	.149	.156	.149	.13$_3$	.11$_1$	.086	.05$_8$	.02$_9$	.000
Mean	..	.000	.063	.11$_0$	.156	.181	.194	.187	.162	.125	.08$_1$	.03$_3$	.000
Std. dev. of mean	..	—	±.005	±.008	±.014	±.018	±.025	±.028	±.026	±.022	±.011	±.005	—

TABLE 4(B).—VALUES OF VISCOSITY (IN STOKES) AND OF $\Delta\psi_{0.33}$ FOR CASHEW SHELL LIQUID.

100x = wt % Mixture with....		0	5	10	20	30	40	50	60	70	80	90	100
Oil blend (1)	..	1.14$_0$	1.03	0.97	0.94	0.93	0.92	0.91$_5$	0.93	0.95	1.00	1.05$_5$	1.12$_2$
Oil blend (2)	..	1.13$_8$	1.06$_5$	1.01	0.97	0.95$_5$	0.95	0.95$_5$	0.96$_5$	0.99	1.02$_5$	1.07$_5$	1.12$_2$
Oil blend (3)	..	1.12$_5$	1.06	1.00$_5$	0.98	0.97	0.97	0.98	0.99	1.01$_5$	1.04$_5$	1.08$_5$	1.12$_2$
Mean viscosity	..	1.13$_4$	1.05$_2$	0.99$_5$	0.96$_3$	0.95$_2$	0.94$_7$	0.95$_0$	0.96$_2$	0.98$_5$	1.02$_3$	1.07$_2$	1.12$_2$
Mean $\Delta\psi_{0.33}$	..	0.000	0.074	0.125	0.159	0.171	0.175	0.169	0.158	0.131	0.093	0.046	0.000

TABLE 4(C).—STANDARD DEVIATIONS OF THE VARIOUS CURVES.

100 x :—		0	5	10	20	30	40	50	60	70	80	90	100
Std. deviation of the individual curves	(1) Bhilawan series	—	0.010	0.016	0.029	0.037	0.050	0.057	0.052	0.045	0.022	0.010	—
	(2) Cashew	—	0.020	0.023	0.020	0.020	0.024	0.029	0.026	0.029	0.020	0.014	—
Mean	..	—	0.015	0.020	0.024	0.029	0.037	0.043	0.039	0.037	0.021	0.012	—
Mean (as % of mean $\Delta\psi_{0.33}$)	—		22	17	15	17	20	24	24	29	24	29	—

other hand is subject to neither of these two errors, and is probably the best quantity to use, especially over small ranges of variation of the viscosity, because it can be determined very accurately by taking measurements with two or three compositions in the vicinity of the com-position for maximum $\Delta \psi$.

The foregoing results have been obtained with phenolic compounds having a long $C_{15}H_{27}$ side chain, containing two double bonds. In order to establish these results on a firm basis, it is desirable to extend the experiments to phenolic compounds with shorter chain lengths and also to study the effect of the number and position of the double bonds in this side chain. This work is in progress and the results on the allyl series of phenolic compounds will be reported soon.

Acknowledgements

References

1. M.M. Qurashi, Pakistan J. Sci. Ind. Research, **1,** 7 (1958).
2. H.H. Mathur, J.S, Aggarwal and S. Siddiqui, J. Sci. Ind. Research, (India) **9B**, 121 (1950).
3. S. Glasstone and Taylor, *Treatise on Physical Chemistry* (1951).

Appendix

Accuracy of the Correction for Difference of Viscosity between the Two Constituents

We consider the equation
$$-\ln\eta = \ln \varphi = x_A \ln \varphi_A + x_B \ln \varphi_B = - x_A \ln \eta_A - x_B \ln \eta_B, \qquad (2)$$
because it is the more nearly correct one for non-polar liquids. If we replace this by the approxi-mate equation
$$\eta' = x_A \eta_A + x_B \eta_B \qquad (3)$$
then the error caused by this approximation is

$$\eta' - \eta = (x_A\eta_A + x_B\eta_B) - \exp [x_A\ln\eta_A + x_B\ln\eta_B]$$
$$= \eta_A + x_B (\eta_B - \eta_A) - \exp [\ln\eta_A + x_B (\ln\eta_B - \ln\eta_A)]$$
$$= x_B(\eta_B - \eta_A) - \eta_A[\exp(x_B\ln\eta_B/\eta_A) - 1]$$
$$= x_B(\eta_B - \eta_A) - \eta_A[(\eta_B/\eta_A)x_B - 1)]$$
$$= x_B(\eta_B - \eta_A) - x_B(\eta_B - \eta_A) + \frac{x_B(1 - x_B)}{2} \frac{(\eta_B - \eta_A)^2}{\eta_A} + \cdots$$
$$= \eta_A \frac{x_B(1 - x_B)}{2} \left(\frac{\eta_B - \eta_A}{\eta_A} \right)^2$$

$+$ higher powers of $(\eta_B - \eta_A) / \eta_A$

This expression has its maximum value for $x_B = 1 - x_B = \frac{1}{2}$,
so that the maximum fractional error is given by

$$\left(\frac{\eta' - \eta}{\eta} \right)_{max} \sim \frac{\frac{1}{2} \times \frac{1}{2}}{2} \left(\frac{\eta_B - \eta_A}{\eta_A} \right)^2 = \frac{1}{8} \left(\frac{\eta_B - \eta_A}{\eta_A} \right)^2,$$

which is equal to 0.011% for $(\eta_B - \eta_A)/\eta_A = 3\%$. Since the usual experimental errors in the measure-ment of viscosity are seldom much less than 0.3%, it can be seen from the above equation that the approximate correction formula (3) is applicable even when $(\eta_B - \eta_A)/\eta_A$ is as large as 15%.