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INFRARED ABSORPTION STUDY OF THE RELATION BETWEEN VISCOSITY AND INTERMOLECULAR HYDROGEN BOND FORMATION FOR SOLUTIONS OF PHENOLIC COMPOUNDS IN OILS

Part I.—Solutions of Bhilawanol in Mineral Oil

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1. Introduction

Investigations of the viscosity of mixtures of mineral oils with a series of long and short chain phenolic compounds by Qurashi and coworkers have yielded certain significant generalizations regarding the depression in viscosity that occurs in such mixtures.[1,2,3] It has been found[2,3] that the relative depression $-\Delta\nu/\nu$ for any given concentration of phenolic compound is proportional to $\nu^{0.36}$, whence it could be shown that the function $\Delta\psi_{0.36} = \Delta[(\nu^{-0.36} - 1)/0.36]$ is independent of the number of phenolic hydroxyl groups.

In order to elucidate the precise dependence of this depression on the nature of the molecule and the degree of association, it was considered desirable to undertake a quantitative study of the OH and hydrogen bond infrared absorption region in the neighbourhood of 3μ, using mixtures containing various concentrations of the phenolic compounds. The observed intensity of the absorption band depends on the one hand on the concentration of the absorbing molecules and on the other on the percentage of hydrogen bond formation, and the (peak) intensities of the resolved absorption peaks at sufficiently high resolution are mathematically correlated in the present paper with the degree of hydrogen bond formation, and thence with the viscosity depression, by using certain fundamental assumptions regarding the mechanism of the viscosity depression.

2. Experimental Details

The spectral region that is usually considered important in infrared spectrometry extends from about 2μ to 15μ, and, although infrared spectrometers used for measuring absorption spectra in this region do not differ in fundamental principles from those employed in visible and ultraviolet spectrometry, certain physical limitations of the commonly used optical materials and light sources necessitate some radical differences in design, and the best resolution is of the order of 2 to 5 cm.$^{-1}$

A Leitz automatic recording spectrometer with a prism of 15 cm. base was used in the present investigation. With the normal slit programme and a sodium chloride prism, this gives a resolution of about 11 cm.$^{-1}$ in the region of the observed OH and H-bond peaks, which resolution is sufficient for the preliminary study shown in Fig. 1(a). Because of the large aperture of the prism, it is possible to use narrower slits, down to 0.035 mm.; at this width, when using a sufficiently slow recording speed coupled with a 3:1 chart magnification, it is easy to obtain a resolution of somewhat better than 5 cm.$^{-1}$, which is ample for accurate work in the present case, as seen in Fig. 1(b). The standard recording paper is divided linearly from 2μ to 15μ (Fig. 1(a)), and for high resolution measurements, the special recording arrangement extends the spectra to three times their lengths as seen from the graphs of Fig. 1(b).

The liquid samples were contained in disc-type cells with sodium chloride plates separated by spacers, whose thicknesses were chosen in order to produce accurately measurable peaks for the various concentrations. For the measurements with bhilawanol, two cell thicknesses, namely 0.033 mm. and 0.083 mm., were found suitable and were controlled by interference fringe measurements[4] with the empty cells, using the wavelength range 5 to 15μ.

3. Infrared Absorption Curves for Bhilawanol and their Analysis

An organic compound, whether aliphatic or aromatic, containing a free OH group shows a narrow symmetrical absorption band depending somewhat upon the rest of the molecule.[5] The general behaviour of the absorption characteristics of the OH band at various concentrations of bhilawanol in mineral oil is shown in Fig. 1(a). In dilute solutions, the 2.87 μ (3480 cm.$^{-1}$) band of the OH group is quite strong, while the broader band at 3.00 μ (3330 cm.$^{-1}$) due to hydrogen bonding is relatively weak. As the concentration of bhilawanol increases, the relative number of associated molecules becomes greater and the 3.00 μ (3330 cm.$^{-1}$) peak becomes stronger relative to the normal OH peak. In order to make a quantitative study of the OH peak and the hydrogen bonding in detail, the spectra were taken

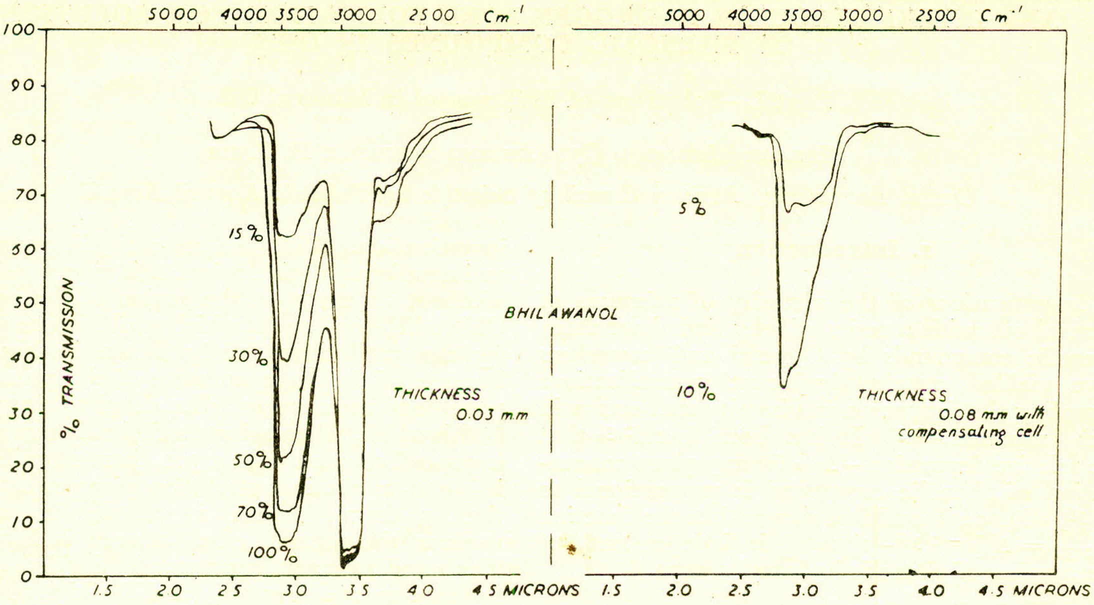

Fig. 1(a).—Preliminary infrared absorption curves in the range of 2 to 4 microns for solutions of bhilawanol in a blend of B.O.C. "90" and "60" mineral oils.

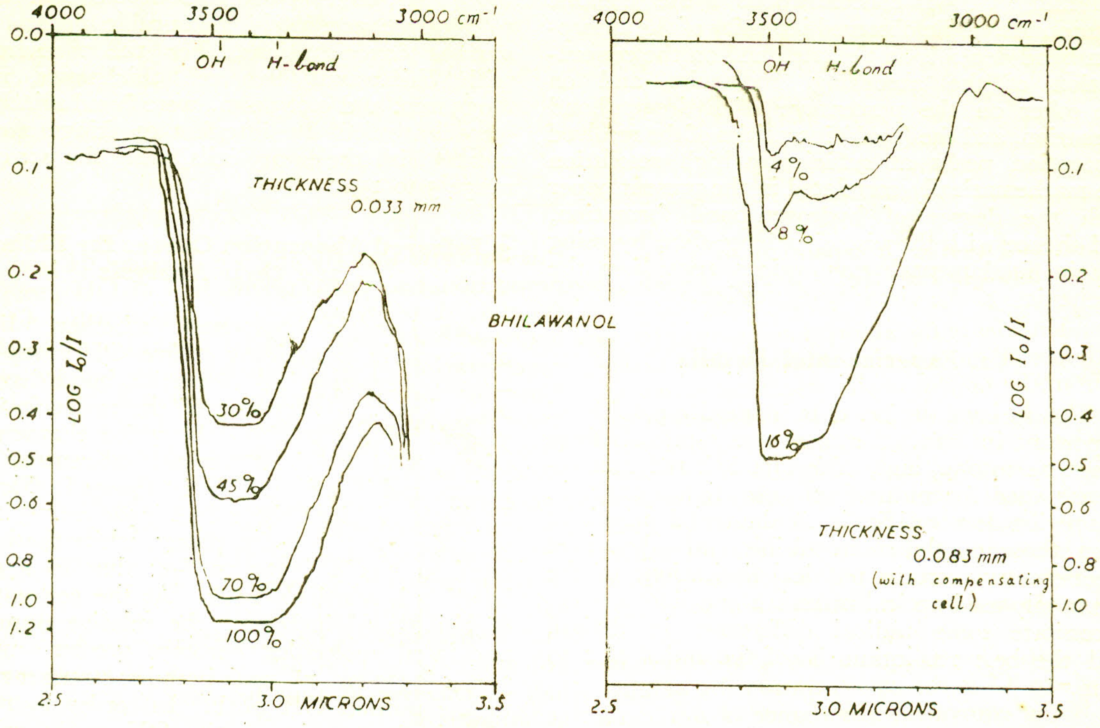

Fig. 1(b).—OH and H-bond peaks at high resolution for various concentrations of bhilawanol in the mineral oil blend.

Table 1.—Peak Heights and Calculated Absorbances for the Sharp OH Peak at 2.87 μ (3480 cm.–1) in Bhilawanol Oil Mixtures.

Cell thickness	% Conc. of bhilawanol (by weight =C)	Unresolved peak height (log I_0/I)	Absorbance (for 1 cm. thickness)	Corrected height (after resolution)	a = Corrected absorbance	log Conc.	log 'a'
0.033mm.	100	1.2	340	0.793	240	2.00	2.38
	70	0.870	264	0.495	150	1.84	2.18
	45	0.497	151	0.310	93.9	1.65	1.97
	30	0.346	105	0.209	63.3	1.48	1.80
0.083mm.	16	0.510	61.4	0.360	43.4	1.20	1.64
	8.0	0.160	19.3	0.130	15.7	0.90	1.20
	4.0	0.061	7.3	0.046	5.5	0.60	0.74

Table 2.—Peak Heights and Calculated Absorbances for the Broad Hydrogen Bond Peak at 3.00μ (3330 cm.$^{-1}$) in Bhilawanol Oil Mixture.

Cell thickness	% Conc. of bhilowanol (by weight) =C	Unresolved peak height (log I_0/I)	Absorbance (for 1 cm. thickness)	Corrected height(after resolution)	a = Corrected absorbance	log Conc.	log 'a'
0.033mm.	100	1.13	342	1.11	336	2.00	2.53
	70	0.878	267	0.855	259	1.84	2.41
	45	0.446	135	0.435	132	1.65	2.12
	30	0.330	100	0.310	93.9	1.48	1.97
0.083mm.	16	0.442	53.2	0.325	39.2	1.20	1.59
	8.0	0.124	14.9	0.104	12.5	0.90	1.10
	4.0	0.045	5.4	0.035	4.2	0.60	0.62

at higher resolution with expansion by a factor of three as shown in Fig. 1(b).

The intensities of the absorption bands in terms of absorbance 'a' for a 1–cm. thickness were determined from the heights of the absorbing peaks by dividing log I_0/I for the peaks by the appropriate cell thickness (in cm.). In order to eliminate errors due to overlapping of the OH and H-bond peaks, graphical resolution of the pairs was carried out: the resolved peaks are shown by thick lines in Fig. 2, and the corrected peak intensities (absorbances)were calculated afresh from these resolved peaks as shown in Tables 1 and 2.

The graphs of log 'C' against log 'a' are shown in Fig. 3, where 'C' is the concentration (by weight) and 'a' is the equivalent absorbance of a 1–cm., thickness of sample. The slope of the graph corresponding to the sharp OH peak is seen to be 1.05 ±0.05, and since the number of OH groups is proportional to the concentration of bhilawanol, this indicates that the intensity of the OH peak is proportional to the concentration of OH groups. We may therefore expect that the intensity of the hydrogen bond peak will be proportional to the concentration of hydrogen bonds in the sample. Now the slope of the graph corresponding to the broad hydrogen bond peak (Fig. 3) is 1.40±0.03, thus indicating that the concentration of hydrogen bonds is proportional to the power 1.40 of the concentration of bhilawanol molecules.* This is to be compared with a theoretical estimate of 2 for the index, in case one H-bond is formed only between pairs of molecules of bhilawanol. The value 1.40 of this index would appear to indicate that hydrogen bond formation between a bhilawanol molecule and an oil molecule is about one-half as effective as that between two molecules of bhilawanol.

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*It is to be noted that, although the concentrations have been taken on a weight basis, these are very close to the molar concentrations, because the molecular weights of bhilawanol and the mineral oil are nearly equal, being 316 and 340, respectively.

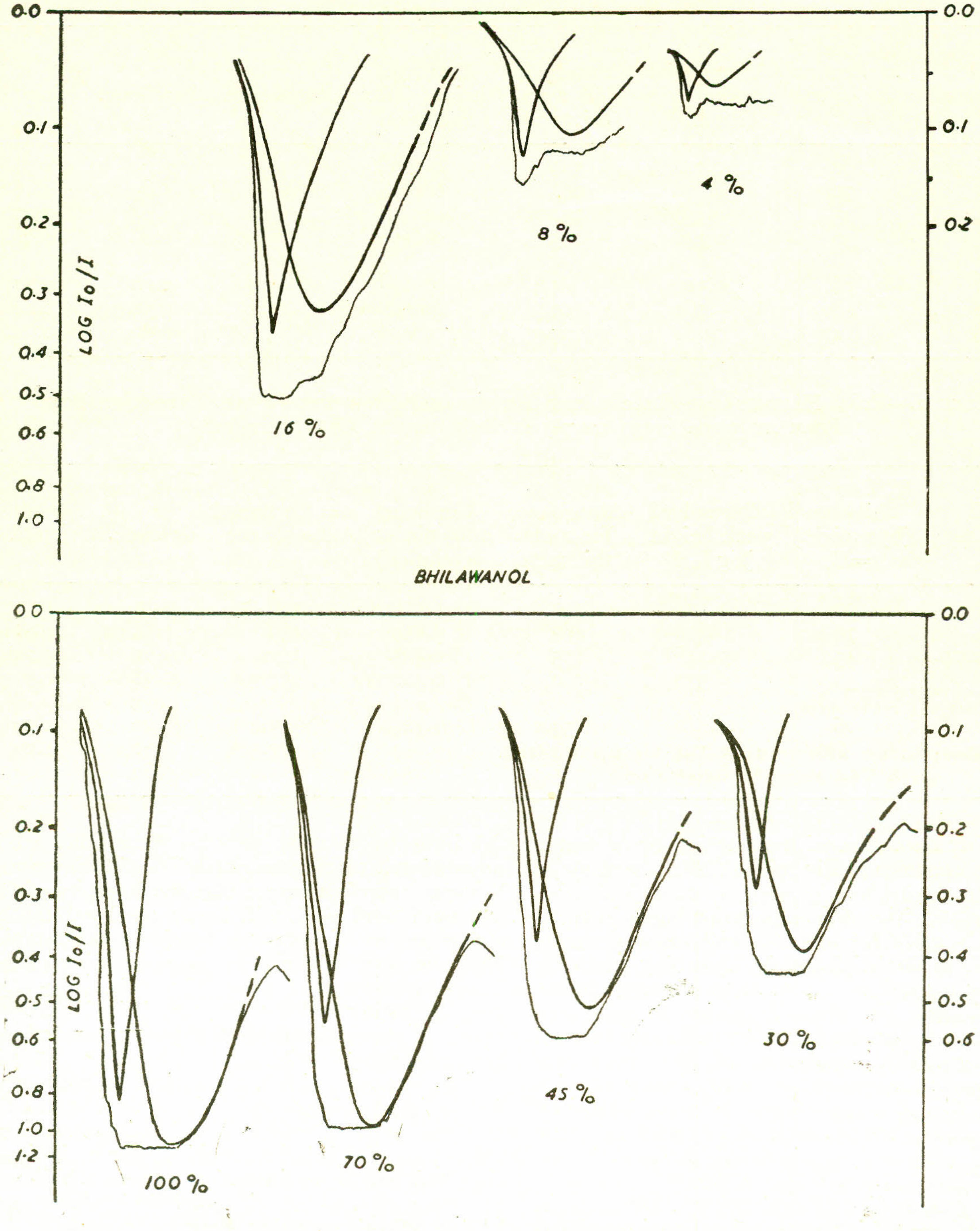

Fig. 2.—Graphical resolution of the curves of Fig. 1(b) into pairs of curves for the OH and H-bond peaks. The ordinate scale is marked in terms of the absorbance, log Io/I.

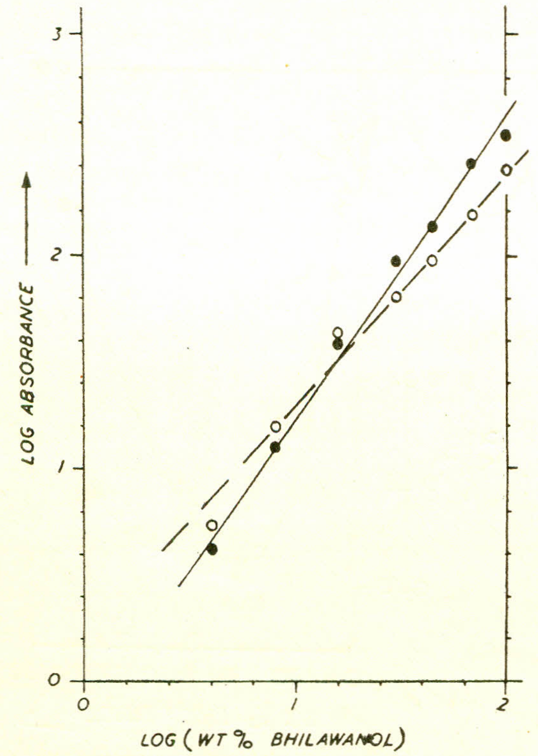

Fig. 3.—Logarithmic plots of peak absorbance (for 1 cm. layer) against weight % bhilawanol for the OH peak (hollow circles, broken line) and the H-bond peak (solid circles, full line). The scatter of the experimental points is mainly attributable to errors in the graphical resolution of peaks (Fig. 2).

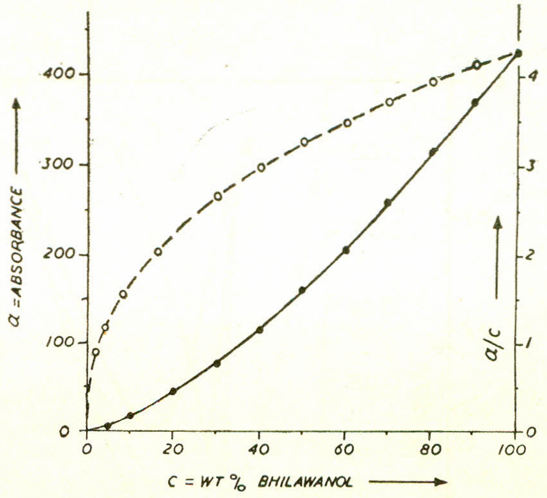

Fig. 4.—Smoothed curves (based on the linear graphs of Fig. 3) for the absorbance 'a' (full line)and for a/C (broken line) against the % concentration 'C' of bhilawanol.

4. Derivation of Formula for Comparison with Viscosity Measurements

On the basis of the data given in Table 2 and Fig. 3, we can now draw a curve showing the absorbance 'a' at the H-bond peak as a function of concentration 'C'. This graph is seen in Fig. 4, together with another graph for a/C against C. Since the OH peak intensity has been found above to be proportional to the concentration of OH groups, we concluded that the intensity of the hydrogen bond peak gives a good measure of the extent of the hydrogen bond formation for bhilawanol in mineral oil. Now, if the viscosity depression $-\Delta\nu$ produced by dilution of the bhilawanol to any concentration is due to the partial dissociation of the hydrogen bonds, we can put $-\Delta\nu/\nu$ varies as (relative change in number of hydrogen bonds per unit volume). (1)

Since $\Delta\nu << \nu$, this will be true regardless of the precise relationship between the viscosity and the hydrogen bond concentration. The change in number of hydrogen bonds is readily calculated by considering the difference between (a) the simple addition of C parts of bhilawanol to (100–C) parts of oil without rupture of the hydrogen bonds, and (b) their mixing with dissemination of the molecules of these C parts over the whole volume of the mixture. In the first case, the number of the H-bonds per unit volume is proportional to C/100 × (conc. of H-bonds)$_{c=100}$, while in the second case it is porportional to (conc. of H-bonds) c%. If a_{100} is the absorbance of the H-bond peak for 100% bhilawanol, and a_c is the corresponding value for the mixture with C% bhilawanol, it follows that

$$-\frac{\Delta\nu}{\nu} = K\left(\frac{C}{100}\,a_{100} - a_c\right) \div a_{100}$$

$$= K\,\frac{C}{100}\left(1 - \frac{a_c/C}{a_{100}/100}\right) \qquad (2)$$

where K is a non-dimensional constant.

5. Application to Bhilawanol Solutions and Discussion

From Fig. 3, log a = 1.40 log C–0.17 for bhilawanol, whence it follows that $(a_c/C) = C^{0.40}/(10)^{0.17} = 0.677\ C^{0.4}$, a graph of which is drawn in Fig. 4. The quantity, $\left[\frac{C}{100}\left(1 - \frac{a_c/C}{a_{100}/100}\right)\right]$ can be calculated from this graph (broken line in Fig. 4), and is plotted in Fig. 5(a) ,while the values of $-\Delta\nu/\nu$ actually obtained from viscosity measurements (at a temperature of 37 °C., which corresponds to that of the I.R. thermostatic chamber) are shown alongside in Fig. 5(b). The

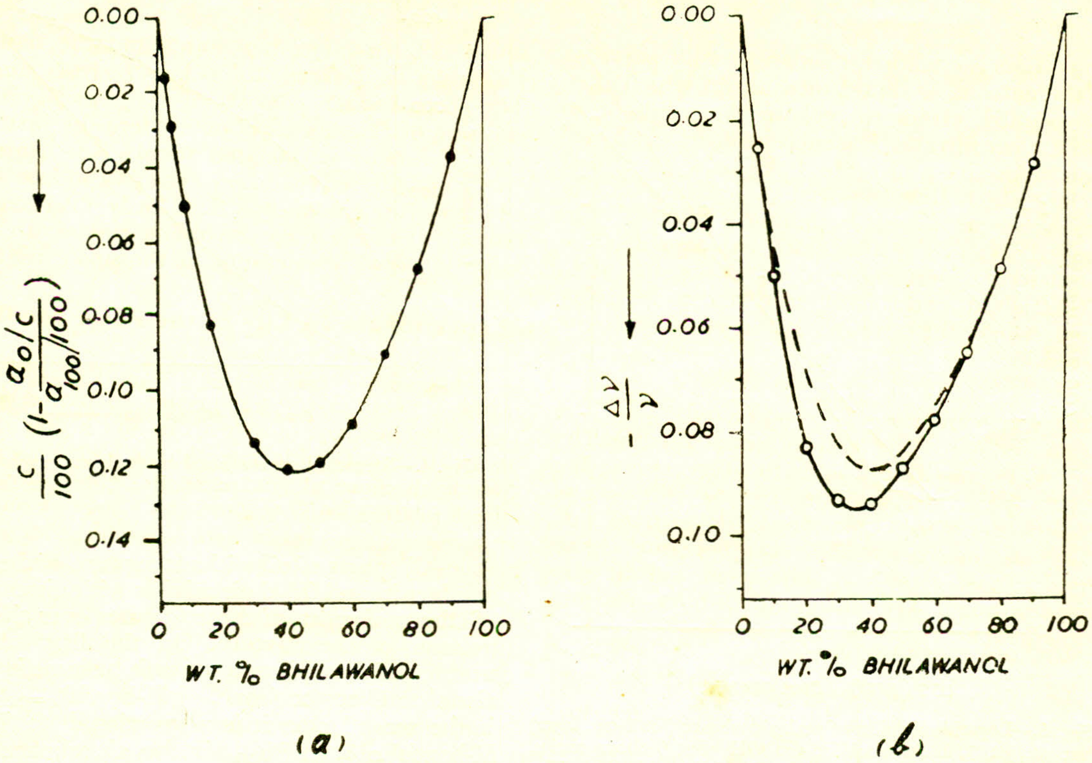

Fig. 5.—Comparison between (a) the value of $\frac{C}{100}\left(1-\frac{a_c/C}{a_{100}/100}\right)$ calculated from the infrared measurements and (b) the value of $(-\Delta\nu/\nu)$ obtained from viscosity determinations on solutions of bhilawanol.

agreement between the two curves is seen to be satisfactory (cf. broken curve), and can be brought within 5% by multiplying the scale for the calculated values by 1.07. This agreement amply justifies the basic theory leading up to the curve of Fig. 5(a). From the ratio between the finally adjusted scales of the two graphs, the *non-dimensional constant* of proportionality, K, in equation(2) comes out to be

$$K = (0.10 \pm 0.005)/0.130 = 0.77 \pm 0.04$$

Further experiments are being carried out with other phenolic compounds in order to determine to what extent K depends on the nature of the compound.

An interesting feature of the foregoing results is the fact that the right-hand side of equation (2) contains the term a_c/C, which varies as $(C/100)^{0.40}$ while the left-hand side, i.e. $-\Delta\nu/\nu$ has previously been shown[3] to vary as $\nu^{0.36}$. It is possible that a study of other phenolic compounds will lead to further elucidation of the significance of these two exponents 0.40 and 0.36.

Acknowledgements

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References

1. M.M. Qurashi, Pakistan J. Sci. Ind. Research, **1**, 7 (1958).
2. Z. Rahman and M.M. Qurashi, ibid., **1**, 214 (1958).
3. Z. Rahman, M.M. Qurashi and G. Hahn, ibid., **1**, 284 (1958).
4. M.P. Lisitia and V.V. Malinko, Optica i Spectrosk, **3**, 294 1957)
5. L.J. Bellamy, *The Infrared Spectra of Complex Molecules* (Methuen & Co. Ltd. 1958), second edition, pp. 95-108.