

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

Part II.—Solutions of Allylphenol in Mineral Oil

MAZHAR M. QURASHI AND SARFARAZ H. ZAIDI

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

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The theoretical formula connecting H-bond absorbance with the relative viscosity depression, viz.

$$-\frac{\Delta v}{v} = K \frac{C}{100} \left(1 - \frac{a_c/C}{a_{100}/100} \right)$$

developed in part I of this paper is now further verified with solutions of allyl phenol in mineral oil. The value of the non-dimensional constant 'K' is found to be 0.83 ± 0.06 , which compares well with the value 0.77 ± 0.04 obtained for bhilawanol, $C_6H_3(OH)_2C_{15}H_{27}$. This suggests that K is a generally applicable constant with a value of 0.80 ± 0.03 .

Introduction

In part I of this paper,¹ some experiments were described on infrared absorption measurements of hydrogen-bond concentration in solutions of bhilawanol in mineral oil. These measurements led to the development of the following equation connecting the absorbance 'a' at the absorption peak with the viscosity depression, $-\Delta v$, observed in the solutions:

$$-\Delta v/v = K \left[\frac{C}{100} \left(1 - \frac{a_c/C}{a_{100}/100} \right) \right] \quad (1)$$

An experimental value of 0.77 ± 0.04 was obtained for the non-dimensional constant K, and, in an effort to study the general applicability of equation (1), the investigations have now been extended to the case of mixtures of mineral oil and allyl phenol, which differs from bhilawanol both in the number of OH groups and the length of the side-chain.

Experimental Results

Samples of allyl phenol prepared for earlier measurements on the viscosity depression^{2,3} were used in the present experiments also. The preliminary infrared curves for a few different concentrations of allyl phenol are shown in Fig. 1(a) and they indicate the desirability of using a cell thinner than 0.03 mm. for the higher concentrations. Accordingly, cells of thicknesses 0.0115 mm. and 0.080 mm. (the thicknesses being obtained from interference measurements) were used for the measurements at high resolution, which gave a lot of fine structure of the OH and H-bond peaks as shown in Fig. 1(b), the peak positions being 2.83μ (3530 cm.^{-1}) and 2.92μ (3420 cm.^{-1}), respectively. The resolution of the absorption curves into the OH and H-bond peaks (ignoring the fine structure) is shown by the thick lines in Fig. 2. The quantitative data obtained from these resolved peaks is arranged in Table I, and

the logarithmic graphs for absorbance against weight % concentration of allyl phenol are shown in Fig. 3. The slope of the graph for the OH peak is 0.96 ± 0.06 and of that for the hydrogen-bond peak is 1.42 ± 0.03 . The former value is in agreement with the theoretical figure of 1.00, while the value 1.42 is in excellent agreement with the corresponding slope (1.40 ± 0.05) previously found for bhilawanol. It is to be noted here that, if molar absorbances are plotted against molar concentrations, then the scales of abscissae and

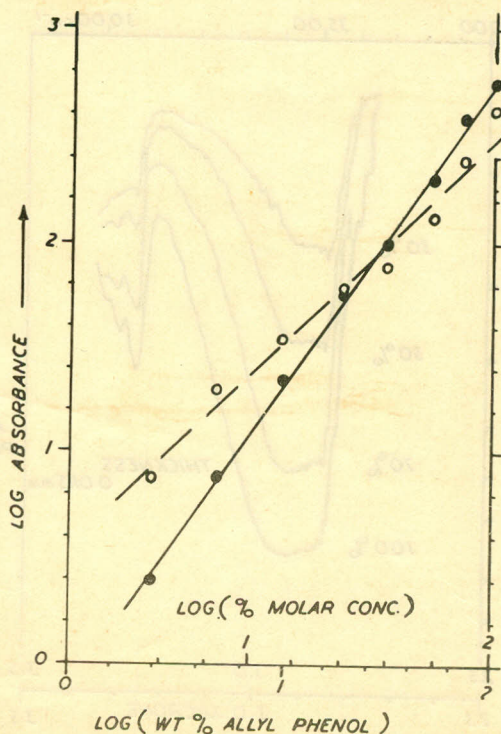


Fig. 3.—Logarithmic plots of absorbance (for 1 cm layer) against wt. % allyl phenol for the OH peak (broken line), and the H-bond peak (full line).

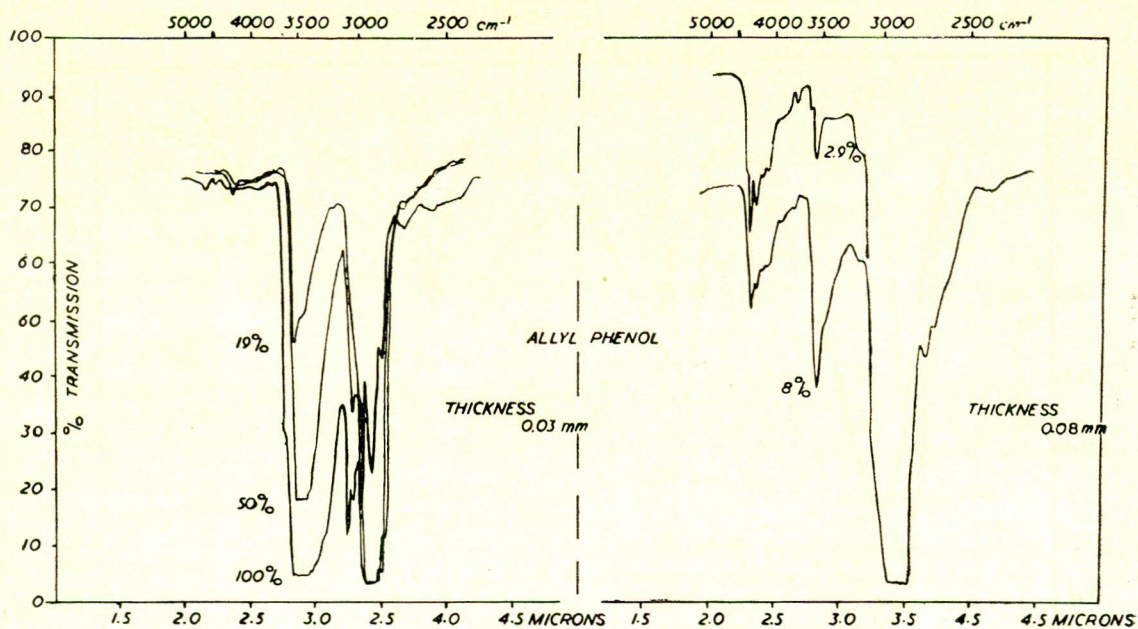


Fig. 1(a).—Preliminary infrared absorption curves for solutions of allyl phenol in H.S.D. oil blend.

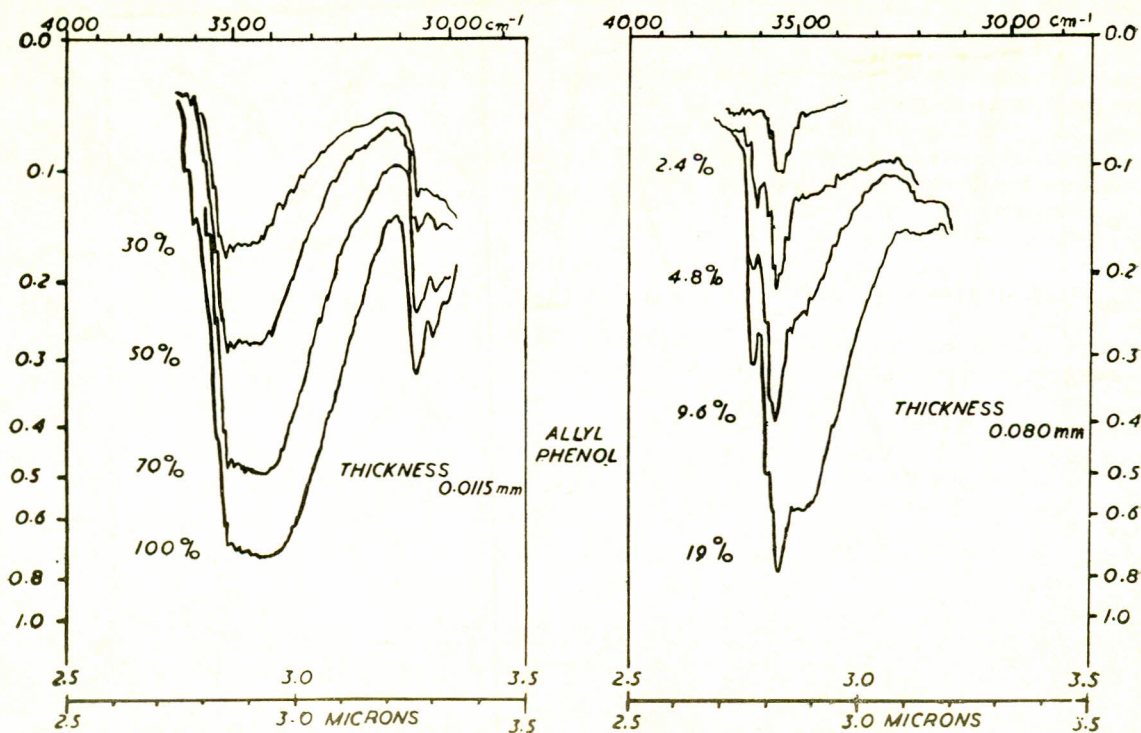


Fig. 1(b).—OH and H-bond peaks at high resolution for various concentrations of allyl phenol in the mineral oil blend.

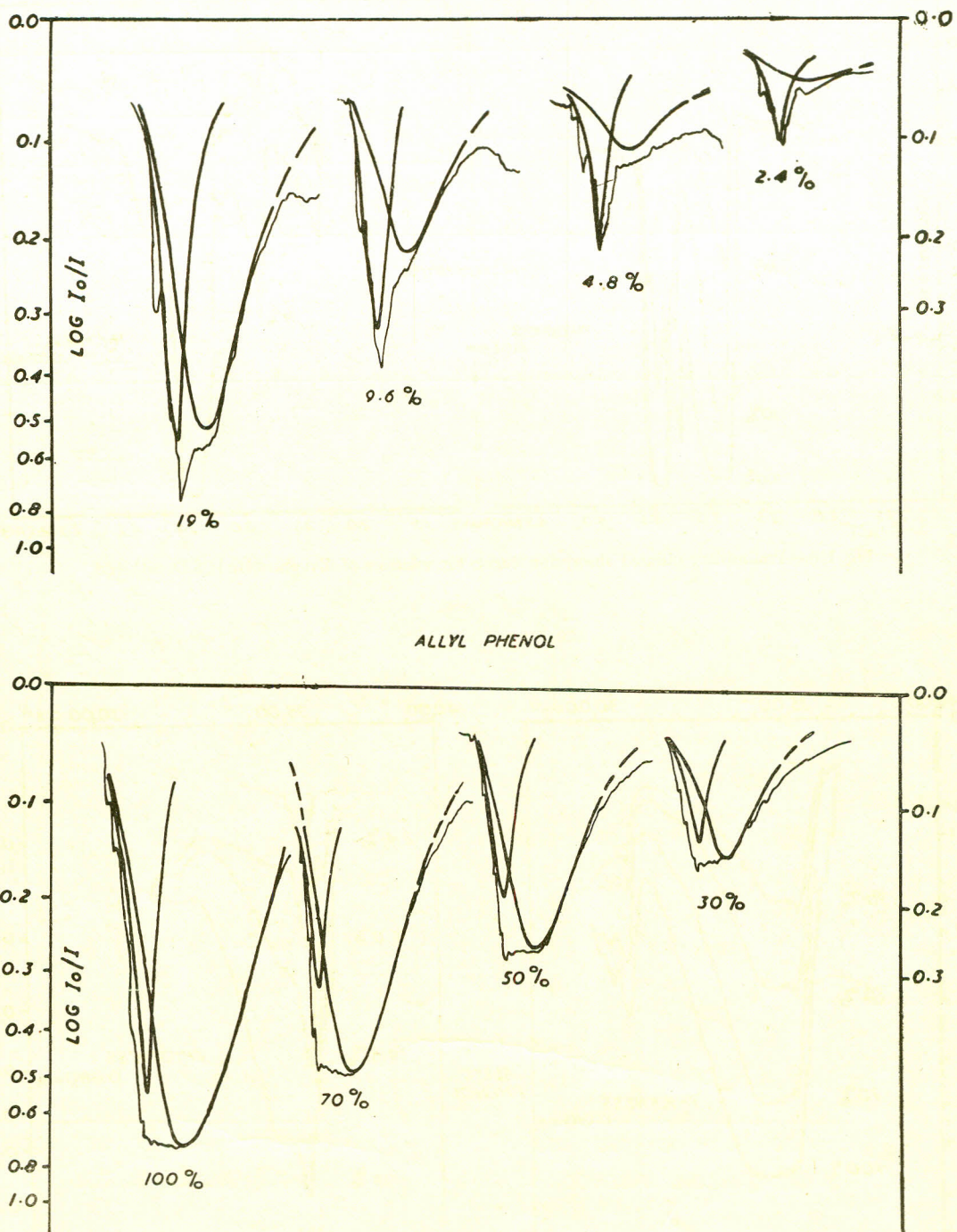


Fig. 2.—Graphical resolution of the curves of Fig. 1(b) into the component OH and H-bond absorption peaks. The ordinate scale is marked in terms of the absorbance, $\log (I_0/I)$.

TABLE I.—OH AND H-BOND PEAK HEIGHTS AND ABSORBANCES IN MIXTURES OF ALLYL PHENOL WITH MINERAL OIL.

Cell thickness mm.	% Conc. allyl phenol =C	Molar % of allyl phenol (M=134, M _{oil} =200)	Resolved peak height (log I ₀ /I)		a _c = Absorbance for 1 cm. layer		Logarithms		
			OH	H-bond	OH	H-bond	% Conc. =C	Absorbance	
								OH	H-bond
0.0115	100	100	0.48	0.645	417	561	2.000	2.620	2.749
	70	78	0.28	0.45	243	391	1.846	2.386	2.582
	50	60	0.152	0.23	132	200	1.699	2.121	2.301
	30	39	0.090	0.115	78	100	1.477	1.893	2.000
0.080	19.2	26	0.50	0.47	62.5	59.0	1.284	1.796	1.771
	9.6	13.6	0.28	0.18	35.0	22.5	0.983	1.544	1.353
	4.8	7.0	0.16	0.06	20.0	7.5	0.681	1.301	0.876
	2.4	3.5	0.06	0.02	7.5	2.5	0.380	0.876	0.398

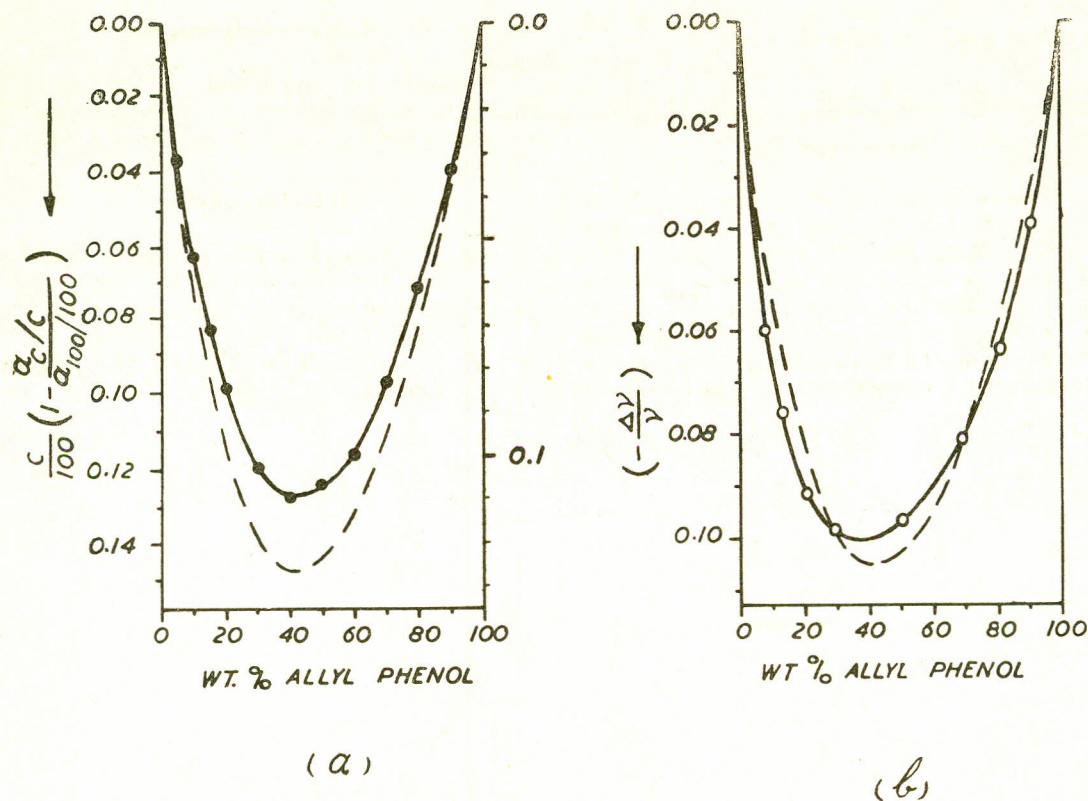


Fig. 4.—Comparison between the values of $\frac{C}{100} \left(1 - \frac{a_c/C}{a_{100/100}} \right)$ calculated from infrared absorption and the graphs of $(-\Delta v/v)$ obtained from viscosity measurements on allyl phenol solutions.

ordinates are both altered in the manner indicated by the second set of markings for the abscissae in Fig. 3. This is approximately equivalent to a shortening of the graphs in both directions by a factor of nearly 0.90, and therefore leaves the slopes of the lines unaltered.

Determination of the Constant K

The values of $\frac{C}{100} \left(1 - \frac{a_c/C}{a_{100}/100} \right)$ calculated from the graph for the hydrogen-bond peak in Fig. 3 are plotted in Fig. 4 alongside of the experimentally determined values of $\Delta\nu/\nu$, at the corresponding temperature³ and give graphs similar to those for bhilawanol (Fig. 5 in part I of this paper). The graph calculated from the infrared measurements is again somewhat shallower than the experimental curve, and needs therefore to be lengthened vertically by a factor of nearly 1.16 in order to obtain good correspondence between the two curves. This adjustment gives agreement to within ± 0.08 in term of $\Delta\nu/\nu$ (cf. broken curves), which is satisfactory, but is somewhat poorer than in the case of bhilawanol. The value of the constant K in equation (1) can be obtained (as before) from a comparison of the graphs of Fig. 4, and comes out to be

$$K = (0.10 \pm 0.007)/0.120 = 0.83 \pm 0.06.$$

Discussion

The value of K obtained above for allyl phenol differs by (0.06 ± 0.07) from the corresponding value (0.77 ± 0.04) for bhilawanol. The difference is thus not statistically significant, and we may therefore take the mean of the two values, namely (0.80 ± 0.03) , as a *generally applicable constant* connecting the relative viscosity depression with the infrared hydrogen-bond peak absorbance

by means of equation (1). Since this conclusion is based on experiments with only two different compounds, it is desirable to investigate mixtures of other hydroxylic compounds with mineral oils in order to place the above formula on a firm footing, and it is hoped to present some further results in this direction in future communications together with their theoretical implications.

It must be mentioned here that the solutions when placed in the infrared cell for absorption measurements will be heated to some extent by the passage of the infrared beam, so their temperature will be above that (37°C.) measured in the thermostatic (beam) chamber, the difference being small, perhaps of the order of 1°C. It can be seen that this will not produce any significant effect on the values found above for K, because the experimental curves for $\Delta\nu/\nu$ are altered by only 0.5% for a 1°C. change in temperature.³ Another point to be noted is that it appears from an examination of the theoretical arguments that the quantity $\Delta\nu/\nu$ in equation (1) should more precisely be $\Delta(\ln \nu)$, but the discrepancy will not be appreciable except when $\Delta\nu/\nu$ is much greater than 0.2.

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References

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