

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

Part III.—Measurement and Analysis of the Viscosity Depression Occurring in Mixtures of Mineral Oils with (A) Allylphenol, (B) Allylbenzene and (C) Allylcatechol*

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I. Introduction

In previous communications of this series,^{1,2} an analysis was given for the viscosity depression produced in mineral oils by the additions of various proportions of bhilawan shell liquid, bhilawanol, and its methylation products. It has been previously suggested by various workers³ that the viscosity depression is attributable to the varying degrees of association of the phenolic component, and this is supported by the fact that the absolute magnitude of the viscosity depression decreases as the number of phenolic OH groups per molecule decreases, from two in bhilawanol to zero in dimethoxybhilawanol.² However, an anomaly presented itself in the cases of (a) bhilawan shell liquid, which exhibits a much larger viscosity depression than bhilawanol, whereas its constituents do not contain more than two hydroxyls per molecule, and (b) dimethoxybhilawanol, which has no free hydroxyl group, but still shows a marked viscosity depression. This led to a consideration of the relation between the viscosity, ν , of the product and the viscosity depression, $\Delta \nu$, produced on mixing it with a mineral oil of the same viscosity. The ultimate conclusion was that this depression is very nearly proportional to the quantity $\nu^{1.33}$ over the whole 75-fold range of viscosities studied, and that it does not show any other direct correlation with the number of free hydroxyl groups in the compounds, whence it was deduced that the function $\Delta \psi_{0.33} = \Delta (\nu^{0.33} - 1)/0.33$ is the same for all these compounds.

Especially significant is the fact that this function $\Delta \psi$ does not become zero suddenly on methylation of both the hydroxyl groups, thus suggesting that ψ measures perhaps a more fundamental property of the liquids. In order to investigate these suggestions further, it was decided to study synthetic phenolic and benzene compounds with short side chains, both saturated and unsaturated. The present communication

deals with the results obtained with allylphenol, allylbenzene and allylcatechol, all of which have the benzene nucleus with a C_3H_5 allyl side chain.

2. Preparation of Compounds

(a) *Allylphenol*.—A mixture of 188 g. of phenol, 242 g. of allyl bromide, 280 g. of finely powdered calcined potassium carbonate and 300 g. of pure dry acetone was refluxed on a steam bath for eight hours. A heavy precipitate of potassium bromide began to form soon after the refluxing started. After cooling, water was added to the reaction mixture, and the product was taken up in ether and washed twice with 10% sodium hydroxide solution. The ethereal solution was dried over potassium carbonate and, after removal of the ether, the residue was distilled under reduced pressure. This gave about 150 g. of allyl phenyl ether, boiling at 85°C./19 mm. of Hg. This is converted into the allyl phenol by the Claisen rearrangement, in which the allyl group migrates only to the ortho position.

The allyl phenyl ether was boiled in a flask with a reflux tube for about 2½ hours, when the rearrangement was substantially complete. The product was dissolved in 20% sodium carbonate solution, the solution was acidified, and the phenol extracted with ether. The extract was dried over calcium chloride and then distilled under reduced pressure. About 90 g. of allylphenol boiling at 103° to 105°C. under a pressure of 19 mm. of Hg were obtained. (Standard data are : b.p., 99°C./12 mm. and 220°C./760 mm. of Hg; $n_D^{20} = 1.5453$). The completion of the rearrangement was confirmed by preparing a derivative, *viz.*, 2-methyl-dihydrobenzofuran, by reaction in acetic acid with 45% aqueous hydrobromic acid, followed by refluxing for twenty minutes, addition of excess water and extraction with ether. The ethereal extract was washed with sodium hydroxide, dried, and distilled to give a 50% yield of material boiling at 86° to 88°C./19 mm. of Hg, a tarry residue being left behind. The viscosity of the allylphenol at 40°C. was found to be 3.107 centistokes.

* The present communication is based in part on a thesis submitted by Zia-ur-Rahman for the M.Sc. degree to the University of Karachi.

(b) *Allylbenzene*.—By reacting 20 g. of magnesium shavings with a mixture of 78.5 g. of pure bromobenzene and 350 ml. of dry ether dropped gradually from a dropping funnel, Grignard reagent was prepared. Through the dropping funnel, 57.5 g. of allyl bromide were added dropwise to the Grignard reagent, and the reaction was completed by heating for half an hour. After adding 100 ml. of water and cooling the flask in ice-cold water, the ethereal layer containing the allylbenzene was separated in a separating funnel, washed with a little water and then dried over calcium chloride. After removal of the ether, the product was distilled in an air bath, the fraction distilling over between 150—160°C./760 mm. of Hg. being collected. By redistillation, the pure substance boiling at 155—158°C. was obtained.

(c) *Allylcatechol*.—132 g. of catechol and 144 g. of pure allyl bromide were dissolved in 220 ml. of pure dry acetone. Finely divided powdered potassium carbonate (freshly heated to remove moisture) was added gradually with constant shaking, and the mixture was refluxed for 7 hours on a water bath, a calcium chloride tube being attached to the condenser. After removal of the acetone and addition of dilute sulphuric acid, the mixture was extracted with ether. By washing with dilute alkali, the monoallyl ether and the unreacted catechol were removed, the ethereal solution being dried and evaporated to give 30 g. of the diallyl ether. The alkali washings were immediately acidified and the oil taken up in chloroform. The catechol having been removed by repeatedly washing with water, the chloroform was evaporated off, and the oil remaining behind was distilled under reduced pressure to give 60 g. of pure mono-allyl ether.

The molecular rearrangement of the mono-allyl ether was carried out by heating it in a flask fitted with a condenser to 170—180°C. in a paraffin bath. The inner temperature rose suddenly to 225°C. with momentary boiling, the colour of the liquid changing to red. After cooling, the product was fractionated under a pressure of 16 mm. of Hg and the fraction boiling

at 142°—159°C./16 mm. was collected. The yield was about 25 g. The viscosity of the compound measured at 40°C. was found to be 13.9 c.s. Some more of the compound was prepared and its viscosity was found to be 18.2 c.s. *i.e.* about 4 c.s. higher than the viscosity of the previous lot. Both were redistilled, after which concordant viscosity measurements were obtained, *viz.* 18.5₈ c.s. for the first lot and 18.5₂ for the second lot.

3. Measurements with Allylphenol

The viscosity of the allylphenol was measured with U-tube viscometer No. 1 of the B.S.S. pattern, supported vertically in a water bath, whose temperature was maintained at 40.0° ± 0.1°C. Drying tubes were connected to the two limbs of the viscometer to prevent the entry of moisture, and the mean of several readings of the time of flow was taken. The mean value obtained for the kinematic viscosity at 40°C. was 3.10₇ c.s.

A straight mineral oil (B.O.C. "H.S.D.") of nearly the same viscosity was selected, and its viscosity was also measured at 40°C. with the above-mentioned viscometer and was found to be 3.18₂ c.s. This was considered close enough to the viscosity of allylphenol for carrying out measurements of viscosity depression produced on mixing. Allylphenol was mixed in various proportions with the mineral oil and the kinematic viscosity of each mixture was measured at the fixed temperature of 40°C. The compositions of the various mixtures were selected in such a way as to obtain a uniform distribution of experimental points over the whole length of the curve. The viscosities of the pure allylphenol and the mineral oil were again measured at the end, and were found to be 3.09₂ and 3.19₈ c.s., respectively. The experimental results are given in Table I.

A small correction is required for the difference of 0.090 c.s. in viscosity between the allylphenol and the oil. As discussed in a previous paper,² this correction can, to a sufficient approximation, be applied by assuming the variation

TABLE I.—VISCOSITY AT 40°C. OF MIXTURES OF ALLYLPHENOL WITH B.O.C. "H.S.D." OIL.

Wt% allylphenol=100 × x	0.0	9.5	18.2	28.5	39.0	50.2	59.3	70.6	81.2	90.8	100.0
Measured viscosity (centistokes)	3.19 ₀	2.97 ₃	2.87 ₂	2.82 ₄	2.817	2.81 ₄	2.81 ₈	2.84 ₀	2.89 ₀	2.96 ₄	3.10 ₀
Viscosity for ideal solution (centistokes)	3.19 ₀	3.180	3.17 ₄	3.164	3.155	3.145	3.137	3.126	3.117	3.10 ₈	3.10 ₀
—Δv=viscosity depression (centistokes)	0.000	0.207	0.30 ₂	0.340	0.338	0.331	0.319	0.286	0.227	0.14 ₄	0.000

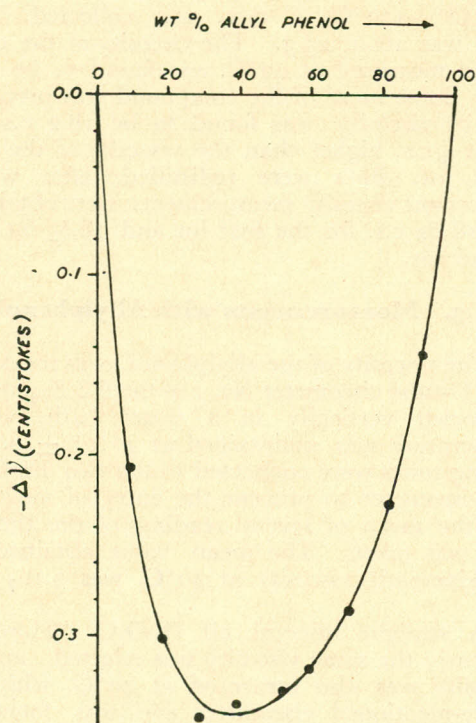


Fig. 1.—Graph showing the viscosity depression, $-\Delta v$, observed in mixtures of allylphenol with mineral oil (B.O.C. "H.S.D"): $\nu=3.19$ c.s.)

of the viscosity for ideal solution to be linear with composition by weight. The values of the depression, $-\Delta v$, obtained are given in the last row of Table 1, and the corresponding graph is seen in Fig. 1. The values of $-(\partial\nu/\partial x)_{x=0}$ where x are the parts by weight of allylphenol, and $(-\Delta\nu_m)$ the maximum depression are obtained from the graph as 2.85 c.s./part and 0.344 c.s., respectively.

It will be noted that the viscosity of the mineral oil used above is about 3% higher than that of the allylphenol. It was therefore thought desirable to repeat the above measurements using an oil with a viscosity lower than that of the allylphenol. Such an oil was prepared by blending the "H.S.D." oil with 1/7 by volume of

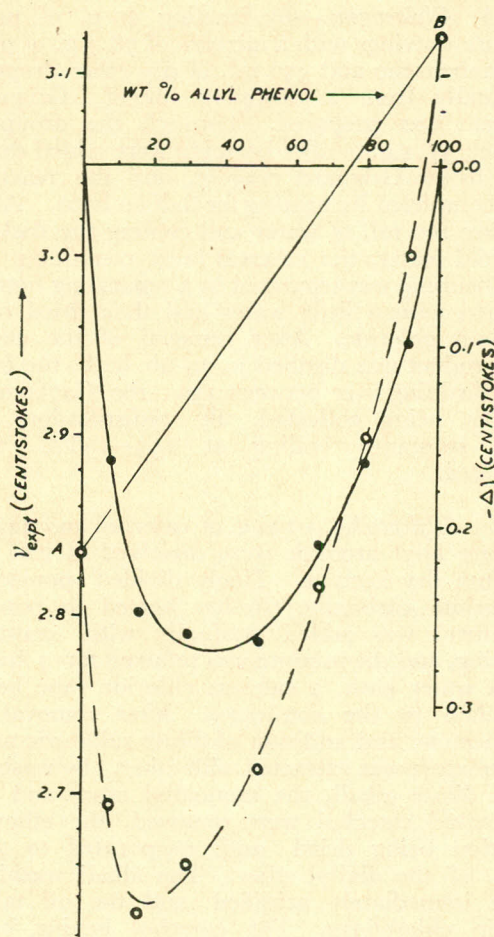


Fig. 2.—Graphs showing the measured viscosities, ν_{expt} , and the calculated viscosity depression for mixtures of allylphenol with a mineral oil blend ($\nu=2.835$ c.s.). ν_{expt} : hollow circles and broken line graph. $-\Delta v$: solid circles and full line graph.

kerosene oil having a viscosity of 1.15 centistokes, and the blend was found to have a viscosity of 2.84 centistokes. The measurements for the mixtures with allylphenol at 40°C. (corrected for changing viscosity* of the blended oil) are given in Table 2, and are plotted in Fig. 2 (broken line).

*It was found that the viscosity of the mineral oil blend increased slowly during the course of the experiment, probably due to loss of the more volatile kerosene oil.

TABLE 2.—VISCOSITY AT 40°C. OF MIXTURES OF ALLYLPHENOL WITH MINERAL OIL BLEND.

Wt. % allylphenol=100x	0.0	8.0	16.0	30.1	50.3	67.0	80.0	92.0	100.0
Measured viscosity (centistokes)	2.835	2.694	2.633	2.661	2.715	2.817	2.900	3.001	3.122
Calculated viscosity for ideal solution (centistokes)	2.835	2.858	2.881	2.921	2.979	3.027	3.065	3.099	3.122
Depression $-\Delta v$	0.000	0.164	0.248	0.260	0.264	0.210	0.165	0.098	.000

The slightly higher value for the viscosity of the allylphenol in this second set of experiments may be due to partial oxidation as in the case of bhilawanol.¹ The values of viscosity of the various compositions on the basis of ideal solution are given as before by the straight line AB, and are to be found in the third row of Table 2, while the deduced viscosity depression, $-\Delta v$, is given in the fourth row of the table. The graph for Δv is plotted in Fig. 2 (full line), and from it we obtain $-(\partial v/\partial x)_{x=0} = 2.40$ c.s./part ($-\Delta v_m$) = 0.268 c.s., which are both lower than the previous values by about 20%. This is quite satisfactory when we remember that in Fig. 2 the correction for the difference of viscosity between the two components of the mixture is about 0.1 centistokes as against the corrected value of 0.268 c.s. for $-\Delta v_m$. In fact, the degree of agreement between the two sets of values (from Figs. 1 and 2) affords confirmation of the essential validity of the corrections. The means of the two values are: $[-(\partial v/\partial x)_{x=0}] = 2.6_2 \pm 0.22$ c.s./part and $-\Delta v_m = 0.30_6 \pm 0.038$ c.s.

It is to be noted here that when the more accurate procedure is adopted and v_{ideal} is taken to vary linearly with mole fraction (instead of weight%), the mean values obtained above remain unchanged, but the standard errors are reduced to two-thirds.

4. Measurements with Allylbenzene

The measurements for allylbenzene were also made by mixing it with two different oil blends, namely, (1) kerosene oil and *n*-heptane, and (2) kerosene oil and petroleum ether. The viscosities were measured with a semi-micro viscometer of 1.5 ml. capacity, which had previously been calibrated with distilled water at several temperatures from 40°C. to 70°C., giving the following values of the constants

$$A = 0.009,52$$

$$B/50^2 < 0.000,05$$

Allylbenzene was found to have a viscosity of 0.724 c.s. at 40°C., and a blend of kerosene oil ($v = 1.15$ c.s.) with *n*-heptane ($v = 0.33$ c.s.) in the ratio of 2:3 had a viscosity of 0.728 c.s. measured at 40°C. in the same viscometer. Allylbenzene was mixed in various proportions (increasing by steps of 10%) with this blended oil, with gentle shaking in a stoppered bottle to avoid loss of the volatile heptane. As a further precaution against such a loss during the experiment, a fresh mixture was prepared for each concent-

ration of allylbenzene in place of the more economical method of adding more allylbenzene to the mixture used for the lower concentration. At least three measurements of the time of flow concordant to 1/2% were taken for each concentration, and their mean was used to calculate the viscosity as $v = At$, the kinetic energy term, B/t^2 , being negligible with the viscometer used here. The viscosities of allylbenzene and the oil blend were measured at the end of the experiment and the overall mean values were used. The measured viscosities are given in Table 3, and are plotted against wt.% allylbenzene in Fig. 3 (hollow circles, broken line). A satisfactorily smooth curve can be drawn through the points, the standard deviation of the points from this curve being nearly 0.003 c.s., which corresponds to 0.4% of the mean viscosity (0.70 c.s.). This compares satisfactorily with the experimental accuracy of each viscosity measurement which is of the order of 1/4%. As before, the line $A_1 B_1$ represents the viscosity of ideal mixtures of allylbenzene with the blended oil, and both $-(\partial v/\partial x)_{x=0}$ and $-\Delta v_m$ can be reckoned from this line as reference, giving

$$-(\partial v/\partial x)_{x=0} = 0.22 \pm 0.05 \quad \text{and}$$

$$-\Delta v_m = 0.039_5 \pm 0.004.$$

The whole series of observations was repeated with another oil blend of viscosity 0.727 c.s. made

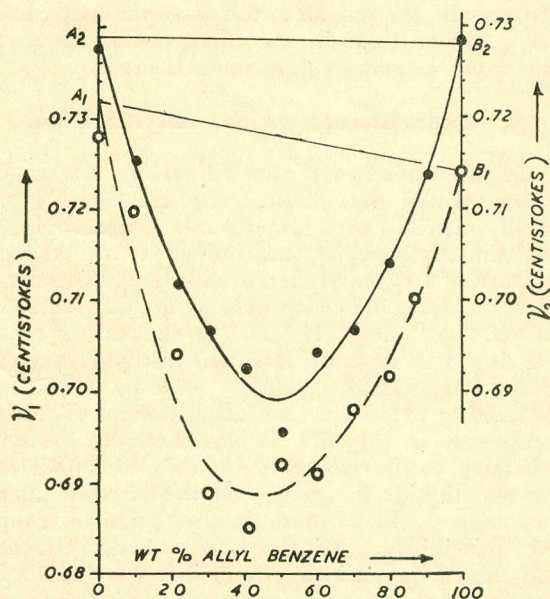


Fig. 3.—Graphs for viscosity depression, $-\Delta v$, observed in mixtures of allylbenzene with (a) blend of kerosene oil and *n*-heptane, shown by the broken line, and (b) blend of kerosene oil and petroleum ether, shown by the full line curve.

TABLE 3.—VISCOSITY AT 40°C. OF MIXTURES OF ALLYL-BENZENE WITH TWO MINERAL OIL BLENDS.

Mixtures with the oil-heptane blend	100 x = Wt. % allyl- benzene	0	10.0	21.4	30.1	41.3	49.9	59.8	70.0	80.1	87.0	100
	Viscosity	0.728	0.719 ₅	0.704	0.698	0.685	0.692	0.691	0.698	0.701 ₅	0.710	0.724
Mixtures with the oil-petroleum ether blend	100 x = Wt. % allyl- benzene	0	10.3	21.2	30.2	40.1	50.4	60.0	70.0	80.0	90.3	100
	Viscosity	0.727 ₅	0.715	0.701 ₅	0.696 ₅	0.692 ₅	0.685 ₅	0.694	0.6965	0.704	0.713 ₅	0.728 ₅

from the kerosene oil and petroleum ether (*i.e.* low-boiling petroleum fraction, b.p. 60–80°C. $v_{40}=0.44$ c.s.) in the ratio of 3:2. The measured viscosities of mixtures of this blend with allylbenzene are given in the lower half of Table 3, and are shown graphically in Fig. 3, full line curve. The standard deviation of the points about this curve is 0.002 c.s., *i.e.* $2/3$ of that with the previous blend, and the graph yields

$$\begin{aligned} - (\partial v / \partial x)_{x=0} &= 0.15 \pm 0.03 \text{ and} \\ - \Delta v_m &= 0.0394 \pm 0.003. \end{aligned}$$

This gives the following overall mean values :

$$\begin{aligned} \text{Mean } - (\partial v / \partial x)_{x=0} &= 0.185 \pm 0.035 \text{ and} \\ \text{mean } - \Delta v_m &= 0.0394 \pm 0.0025. \end{aligned}$$

It is to be noted that the viscosity of allylbenzene in the second graph is apparently about 0.6% higher than in the first, which may be attributed largely to experimental error.

5. Experiments with Allylcatechol

(a) *Determination of the Miscibility Curve.*—It was suspected that allylcatechol might not be as readily miscible with mineral oils as are allylphenol and allylbenzene, and indeed a well shaken mixture of 10% allylphenol with 90% of mineral oil of viscosity 19 centistokes at 40°C. (blend of B.O.C. "50" and "H.S.D." in the ratio of 10:1) was found to separate into two distinct layers at room temperature (nearly 30°C.). However, on heating to 80°C., the allylcatechol dissolved completely in the oil. It was therefore thought necessary to determine the miscibility curve for the two liquids in order that the viscosity measurements could be made in the region of complete miscibility. Mixtures of the allylcatechol and the oil in various proportions were taken in test tubes, and were slowly heated (with constant stirring) in a water bath, and the temperature at which the turbidity disappeared was noted for each mixture. The bath was allowed to cool,

and the temperature at which turbidity re-appeared was noted, the mean of the two temperatures being taken as the miscibility temperature for the particular mixture. The results are given in Table 4, and the miscibility curve is drawn in Fig. 4. The standard deviation of the points about the curve is less than 2°C., which agrees well with that estimated from the measurements in Table 4. It follows from an inspection of Fig. 4 that we must work at a temperature of over 125°C. in order to obtain a reliable value for $-\Delta v_m$, which can then be extrapolated to 40°C., if we at the same time determine experimentally the temperature variation of the viscosity depression. For obtaining $-(\partial v / \partial x)_{x=0}$ we require measurements in the range 0–15% allylcatechol, and therefore we need not go much above 90°C.

(b) *Viscosity Measurements.*—For these measurements, a B.S.S. pattern U-tube viscometer No. 2 was used, which has the advantage of a wide capillary, thus lessening the danger of clogging errors caused by possible decomposition at the elevated temperatures necessary for the present measurements. The times of flow are also small, of the order of 1 minute, which necessitates use of the kinetic energy correction, but

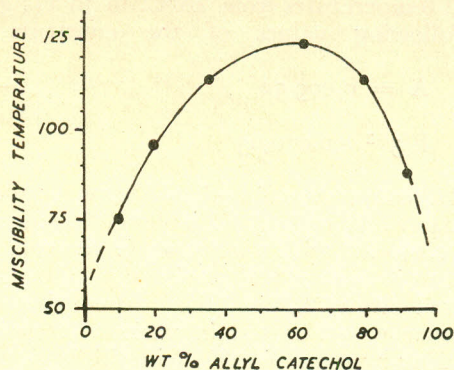


Fig. 4.—Miscibility curve for mixtures of allylcatechol with mineral oil of viscosity 19 centistokes at 40°C., showing that the critical solution temperature is 125°C.

TABLE 4.—MISCIBILITY TEMPERATURES OF MIXTURES OF ALLYL-CATECHOL WITH MINERAL OIL.

Wt. % allylcatechol	9.8	19.6	35.5	62.5	79.8	91.9
Turbidity disappears at (°C.) ..	88	106	120	125	115	90
Turbidity appears at (°C.) ..	62	86	109	124	112	86
Mean miscibility temperature (°C)	75	96	114	124	114	88

provides a compensating advantage in that the time for which the mixtures are to be heated to any one temperature is small, thus lessening the errors due to polymerization and decomposition.

The viscosity of the allylcatechol was measured every 20°C. from 40°C. upto 180°C., and an oil blend was prepared by mixing B.O.C. "50" and "H.S.D." oils in proportions of 3 to 2, so as to have the same viscosity as the allylcatechol in the middle of this temperature range, *i.e.*, at 110°C. This adjustment helps to keep down the corrections for difference of viscosity between the allylcatechol and the oil blend, which are seen in Table 5 below to be less than 10% at the extremes of the temperature range. Since it was desired to measure $-(\partial v / \partial x)_{x=0}$ and $-\Delta v_m$, most of the observations were in the first instance made with concentrations of allylcatechol between 0% and 40% by weight, only one mixture being made in the range 40% to 100%. The quantity of allylcatechol available barely sufficed for these measurements, because (a) the capacity of the viscometer was about 11 c.c. and (b) fresh oil and allylcatechol had to be used for each mixture in order to avoid error due to increase in viscosity consequent upon heating which is of the order of 3% per heating in the present case. Each mixture was prepared by weighing out the constituents in a covered weighing bottle, which was then heated rapidly with occasional shaking to nearly 15°C. above the corresponding miscibility temperature. The clear solution was then sucked up into an air-jacketted pipette (Fig. 5) and immediately transferred into the viscometer, already fixed in the bath, which was maintained about 10°C. above

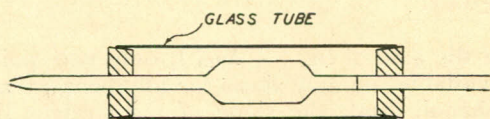


Fig. 5.—Sketch of air-jacketted pipette for transferring hot solutions into the viscometer.

the miscibility temperature. (During the transfer the temperature of the solution fell by less than 10°C., as was determined by a separate experiment.) After allowing fifteen minutes for the attainment of a steady temperature, the viscosity measurements were carried out as before, the mean of five to ten observations of the flow time being taken as the correct value. The process was repeated at all the desired temperatures, care being taken to remain at least 5 to 10°C. above the miscibility temperature, so as to avoid all possibility of separation of the two constituents inside the viscometer. (A redetermination of the (maximum) miscibility temperature with the oil blend used in the viscosity measurements gave a figure of $120 \pm 2^\circ\text{C}$. for 60% allylcatechol, which is 5 degrees lower than the value in Fig. 4.) The measured viscosities are given in Table 5, and their standard deviation has been estimated as varying from 0.006 c.s. at the lower temperatures to 0.003 c.s. at the highest temperature.

Since the molecular weight of allylcatechol is 150, which differs considerably from that of the oil blend, estimated at 250 from cryoscopic measurements, the values of v_{ideal} for an ideal mixture have been calculated in Table 5 by using molecular proportions in the formula $v_{\text{ideal}} = x_A v_A + x_B v_B$. The deviation Δv of the measured viscosity from v_{ideal} is calculated as $\Delta v = v_{\text{expt}} - v_{\text{ideal}}$, and it is seen that the values of Δv are negative for small concentrations of allylcatechol, but are predominantly positive in the range 40–80% allylcatechol. This abnormal behaviour is strikingly shown in the plots of Δv against concentration at different temperatures (Fig. 6 (a) and 6 (b)), in which another set of observations made with 60% allylcatechol are also included and the broken lines indicate the general trend in regions not adequately covered by experimental points. The parts of the curves near the origin (*i.e.* for less than 10% allylcatechol) are similar to those for allylphenol and allylbenzene, while the portions between 40 and 80% approach the normal behaviour only at temperatures well above 180°C.

TABLE 5.—MIXTURES OF ALLYL CATECHOL WITH MINERAL OIL.

Experimental viscosities and calculated deviations, Δv , in centistokes. (The standard error of the experimental values varies from ± 0.006 c.s. to ± 0.003 c.s.)

Temperature	100x=Wt. % allylcatechol	0	5.3	10.7	20.0	36.1	83.2	100	$-(\partial v/\partial x)_{x=0}$
80°C.	v_{expt}	3.275	3.166	3.183	—	—	—	3.772	3.5 /part
	v_{ideal}	3.275	3.317	3.358	—	—	—	3.772	
	Δv	0.000	-0.151	-0.175	—	—	—	0.000	
100°C.	v_{expt}	2.293	2.217	2.170	2.218	—	—	2.322	1.62/ ,,
	v_{ideal}	2.293	2.295	2.298	2.302	—	—	2.322	
	Δv	0.000	-0.078	-0.128	-0.084	—	—	0.000	
120°C.	v_{expt}	1.728	1.663	1.621	1.615	1.688	1.611	1.564	1.05/ ,,
	v_{ideal}	1.728	1.714	1.701	1.680	1.648	1.582	1.564	
	Δv	0.000	-0.051	-0.080	-0.065	+0.040	+0.029	0.000	
130°C.	v_{expt}	1.523	—	1.421	—	1.443	—	1.330	—
	v_{ideal}	1.523	—	1.491	—	1.429	—	1.330	
	Δv	0.000	—	-0.070	—	+0.014	—	0.000	
140°C.	v_{expt}	1.360	1.307	1.269	1.241	1.257	1.189	1.155	0.81/ ,,
	v_{ideal}	1.360	1.343	1.326	1.300	1.260	1.177	1.155	
	Δv	0.000	-0.036	-0.057	-0.059	-0.003	+0.012	0.000	
160°C.	v_{expt}	1.096	—	1.038	1.006	0.997	0.932	0.920	0.45/ ,,
	v_{ideal}	1.096	—	1.067	1.044	1.011	0.939	0.920	
	Δv	0.000	—	-0.029	-0.038	-0.014	-0.007	0.000	
180°C.	v_{expt}	0.896	—	0.866	0.835	0.813	—	0.787	—
	v_{ideal}	0.896	—	0.878	0.864	0.843	—	0.787	
	Δv	0.000	—	-0.012	-0.029	-0.030	—	0.000	

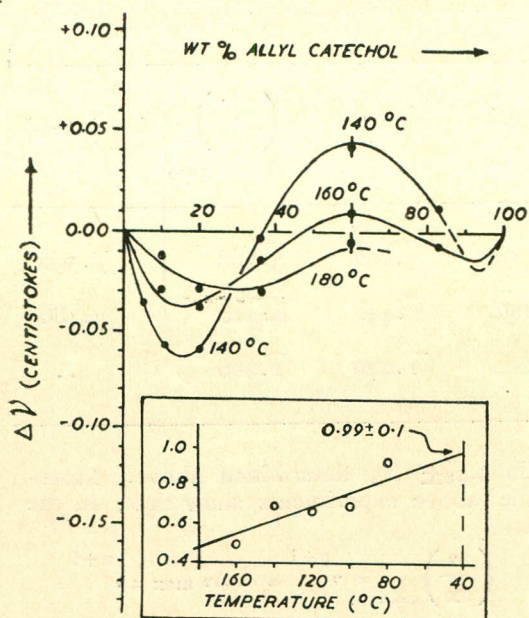
This is very surprising, since the miscibility temperature in this range of compositions lies between 115°C. and 125°C., and the experimental results therefore indicate the existence of some special effect that persists far above the miscibility temperature. The nature of this effect is being studied further, and will be discussed separately. (It is also to be noted that the minimum near 95% allylcatechol seems to be present in all the curves, and probably corresponds to the other minimum on the oil-rich side.) Here, it is sufficient to note that (a) the value of $-\Delta v_m$ cannot be estimated with any reliability from the above experimental data, and (b) the value of $-(\partial v/\partial x)_{x=0}$ appears to be nearly independent of the disturbing effect noted above, because the positive departure of Δv is seen to drop very rapidly as the concentration moves away from that for the maximum, namely 60% allylcatechol. Since $-(\partial v/\partial x)_{x=0}$ varies very rapidly with temperature, the quantity $-(\partial v/\partial x)_{x=0}/v_{\text{catechol}}$ which has a much slower variation, was calculated from the various graphs and plotted against temperature for extrapolation to 40°C. (inset to Fig. 6 (a)). The linearly extrapolated value of $-(\partial v/\partial x)_{x=0}/v_{\text{catechol}}$ is found to be 0.99 ± 0.10 . If we allow a further uncer-

tainty of ± 0.10 due to the possible non-linearity of the actual curve, the standard error becomes ± 0.14 . The extrapolated value of $-(\partial v/\partial x)_{x=0}$ for 40°C. is thus found to be 18.5 ± 2.6 c.s./part.

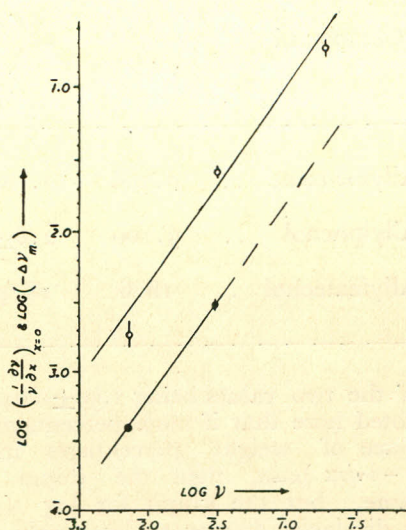
6. Conclusions and Discussion

The data obtained above on the three members of the allyl series of phenolic compounds are collected in Table 6, together with their logarithms, which are plotted in Fig. 7 (a), the short vertical lines indicating the estimated standard deviations of the corresponding measurements. It is seen that a satisfactory straight line can be drawn through the three points for $\log(-\partial v/\partial x)_{x=0}$, the deviation from the points being about $1\frac{1}{2}$ times the estimated experimental error. The slope of the best straight line is found to be 1.37 ± 0.07 .

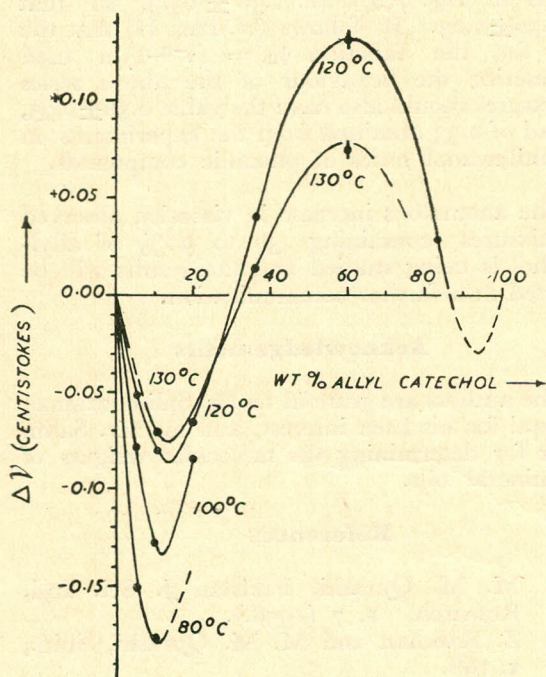
In the case of $\log(-\Delta v_m)$, only two points are available, namely those for allylbenzene and allylphenol, and the slope of the straight line joining these two points is 1.41 ± 0.07 , which agrees very well with that found above for the logarithmic plot of $(-\partial v/\partial x)_{x=0}$, the mean



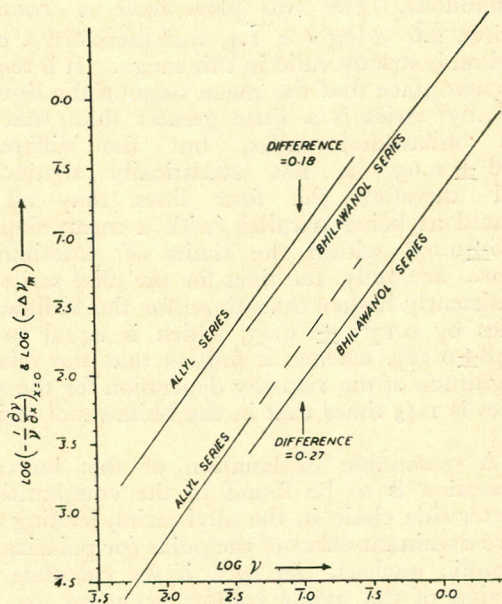
(a)



(a)



(b)



(b)

Fig. 6.—Graphs showing $\Delta\gamma$, the departure from linearity of the viscosity of mixtures of allylcatechol with mineral oil at various temperatures (a) from 140°C. to 180°C. and (b) from 80°C. to 130°C. The inset to Fig. 6 (a) shows the extrapolation of $[-(\partial\gamma/\partial x)_{x=0}]_{\text{catechol}}$ to a temperature of 40°C.

Fig. 7.—Logarithmic plots of the viscosity depressions, showing (a) the close parallelism of the linear plots for the origin slopes and the maximum depression in the allyl series, and (b) the near parallelism of the two pairs of lines for the bhlawanol series with those of the allyl series, and the upward displacement of the lines for the allyl series.

TABLE 6.—COLLECTED DATA ON VISCOSITY DEPRESSION IN THE ALLYL SERIES (VISCOSITY IN STOKES).

Compound	$\nu \times 100$	$-\left(\frac{\partial \nu}{\partial x}\right)_{x=0} \times 100$	$-\Delta \nu_m \times 100$	$\log \nu$	$\log\left(-\frac{\partial \nu}{\partial x}\right)_{x=0}$	$\log(-\Delta \nu_m)$
Allylbenzene ..	0.726	0.185 ± 0.035	0.0394 ± 0.025	$\bar{3}.862$	$\bar{3}.268$	$\bar{4}.596$
Allylphenol ..	3.100	2.62 ± 0.22	0.306 ± 0.038	$\bar{2}.492$	$\bar{2}.418$	3.486
Allylcatechol ..	18.6	18.4 ± 2.8	..	$\bar{1}.270$	$\bar{1}.266$..

of the two values being 1.39 ± 0.04 . It is to be noted here that if mole percentages are used in place of weight percentages in calculating $(-\partial \nu / \partial x)_{x=0}$, then the slopes remain the same, but the graph for $\log(-\partial \nu / \partial x)_{x=0}$, is displaced downward by nearly 0.20 units.

In Fig. 7 (b) the two straight-line plots obtained for the allyl series are compared with the corresponding linear plots for the bhilawanol series of compounds. The two plots have a common region, $2.6 < \log \nu < 1.4$, and therefore a comparison is strictly valid in this range. It is seen in the first place that the mean slope of the lines for the allyl series is a little greater than that for the bhilawanol series, but the difference, 0.06 ± 0.05 , is not statistically significant, and therefore the four lines may all be treated as being parallel (with a mean slope of 1.36 ± 0.03) within the limits of experimental error. Secondly, the lines for the allyl series are consistently higher than those for the bhilawanol series by $0.17^* \pm 0.05$, which is equal to $\log(1.48 \pm 0.16)$, whence it follows that the relative magnitude of the viscosity depression for the allyl series is 1.48 times that in the bhilawanol series.

A reasonable explanation of this increased depression is to be found in the comparatively shorter side chain in the allyl series, leading to a more dominant effect of the polar (or polarizable) phenolic nucleus. In fact, if we calculate the fraction of the molar volume occupied by the nucleus in the two series, we get for allylphenol and dimethoxybhilawanol the values, 0.8 and 0.4, respectively, whose ratio is comparable with

the ratio 1.48 ± 0.15 determined above. Moreover, the above experiments show that, in the relations,

$$\left(\frac{\partial \nu}{\partial x}\right)_{x=0} \propto \nu^{n+1} \quad \text{and} \quad \Delta \nu_{\max} \propto \nu^{n+1},$$

the value of 'n' is tolerably independent of the length of the side chain, the best experimental value for $n+1$ being the mean of the slopes of the graphs of Fig. 7(b), *i.e.* 1.36 ± 0.03 , so that $n = 0.36 \pm 0.03$. It follows (cf. Part II) that the 'n' for the function $\psi_n = (\nu^{-n} - 1)/n$ used to describe the behaviour of the above series of mixtures should also have the value 0.36 ± 0.03 , instead of 0.33 obtained from the experiments on the bhilawanol series of phenolic compounds.

The anomalous increase in viscosity observed in mixtures containing 30 to 90% of allylcatechol is being studied and the results will be reported in a further communication.

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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**, 198.
3. H. H. Mathur, J. S. Aggarwal and S. Siddiqui, J. Sci. Ind. Research (India), **9B**, 121 (1950).

* The figure given is the mean of those with 'x' as mole fraction and as parts by weight.