STUDIES IN THE INFLUENCE OF LONGCHAIN PHENOLIC ADDITIVES ON THE VISCOSITY OF MINERAL OILS

Part IV.—Temperature Variation of the viscosity depression in mixtures of bhilawanol and allyl phenol with mineral oils.*

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1. Introduction

In previous communications of this series, [1,2,3] a study has been made of the departure from linearity of the graphs for viscosity against concentration for mixtures of mineral oils with several phenolic compounds of the bhilawanol series, having a $C_{15}H_{27}$ side chain containing two double bonds, and of the allyl series with a short C_3H_5 side chain. From these experiments, a generalized law governing the dependence of this departure from linearity, or viscosity depression, in this series of compounds was derived. At first it was thought that the viscosity depression was dependent only on the number of hydroxyls per molecule, but this produced some anomalies that led to consideration of a direct relation between the viscosity, v, of the product and the viscosity depression, $\triangle v$, produced on mixing it with a mineral oil of the same viscosity.

It was found [2,3] that $\triangle v$ is proportional to $v^{1.36}$, and, on putting $\Psi_{0.36}=(v^{-0.36}-1)/0.36$, the depression was shown to be governed by the law that $\triangle\Psi_{0.36}$ is very nearly the same function of concentration for all the compounds of one series. Now, apart from changing the number of hydroxyl groups, another method of varying the strength of the polar inter-molecular interaction is to alter the temperature (while keeping the number of OH groups per molecule fixed), and it was thought desirable to study the applicability of the above law in this direction. Accordingly, experiments were conducted to determine the law governing the temperature dependence of the viscosity depression for two typical compounds :

(1) re-distilled bhilawanol with a long $C_{15}H_{27}$ side chain, and

(2) allyl phenol with a short C_3H_5 side chain.

2. Experimental Data for Bhilawanol

The general technique of conducting these experiments was essentially the same as described in parts I and II for bhilawanol and its methyl ethers,[1,2] except that measurements with each mixture were all repeated at intervals of 10°C., starting from 25°C. and going up to 75°C. This range of 50°C. was considered large enough for the present purpose because it corresponds to a ten-fold decrease in the viscosity of bhilawanol. To begin with, the viscosities of the bhilawanol sample and of the mineral oil blend to be mixed with it were measured at the six temperatures selected, the temperature in each case being controlled to within ± 0.02°C. The measurements were then repeated with mixtures prepared so as to cover the entire composition range in ten steps, with an extra step at 5% bhilawanol. The experimental results are plotted in the form of six curves on semi-logarithmic paper in Fig. 1.

It is to be noted that the viscosity of this sample of bhilawanol when measured at 40°C. comes out to be nearly 51 centistokes, as against the value of 80 centistokes for the sample used in earlier experiments. [1,2] This difference is attributable largely to the time for which the extracted shell liquid and the distilled bhilawanol was left standing in the earlier experiments, thus producing an increase in the viscosity due to auto-oxidation, which effect was actually observed in the course of the measurements[1].
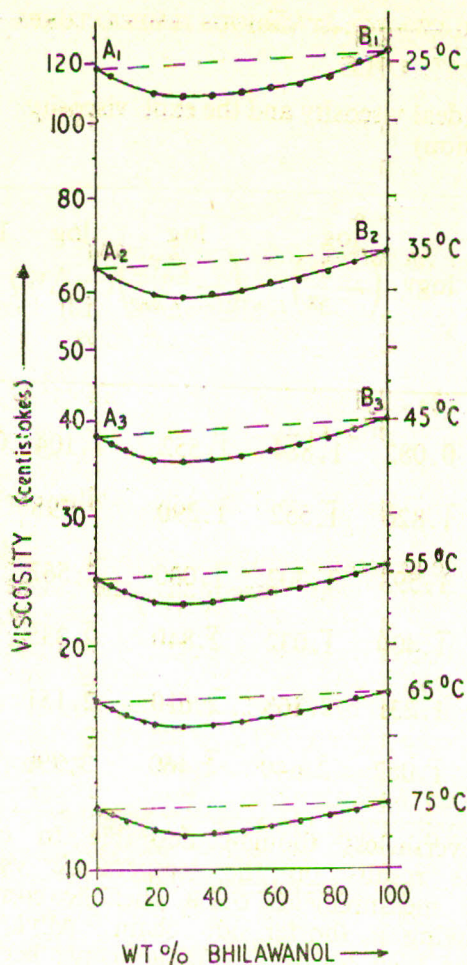

Fig. 1.—Viscosity curves for bhilawanol in mineral oil at various temperatures.

It is clear from Fig. 1 that all the curves are similar in shape, but they become somewhat flatter at higher temperatures, i,e. for lower viscosities of the constituents. Since the viscosity scale is logarithmic, this means that $\triangle v$ varies somewhat faster than v.

3. Determination of the Law of variation

In order to determine the law of this variation more precisely, we calculate the quantity, (v_{expt}/v_{ideal}), where v_{ideal} is the viscosity of an ideal (i.e. non-interacting) mixtulre of the two constituents, and can be calculated to a sufficient degree of accuracy by means of the formula (3) discussed previously[2] in connection with the experiments with dimethoxy-bhilawanol. This corresponds essentially to linear interpolation along the lines A_1, B_1, A_2B_2, etc. in Fig. 1.
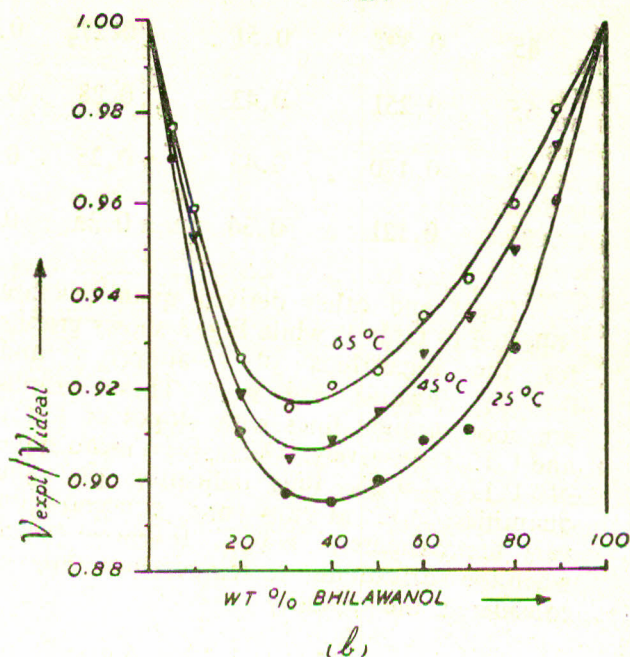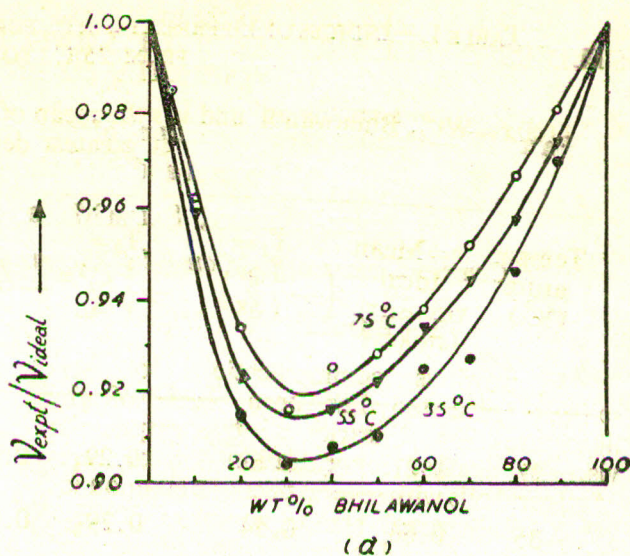

Fig. 2(a) and (b)—Graphs for v_{expt}/v_{ideal} calculated from the data of Fig. 1.

The graphs of (v_{expt}/v_{ideal}) are shown in Figs. 2(a) and 2(b), from which we can readily calculate the three significant quantities,.

$$I_1 = \left(-\frac{1}{v}\frac{\partial v}{\partial x}\right)_{x=0} = -(\text{slope at the origin}),$$

$$-\frac{\triangle v_m}{v} = 1 - (v_{expt}/v_{ideal})_{mIn},$$

$$I_2 = -\frac{1}{v}\frac{\triangle v_m}{x_m} = -\frac{\triangle v_m}{v}\bigg/ x_m.$$

TABLE 1.—INDICES OF DEPRESSION, ETC., FOR BHILAWANOL AT VARIOUS TEMPERATURES FROM 25°C. TO 75°C.

($100x$ = Wt% Bhilawanol and $\bar{v}$ is the mean of the ideal viscosity and the expt. viscosity at greatest depression)

Temperature (°C.)	v = Mean Ideal viscosity (stokes)	$I_1 = \left(-\dfrac{1}{v}\dfrac{\partial v}{\partial x}\right)_{x=0}$	$I_2 = -\dfrac{1}{v}\dfrac{\triangle v_m}{x_m}$	$-\dfrac{\triangle v_m}{v}$	$\log v$	$\log\left(-\dfrac{\partial v}{\partial x}\right)_{x=0}$	$\log\left(-\dfrac{\triangle v_m}{x_m}\right)$	$\log(-\triangle v_m)$	$\log \bar{v}$
25	1.21	0.63	0.29_5	0.105	0.082	$\bar{1}.884$	$\bar{1}.552$	$\bar{1}.104$	$\bar{0}.058$
35	0.66_0	0.54	0.29_5	0.095	$\bar{1}.820$	$\bar{1}.552$	$\bar{1}.290$	$\bar{2}.798$	$\bar{1}.800$
45	0.392	0.51	0.27_5	0.093	$\bar{1}.593$	$\bar{1}.302$	$\bar{1}.030$	$\bar{2}.562$	$\bar{1}.574$
55	0.251	0.43	0.28	0.086	$\bar{1}.400$	$\bar{1}.032$	$\bar{2}.840$	$\bar{2}.335$	$\bar{1}.380$
65	0.170	0.43	0.25	0.083	$\bar{1}.231$	$\bar{2}.868$	$\bar{2}.610$	$\bar{2}.151$	$\bar{1}.211$
75	0.121	0.36	0.25	0.081	$\bar{1}.082$	$\bar{2}.640$	$\bar{2}.460$	$\bar{3}.990$	$\bar{1}.061$

These and other derived quantities are collected in table 1, while Fig. 3 shows graphs for the logarithms of $(-\partial v/\partial x)_{x=0}$ and $(-\triangle v)_m$ against log v. These graphs are good straight lines with slopes of 1.22_5 and 1.12, respectively, which give a mean slope of $1.17_2 \pm 0.05$, thus indicating that the quantities, $\triangle v$, at any one concentration vary approximately as $v_{1.17}$. It follows that, when the varition due to temperature only is considered, the quantity

$$\triangle \Psi_{0.17} = \triangle (v^{-0.17}-1)/1.17 \simeq \triangle v/v^{1.17}$$

is a constant. This is to be compared with the generalized law of variation for the two series of phenolic compounds at a fixed temperature of 40°C., which is that $\triangle \Psi_{0.36}$ is a constant[2]. Although the difference between the index 0.17 ± 0.05 for the temperature variation, and the index 0.36 ± 0.03 for variation in the number of OH groups is seen to be a little grater than three times the standard error $([(0.05)^2+(0.23)^2]^{\frac{1}{2}}=0.006)$, it was nevertheless thought desirable to confirm the results on the temperature variation by measurements on a phenolic compound having a shorter side chain. Allyl phenol was used for these measurements because it differs from bhilawanol both in the number of phenolic hydroxyl groups and in the length of the aliphatic side chain (C_3H_5 against $C_{15}H_{27}$ in bhilawanol). The preparation and confirmation of the allyl phenol as well as some viscosity measurements at 40°C. have been described in part III of this series[3].

4. Experimental Results with Allyl Phenol

Because of the higher ambient temperature when these experiments were performed, it was only possible to work above 35°C., but the upper limit of the temperature range was pushed up to 85°C. in order to compensate for this. The experimental technique was exactly as for the foregoing measurements with bhilawanol, except that, due to the shortage of allyl phenol, the concentrations
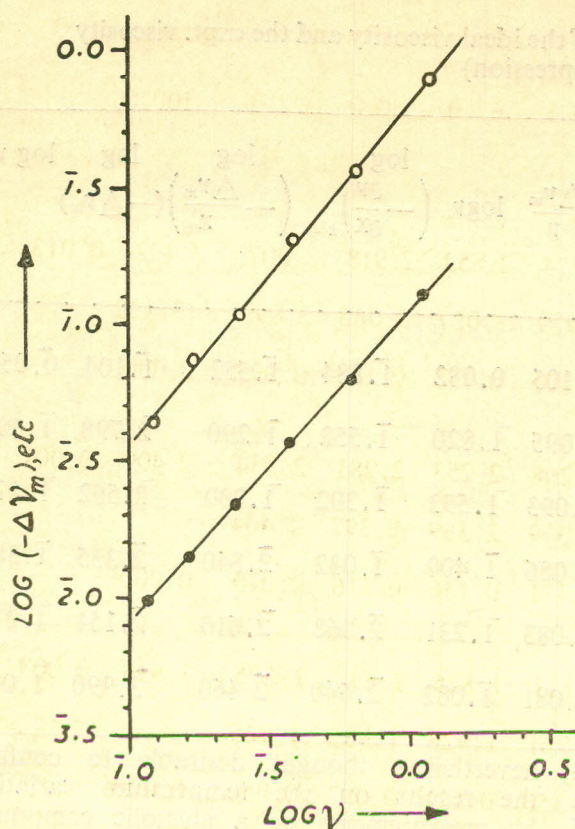
Fig. 3.—Linear graphs of log $(-\triangle v/\triangle x)_{x=0}$ (hollow circles) and log $(-\triangle v_m)$ (solid circles) against log v for bhilawanol in mineral oil.

of the mixtures were spaced rather further apart than with bhilawanol. The mineral oil blend used in this experiment had a smaller temperature coefficient of viscosity than allyl phenol, the viscosities of the two being identical in the neighbourhood of 55°C. The oil blend consisted of 93.5 parts of B. O. C. "H.S.D." oil and 6.5 parts of kerosene oil. The viscosity of the allyl phenol was measured both in the beginning and at the end of the whole experiment, and the two sets of values were found to agree to better than 1%, so that the effect of oxidation of the phenolic OH group was negligible. The mean values are quoted in table 2 below, which gives the measured viscosities for the series of mixtures together with the value calculated for ideal solution[2] and the calculated depression, $\triangle v$, obtained as the

difference of these two values. These values of $\triangle v$ are plotted as crosses in Figs. (4a), (4b) and (4c), for the pairs of temperatures, 40° and 70°C., 50° and 80°C. and 60°C and 85°C., respectively. The curves have a peculiar distorted appearance in the range of 30% to 80% allyl phenol, suggesting that the viscosity of one of the components had increased considerably during the experiment. Since the allyl phenol had already been checked for such an effect, with a negative result, the viscosity of the blended mineral oil was redetermined at all the temperatures used in table 2, and considerably higher values were obtained as shown in table 3. This increase in viscosity is probably due to the gradual loss of some of the more volatile component (viz., the kerosene oil) in the blend during the experiment, which was spread over a period of about 25 days. A correction was applied to all the calculated values of $\triangle v$ by means of the formula,

Correction = (wt. fraction of oil) × (Increase in Viscosity of oil in 25 days) × $\left(\dfrac{\text{no. of days elapsed.}}{25}\right)$.

The maximum corrections were obtained for the 50% mixture, and amounted to about 1/3 of the total observed increase in viscosity of the oil blend.

The corrected values of $\triangle v$ are plotted in solid circles in Figs. 4(a), 4(b) and 4(c), and give satisfactory graphs, very similar in shape to those for bhilawanol, the minima occurring at about 35% of allyl phenol. The values of the maximum depression $\triangle v_m$ obtained from these graphs are given in table 4 together with the values of $(-\triangle v/x)_{x=0.1}$, which have been chosen in preference to $(-\partial v/\partial x)_{x=0}$ because of the relatively large errors in fixing the tangent at the origin in the present case. Since the minima occur at x—0.35, the quantity $(-\triangle v/x)_{x=0.1}$ will be intermediate between $(-\partial v/\partial x)_{x=0}$ and $(-\triangle v_m/x_m)$. Table 4 also gives the values of the logarithms of these quantities, from which graphs for log $(-\triangle v/x)_{x=0.1}$ against log v and log $(-\triangle v_m)$ against log v have been plotted in Fig. (5).

TABLE 2.—EXPERIMENTAL VISCOSITY AND DEPRESSION, $\triangle v$, FOR ALLYL PHENOL AT TEMPERATURES OF 40°C. TO 85°C.]

100x =Wt% Allyl Phenol	0.0	8.1	16.0	30.1	50.3	67.0	80.0	92.0	100.0
40°C. v_{expt}	2.835	2.706	2.655	2.684	2.774	2.852	2.918	3.007	3.122±0.013
v_{ideal}	2.835	2.858	2.881	2.921	2.979	3.027	3.065	3.099	3.122
—$\triangle v$	0.000	0.152	0.226	0.237	0.205	0.175	0.147	0.092	0.000
50°C. v_{expt}	2.348	2.232	2.193	2.168	2.208	2.253	2.281	2.334	2.409±0.001
v_{ideal}		2.353	2.358	2.367	2.379	2.389	2.397	2.404	
—$\triangle v$	0.000	0.121	0.165	0.199	0.171	0.136	0.116	0.070	0.000
60°C. v_{expt}	2.003	1.874	1.817	1.805	1.811	1.825	1.838	1.875	1.918±0.003
v_{ideal}		1.996	1.989	1.977	1.961	1.926	1.935	1.925	
—$\triangle v$	0.000	0.122	0.172	0.172	0.150	0.121	0.097	0.050	0.000
70°C. v_{expt}	1.732	1.597	1.570	1.528	1.518	1.509	1.510	1.528	1.557±0.009
v_{ideal}		1.718	1.704	1.679	1.645	1.615	1.592	1.571	
—$\triangle v$	0.000	0.121	0.144	0.151	0.126	0.106	0.082	0.043	0.000
80°C. v_{expt}	1.487	1.398	1.351	1.304	1.286	1.282	1.278	1.288	1.296±0.004
v_{ideal}		1.472	1.456	1.430	1.392	1.359	1.334	1.311	
—$\triangle v$	0.000	0.074	0.105	0.126	0.106	0.077	0.056	0.023	0.000
85°C. v_{expt}	1.396	1.313	1.278	1.225	1.194	1.177	1.184	1.183	1.190±0.004
v_{ideal}		1.380	1.363	1.331	1.294	1.258	1.231	1.206	
—$\triangle v$	0.000	0.067	0.085	0.106	0.100	0.081	0.047	0.023	0.000

TABLE 3.—REPEATED MEASUREMENTS OF THE VISCOSITY OF THE BLENDED MINERAL OIL.

Temperature (in °C.)		40	50	60	70	80	85
Final Viscosity	..	3.000	2.473	2.083	1.782	1.530	1.436
Intial Viscosity	..	2.835	2.348	2.003	1.732	1.487	1.396
Increase	..	0.165	0.125	0.080	0.050	0.043	0.040

TABLE 4.—VALUES OF $(-\triangle v/x)_{x=0\cdot1}$ $(-\triangle v_\mathrm{m})$, ETC., AND THEIR LOGARITHMS FOR ALLYL PHENOL AT VARIOUS TEMPERATURES.

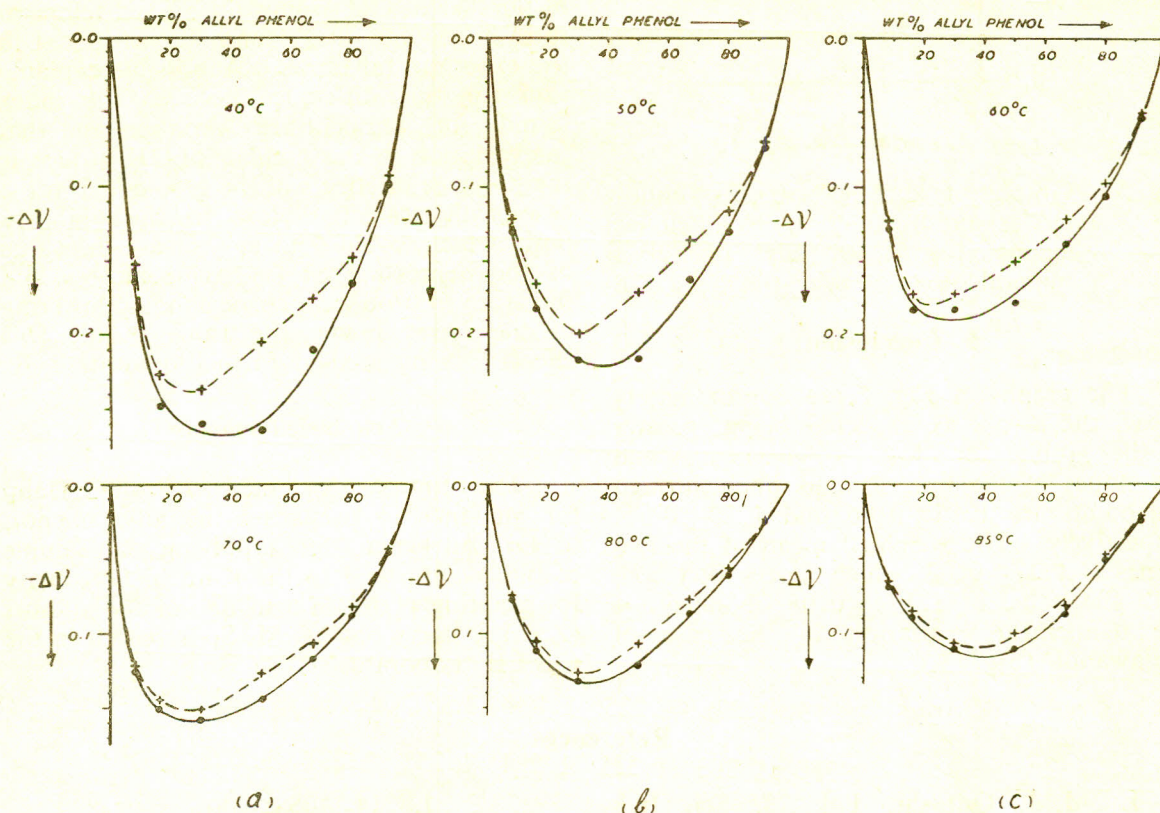| Temper-ture (°C.)	v_{ideal} (stokes)	$-(\triangle v/x)_{x=0\cdot1}$ stokes/part	$-\triangle_\mathrm{m}$ (stokes)	$\log v$	$\log(-\triangle v/x)_{x=0\cdot1}$	$\log(-\triangle v_\mathrm{m})$
40	0.0287	0.0198	0.00268	$\bar{2}.457$	$\bar{2}.297$	$\bar{3}.428$
50	0.0235	0.0149	0.00222	$\bar{2}.371$	$\bar{2}.174$	$\bar{3}.347$
60	0.0199	0.0150	0.00190	$\bar{2}.299$	$\bar{2}.176$	$\bar{3}.279$
70	0.0177	0.0135	0.00159	$\bar{2}.233$	$\bar{2}.131$	$\bar{3}.202$
80	0.0147	0.0090	0.00134	$\bar{2}.168$	$\bar{3}.955$	$\bar{3}.128$
85	0.0138	0.0075	0.00116	$\bar{2}.141$	$\bar{3}.876$	$\bar{3}.065$

Fig. 4.—Viscosity curves for allyl phenol in mineral oil; full line, corrected and broken line, uncorrected.
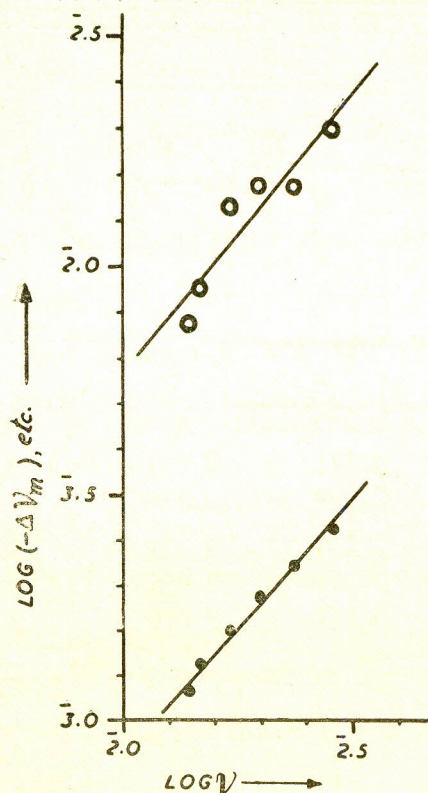
Fig. 5.— Graphs of log $(-\triangle v/x)_{x=0.1}$ (hollow circles) and log $(-\triangle v_m)$ (solid circles) against log v for allyl phenol in mineral oil.

5. Conclusion

The graphs of Fig. 5 are approximately linear, the errors as expected being greater in the graph for log $(-\triangle v/x)_{x=0.1}$, and the slopes of the best straight lines through the points are 1.15 ± 0.06 and 1.20 ± 0.15, respectively. The weighted mean of the two slopes is 1.17 ± 0.03, which agrees very well with the value of $1.17_2\pm0.05$ obtained for the temperature variation in the case of bhilawanol (Fig. 3.).

The good agreement between the mean values of the slopes otained with bhilawanol and with allyl phenol is all the more significant because the two experiments cover different viscosity ranges, viz. 120 c.s. to 12 c.s., and 3 c.s. to 1.3 c.s., respectively, so that, over this whole range, we get the mean slope as 1.17 ± 0.03, showing that

$$\triangle v \propto v^{1.17\pm0.05} \qquad (4)$$

for temperature variation only, whence we conclude that

$$\triangle \Psi_{0.17} = \triangle(v^{-0.17}-1)/0.17 = \text{constant}.$$

Since the standard error of the mean value of the index (0.17) is now 0.03, it follows that the difference of 0.19 between this and the value of 0.36 ± 0.03 obtained for the variation of number of OH groups (at a fixed temperature) is genuine, and cannot be attributed to the experimental errors. A possible explanation for this difference between the index found for temperature variation and that for variation in the number of OH groups is the presence of effects of the type noted in the case of allyl catechol[3] close to the solubility limit, which would tend to decrease the value of the depression at low temperatures and therefore to produce a corresponding lowering of the index below the value 0.36. This effect is being studied further quantitatively.

References

1. M.M. Qurashi, Pak. 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).