

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

Part V.—Phenomena occurring in the Proximity of the Miscibility Limit in Mixtures of Allyl Catechol and Mineral Oil

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Earlier experiments on the viscosity depression occurring in solutions of allyl catechol in mineral oil have been extended, and the results are analyzed to investigate the nature of the large anomalous increase in viscosity noticed in the range of 30% to 80% allyl catechol. This increase above the normally depressed value has been estimated as a Reduced Viscosity i.e. $(\Delta v/v) \div$ concentration, and plotted as a function of the temperature excess, ΔT , above the miscibility temperature for four different concentrations of allyl catechol varying from 20% to 70%. From this data, the graph for Intrinsic Viscosity (i.e. the limit of reduced viscosity at zero concentration) as a function of ΔT is obtained, which lends itself to an interpretation of the phenomenon as an incipient separation into macro-molecules of the two components. The Intrinsic Viscosity for $\Delta T \rightarrow 0$ is about 0.3, and, by using Staudinger's equation for the degree of polymerization in colloids, it is possible to estimate the number of molecules in each macro-molecule as about 70 when just above the miscibility temperature.

On the basis of these experimental data, an attempt is made to explain the different values of the coefficient of the quantity, $\ln v$, in the empirical equation, $\ln(-\Delta v) = K + A \ln v$, in the case of (i) variation of number of OH groups in a single series of phenolic compounds, and (ii) variations of temperature for a given binary system.

Introduction

Some measurements on the viscosities of mixtures of allyl catechol with mineral oil at various temperatures were presented in an earlier communication,¹ dealing with the development of a law governing the viscosity depression that occurs when a phenolic compound is mixed with a

mineral oil blend of the same viscosity. Whereas the curves for the other compounds studied were of the expected character with a (single) minimum of viscosity near the middle, those for allyl catechol showed an anomalous increase in viscosity in the region of 30% to 85% allyl catechol (Fig. 1(a)). The relative magnitude of this anomalous rise was found to increase as the temperature was decreased towards the miscibility temperature (Fig. 1(b)) for the corresponding concentration of allyl catechol.

Since the normal drop in viscosity is approached at temperatures far above the miscibility limit for a particular binary mixture (cf. Figs. 1(a) and 1(b)), it appears that the total change in viscosity

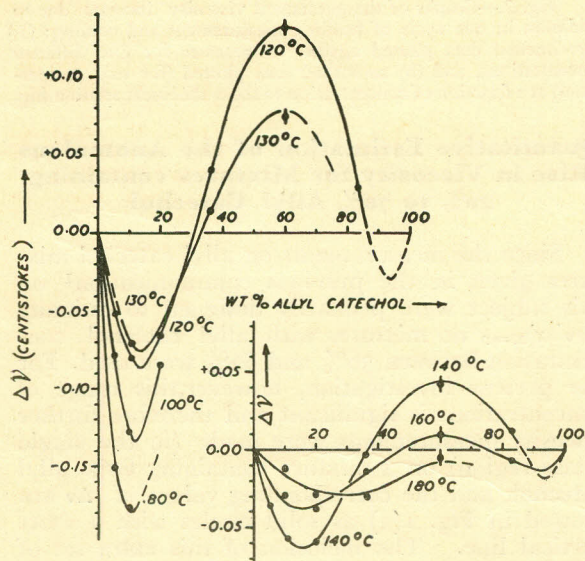


Fig. 1(a).—Experimentally observed viscosity depression and the anomalous viscosity increase in mixtures of allyl catechol and mineral oil at various temperatures from 80°C. to 180°C.

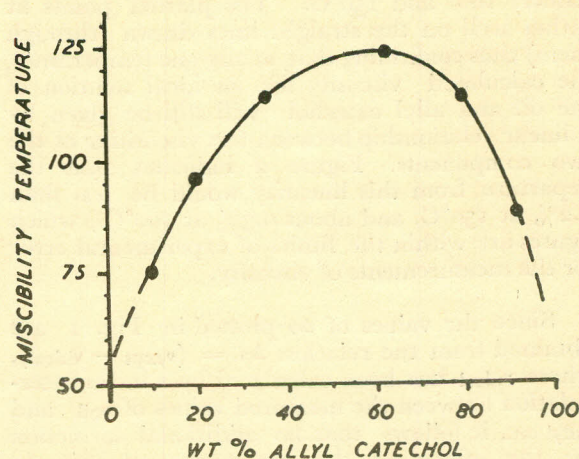


Fig. 1(b).—Phase diagram, showing miscibility temperatures in the allyl catechol-mineral oil system.

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can be represented as the sum of (a) the normal viscosity depression, and (b) the anomalous rise, which depends on the proximity of the miscibility temperature. It was therefore considered of interest to separate these two effects quantitatively, and to study the dependence of the viscosity increase on the concentration of the allyl catechol and on the departure from the miscibility temperature.

Effect of Oxidation of the Allyl Catechol

For quantitative interpretation of the graphs of Fig. 1(a), it is important to note that at the elevated temperatures of these measurements, the viscosities of both the mineral oil blend and the allyl catechol increases continuously with heating, due mainly to loss of the volatile components in the first case and oxidation in the second case. In order to measure this permanent increase (in viscosity) and to estimate its dependence on concentration of the catechol in the mixture of oil and allyl catechol, some of the mixtures were heated two or three times over the range of temperatures used in the experiments of Fig. 1, and the mean percentage increase in viscosity at several temperatures was calculated for one heating. These results are plotted against temperature in Fig. 2(a) and the best lines have been drawn through the points for each concentration, the uppermost line being for 100% allyl catechol. These graphs approximate to a pencil of straight lines meeting at a point somewhat above 200°C., and their spacing indicates that the increase in viscosity at any one temperature is roughly proportional to the concentration of allyl catechol plus a constant. Fig. 2(b) shows plots of this increase as a function of concentration at two different temperatures, namely 100° and 150°C. The plotted points fit rather well on the straight lines drawn (through them) thus confirming that, at any one temperature, the calculated viscosity for an ideal solution of the oil and allyl catechol will still be given by a linear relationship between the viscosities of the two components. Figure 2 indicates that the departure from this linearity would be less than 0.2% at 150°C. and about 0.3% at 100°C., which figures are within the limits of experimental error for the measurements of viscosity.

Since the values of Δv plotted in Fig. 1 are obtained from the relation $\Delta v = (v_{\text{expt}} - v_{\text{ideal}})$, where v_{ideal} has been calculated by a linear interpolation between the measured values of v_{oil} and $v_{\text{allyl cat.}}$, it follows that no additional correction for the effects of the permanent change in viscosity discussed above is required for these values of Δv .

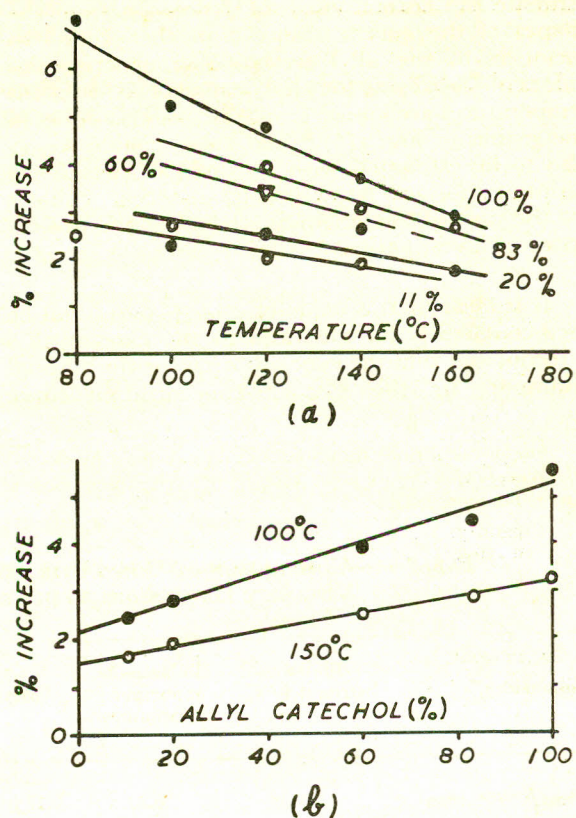


Fig. 2.—Graphs of the permanent viscosity increase due to oxidation in one cycle of heating, measurement and cooling: (a) experimental data plotted against temperature for five different concentrations, and (b) smoothed data plotted (for two temperatures) as a function of concentration to show the linear relationship.

Quantitative Estimation of the Anomalous Rise in Viscosity for Mixtures containing 20% to 70% Allyl Catechol

Since the measurements on allyl catechol mixtures given in the previous communication¹ on this subject were primarily designed to estimate $-(\partial v/\partial x)_{x=0}$ no mixtures with allyl catechol concentration between 36% and 82% were used. For the present investigation, however, this range of concentrations is significant and therefore further viscosity measurements were made (in the single phase region) on a mixture containing 60% allyl catechol, and the corresponding values of Δv are plotted in Fig. 1(a) as solid circles with a short vertical line. The inclusion of this extra set of points makes it possible to draw the complete variation of Δv quite satisfactorily, even (in some cases) beyond 80% allyl catechol.

In order to determine the magnitude of the anomalous rise in viscosity, it is first necessary to

estimate the normal viscosity depression from the shapes of the curves observed in the other two members of the allyl series. The experimental values of $(\partial v/\partial x)_{x=0}$ for allyl catechol at different temperatures are known from the original slopes of the graphs in Fig. 1(a),* and these enable Δv_{\max} also to be estimated with the help of the known ratios of Δv_{\max} to $(\partial v/\partial x)_{x=0}$ tabulated in Table 1 for the phenolic compounds studied in the present series of investigations.

It is clear that a value of 0.14 ± 0.015 can be used confidently for this ratio in the case of allyl catechol and that the concentration for the normal minimum in the viscosity-concentration curve

can be taken as $40\% \pm 3\%$. With the help of this data, and using the additional information (last row of Table 1) that $(\partial v/\partial x)_{x=100\%} \approx 0.39(-\partial v/\partial x)_{x=0}$, the "normal" curves to be expected for allyl catechol can be drawn reasonably accurately, at least upto 70% allyl catechol, as shown by the broken lines in Figs. 3(a), 3(b) and 3(c) where the experimental graphs are indicated by solid lines. The differences, δv , between these experimental graphs and the calculated "normal" curves can be measured, and are given in Table 2, together with the values of the (fractional) specific viscosity increase, $\delta v/v_{\text{mean}}$, for four different concentrations of allyl catechol, namely 20%, 35%, 50% and 70%.

It is seen that the specific viscosity increase is strongly dependent on both the concentration of the allyl catechol and on the proximity to the

*In the calculations, the smoothed values obtained by plotting $(\partial v/\partial x)_{x=0}/v$ allyl cat. against temperature have been used as being rather more reliable.

TABLE 1.—COMPARISON OF CONSTANTS DETERMINING THE SHAPE OF THE CURVE FOR VISCOSITY DEPRESSION Δv IN SEVERAL PHENOLIC COMPOUNDS.

Compounds :	Bhilawan series at 40°C.	Bhilawanol at various temperatures	Mean	Allyl series at 40°C.	Allyl phenol at various temperatures	Mean	Overall Mean
$\Delta v_{\max}/(\partial v/\partial x)_{x=0}$	0.14	0.20	0.17 ± 0.03	0.155	0.125	0.14 ± 0.015	0.15 ± 0.02
100 (x) _{max}	39 ± 4	35 ± 2	37 ± 2	43 ± 3	36 ± 5	40 ± 3	38 ± 2
$-(\frac{\partial v}{\partial x})_{x=100\%} \div (\frac{\partial v}{\partial x})_{x=0}$	0.20 ± 0.03	0.45 ± 0.05	0.32 ± 0.1	0.55 ± 0.1	0.35 ± 0.1	0.45 ± 0.05	0.39 ± 0.06

TABLE 2.—MEASURED VALUES OF THE ANOMALOUS INCREASE IN VISCOSITY AND THE CORRESPONDING SPECIFIC VISCOSITY FOR ALLYL CATECHOL-MINERAL OIL MIXTURES AT SEVERAL TEMPERATURES.

Temperature (°C.)		180	160	140	130	120	100	80	Miscibility temperature
Anomalous increase in viscosity	20% allyl cat.	.008	.013	.021	.034	.056	(.115)	(.30)	94°C.
	35% " "	.017	.050	.091	.128	.182	(.35)	—	112°C.
	50% " "	.031	.070	.132	.180	.260	—	—	120°C.
	70% " "	.026	.052	.108	.152	.215	—	—	120°C.
v_{mean} = mean viscosity of oil & allyl catechol		0.84	1.01	1.26	1.43	1.65	2.31	3.52	
Specific viscosity increase = $\delta v/v_{\text{mean}}$	20% allyl cat.	.009	.013	.017	.024	.034	.050	(.085)	94°C.
	35% " "	.020	.050	.072	.090	.110	(.15)	—	112°C.
	50% " "	.037	.069	.105	.126	.158	—	—	120°C.
	70% " "	.031	.051	.086	.106	.130	—	—	120°C.

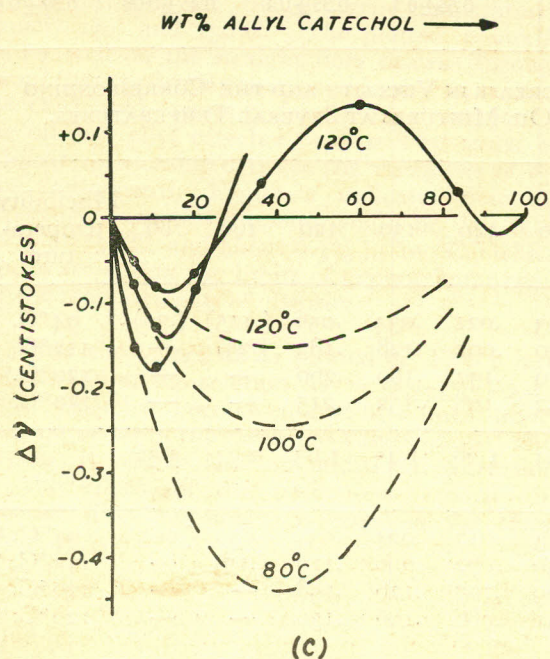
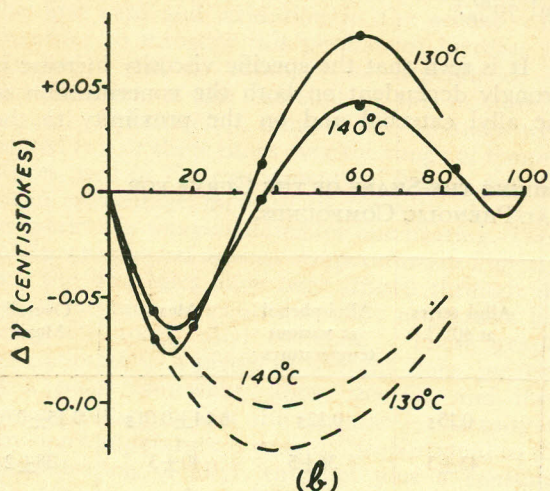
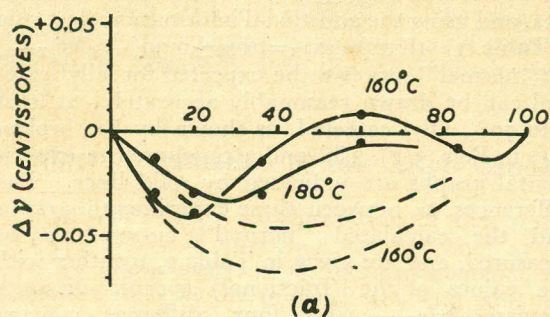


Fig. 3.—Curves for the quantitative estimation of the anomalous

miscibility temperature for the particular concentration. When allowance is made for the difference in miscibility temperatures for the four concentrations, it appears that, for concentrations below 50% allyl catechol, the specific viscosity $\delta\nu/\nu_{\text{mean}}$ is roughly proportional to the concentration, reaching a maximum at about 50% catechol, after which it decreases with increasing catechol concentration. This behaviour can to some extent be compared with the viscosity of a dilute suspension of small particles in a liquid, for which the specific viscosity is proportional to the concentration of these small particles, as given by Einstein's equation.² An explanation of the anomaly was therefore sought along these lines.

Interpretation in Terms of Einstein's Equation for Suspensions

For the case of solid spherical particles, the theoretical relation developed by Einstein² and other workers³ for the relative viscosity η/η_0 is

$$\eta/\eta_0 = 1 + 2.5 \times (\text{Vol. concentration}) + \alpha (\text{Vol. Conc.})^2, \quad (1)$$

$$\text{i.e. Specific Viscosity} = (\eta - \eta_0)/\eta_0 = \delta\eta/\eta_0 = 2.5 (\text{Vol. Conc.}) + \alpha (\text{Vol. Conc.})^2 \quad (2)$$

$$\text{whence Reduced Viscosity} = (\delta\eta/\eta_0)/\text{Conc.} = 2.5 + \alpha (\text{Vol. Conc.}). \quad (3)$$

The above relations hold for (volume) concentrations of much less than 50%. If now we postulate that, at temperatures only slightly above the miscibility temperature for a given concentration of allyl catechol, the molecular aggregates of the catechol behave to some extent like a suspension of very small particles in the oil, then equation (3) may be assumed to apply, albeit with a smaller value of the constant than 2.5, because the "particles" in this case are not *solid* spheres. The experimental value of this constant should be expected to increase rapidly as the miscibility temperature is approached. In order to test these ideas, the Reduced Viscosity has been calculated as $\{(\delta\nu/\nu_{\text{mean}})/\text{concentration}\}$ in Table 3, $\delta\nu/\nu$ and concentrations by weight being taken as a sufficiently good approximation to $\delta\eta/\eta$ and volume concentrations, respectively, because of the small difference in density.

The reduced viscosity for any particular temperature excess above the miscibility temperature

viscosity increase above the normal depression. Broken lines, calculated "normal" curves; solid lines, experimental graphs of Fig. 1(a): the differences between corresponding solid and broken lines give the anomalous increase.

TABLE 3.—THE REDUCED VISCOSITY OF ALLYL CATECHOL - MINERAL OIL MIXTURES AT DIFFERENT TEMPERATURES.

Temperature (°C.)		180	160	140	130	120	100	80	Miscibility temperature
Reduced Viscosity $= \left\{ \frac{\delta v/v_{\text{mean}}}{\text{Concentration}} \right\}$	20% allyl cat.	.045	.065	.085	.120	.170	.25	(.42)	94°C.
	35% „ „	.057	.143	.206	.257	.315	(.44)	—	112°C.
	50% „ „	.074	.138	.210	.252	.316	—	—	120°C.
	70% „ „ (100-30)% „ „	.044 .103	.073 .170	.123 .287	.151 .353	.186 .433	— —	— —	120°C. 120°C.

is seen to increase slowly with concentration upto nearly 50% allyl catechol, so that it would tend to a definite non-zero limit (the Intrinsic Viscosity) for small concentrations. In order to determine this limit for various temperatures above the miscibility limit, the following procedure was used:

(a) The reduced viscosity for each of the four concentrations given in Table 3 was plotted against ΔT , the temperature excess above the corresponding miscibility limit. These graphs are seen in Figs. 4(a) and 4(b), where the two points for negative ΔT are estimates based on the general trend of the graphs in Fig. 3(c), and the broken line graph with plotted triangles corresponds to the 70% allyl catechol mixture treated as a suspension of 30% oil in the allyl catechol.

(b) From the graphs of Fig. 4, smoothed values of the reduced viscosity were read off for $\Delta T = 0^\circ, 10^\circ, 20^\circ, 30^\circ$, etc., and plotted as functions of the concentration of allyl catechol in Fig. 5(a), where each of the plots tends to zero at 100% allyl catechol and extrapolates to a non-zero value at very small concentrations. These extrapolated values, which give the Intrinsic Viscosity, are plotted as solid circles in the lower graph of Fig. 5(c), and they show the expected steep rise as ΔT tends to zero. However, since the graphs of Fig. 5(a) have a very sharp peak in the middle, their extrapolation to zero concentration is subject to considerable error.

(c) From a theoretical stand point, it is better to reckon the mixtures with more than 50% allyl catechol as suspensions of oil in the catechol, and then to calculate the Reduced Viscosity in terms of the concentration of oil. This has been done in the last row of Table 3 for the mixture containing 70% allyl catechol. On the above basis, the graph of reduced viscosity against concentration should be symmetrical about the 50% line, and

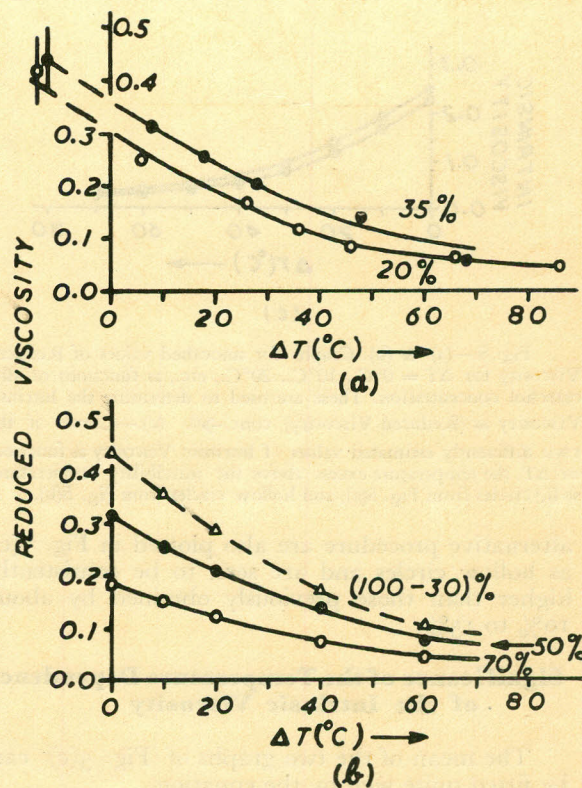


Fig. 4.—Graphs showing the Reduced Anomalous Viscosity as a function of temperature excess, ΔT , above the corresponding miscibility temperature. Reduced Viscosity = $(\Delta v/v) \div$ Concentration of allyl catechol, the concentrations being indicated alongside the respective curves. The broken-line curve is for 70% catechol treated as a 30% solution of mineral oil in allyl catechol.

this serves as an additional criterion for drawing the graphs through the points plotted in Fig. 5(b), where the mean of the values for 50% and (100-30)% allyl catechol has been plotted in order to get an accuracy comparable with the other two points. The values of Intrinsic Viscosity obtained by this

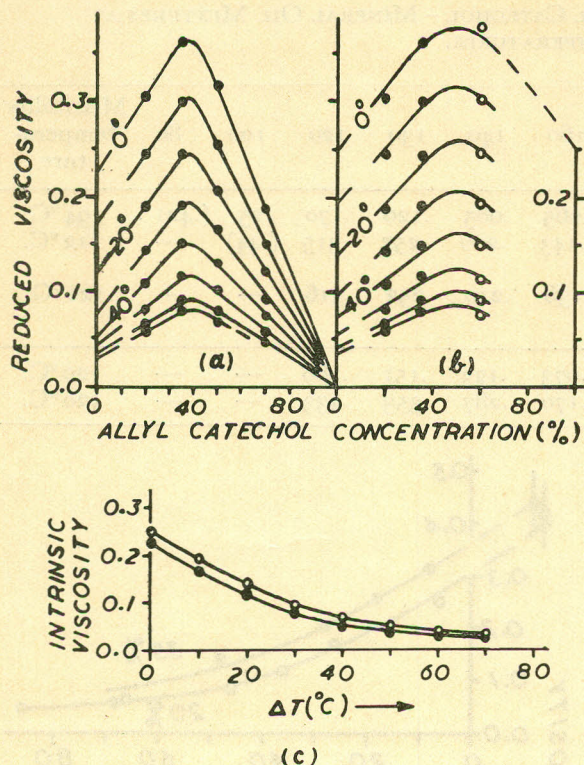


Fig. 5.—(a) & (b). Graphs for smoothed values of Reduced Viscosity for $\Delta T = 0^\circ\text{C}.$, $10^\circ\text{C}.$, $20^\circ\text{C}.$, etc., as functions of allyl catechol concentration. These are used to determine the Intrinsic Viscosity as (Reduced Viscosity) conc. $\rightarrow 0$. (c).—Curves of the two differently estimated values of Intrinsic Viscosity as functions of ΔT , the temperature excess above the miscibility temperature; solid circles from Fig. 5(a), and hollow circles from Fig. 5(b).

alternative procedure are also plotted in Fig. 5(c) as hollow circles and are seen to be consistently higher than those previously obtained by about 10% to 15%.

Significance of the Temperature Dependence of the Intrinsic Viscosity

The mean of the two graphs of Fig. 5(c) can be fitted quite well by the equation.

$$\text{Intrinsic Viscosity} = 0.24 \exp\left(-\frac{\Delta T}{30}\right), \quad (4)$$

which indicates that the seat of the phenomenon is to be found in inter-molecular forces that are still appreciable at temperatures $50^\circ\text{C}.$ to $100^\circ\text{C}.$ above the miscibility temperature. Visualizing the process as an incipient agglomeration of the molecules of allyl catechol near to the miscibility temperature, we may attempt to estimate the degree of this agglomeration or polymerization by means of Staudinger's empirical equation,⁴ viz.,

$$P = k \times \text{Intrinsic Viscosity},$$

in which P is the degree of polymerization and k may be taken as about 300 for the type of molecules (oil and allyl catechol) that we are considering here. This makes P of the order of 3 at $100^\circ\text{C}.$ above the miscibility temperature and about 70 at the miscibility temperature. The first figure of 3 is of the right order for hydrogen-bonding in solutions of allyl catechol in mineral oil, while the figure of 70 indicates the formation of quite a large aggregate at the stage when separation into two distinct phases is just about to occur. It must of course be borne in mind that these figures are to be taken as giving only the order of magnitude.

Application to Calculation of the Formula for Temperature Variation of Viscosity Depression

Since the anomalous viscosity increase analyzed above is found to persist strongly even $50^\circ\text{C}.$ away from the miscibility temperatures, it should produce a significant effect on the temperature dependence of the viscosity depression previously measured with solutions of various phenolic compounds in mineral oils.⁵ In order to estimate the magnitude of this effect, it is useful to study the ratio

$$R = \{(\delta v)_{\text{anomalous}} / (-\Delta v)\}$$

where $(-\Delta v)$ is the "normal" viscosity depression and $(\delta v)_{\text{anomalous}}$ is the value of the anomalous increase in viscosity measured from the "normal" curve (cf. broken line curves in Fig. 3). Values of this ratio 'R' for different temperatures are given in Table 4 for the four concentrations of allyl catechol.

Since the dependence of δv and $-\Delta v$ on temperature is exponential, semi-logarithmic plots are given in Fig. 6 for R against ΔT , the temperature excess above the miscibility temperature. These plots are linear with nearly the same slope in every case, the mean value of the slope being 0.32 ± 0.01 , whence it follows that R is given by the relation (cf. equation 4)

$$R = \frac{\delta v}{-\Delta v} = A \exp\left[-\frac{\Delta T}{62}\right] \quad (5)$$

where 'A' depends on the concentration of the allyl catechol, but shows only a small variation in the range from 30% to 70%. The exceptionally low value of 'A' for 20% allyl catechol may be attributed in part to the fact that the experimental points for concentrations upto 10% have to be used to fix the linear part of the broken line graphs

TABLE 4.—THE RATIO 'R' OF THE ANOMALOUS VISCOSITY INCREASE TO THE NORMAL VISCOSITY DEPRESSION.

Temperature (°Centigrade)		180	160	140	130	120	100	Miscibility temperature
$R = \frac{\delta v_{\text{anomalous}}}{-\Delta v}$	20% allyl catechol	0.22	0.24	0.26	0.35	0.46	0.57	94°C.
	35% " "	0.38	0.76	0.91	1.06	1.20	—	112°C.
	50% " "	0.71	1.10	1.36	1.52	1.75	—	120°C.
	70% " "	0.81	1.10	1.50	1.69	1.96	—	120°C.

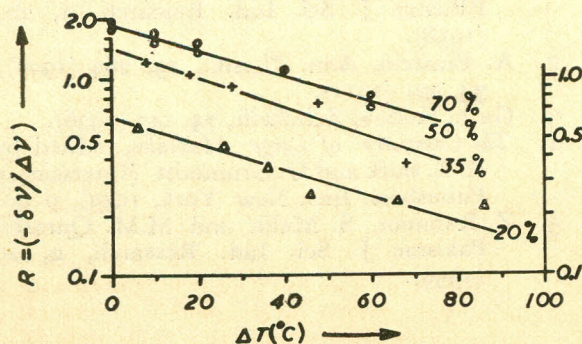


Fig. 6.—Semi-logarithmic plots showing the temperature dependence of the ratio 'R' of the anomalous viscosity increase to the 'normal' viscosity depression for four different concentrations of allyl catechol from 20% to 70%.

of Fig. 3 near the origin, which will lead to a significant underestimation of the values of δv in the region of 15% to 30% allyl catechol. Taking this into account, we may consider the value of 'A' as approximately constant at 1.3 ± 0.3 for mixtures containing 15% to 45% allyl catechol, which are the significant ones for determining the values of $(-\Delta v)_{\text{max}}$ and $(-\partial v/\partial x)_{x=0}$ and their variation with temperature.⁵

In an earlier communication,¹ it was shown that at a temperature of 40°C., the depression, $-\Delta v$, in the allyl series of compounds, (allyl benzene, allyl phenol and allyl catechol) is related to the viscosity v by

$$\ln(-\Delta v) = K + 1.36 \ln v, \quad (6)$$

We may consider this equation to give the ideal value, $(-\Delta v)_{\text{ideal}}$, of the viscosity depression in the absence of the effect of proximity to the miscibility temperature, because this effect was corrected for in allyl catechol and is negligible in allyl benzene. For examining the temperature variation in the case of allyl phenol, we now introduce the anomalous viscosity increase δv , which is appreciable but smaller than $(-\Delta v)$ at 50°C.

to 100°C. above the miscibility temperature. Thus we put

$$\Delta v = (\Delta v)_{\text{ideal}} + \delta v = (\Delta v)_{\text{ideal}} \{1 - \delta v / (-\Delta v)_{\text{ideal}}\}, \quad (7a)$$

and get

$$\begin{aligned} \ln(-\Delta v) &= \ln(-\Delta v)_{\text{ideal}} - \delta v / (-\Delta v)_{\text{ideal}} \\ &= \ln(-\Delta v)_{\text{ideal}} - R, \end{aligned} \quad (7b)$$

Assuming the formula (5) for R determined above for allyl catechol to apply also in the case of allyl phenol as a first approximation, we can differentiate (7) with respect to T, to obtain

$$\begin{aligned} \frac{\partial \ln(-\Delta v)}{\partial T} &= \frac{\partial}{\partial T} \ln(-\Delta v)_{\text{ideal}} + \frac{R}{62} \\ &= \frac{\partial K}{\partial T} + 1.36 \frac{\partial \ln v}{\partial T} + \frac{R}{62} \quad \text{from (6)} \\ &= \frac{\partial \ln v}{\partial T} \left\{ 1.36 + \frac{R}{62 \partial \ln v / \partial T} + \frac{\partial K / \partial \ln v}{\partial T} \right\} \quad (8) \end{aligned}$$

Comparison with Experiments on Allyl Phenol

Examination of equation (8) shows that the quantity in curly brackets will give the value of the coefficient in an equation similar to (6) and applicable when temperature variation of $(-\Delta v)$ is considered for one particular compound. Since $\partial \ln v / \partial T$ is of the order of $-1/50$, the effect of the second term is to decrease the value of the coefficient appreciably below 1.36, as has been experimentally observed in the case of allyl phenol and bthlanol.⁵ A quantitative estimate can be made by ignoring the third term in equation (8) and taking for $\partial \ln v / \partial T$ the average value, $-1/46$, obtained in the case of allyl phenol in the range of 40°C. to 85°C. This yields

$$\frac{\partial \ln(-\Delta v)}{\partial T} = \frac{\partial \ln v}{\partial T} \left\{ 1.36 - \frac{46}{62} R \right\} \quad 9(a)$$

The miscibility temperatures of various concentrations of allyl phenol in the corresponding oil blend were determined experimentally to be in the region of -6°C. to -30°C. , with an average of -18°C. , so that the mean value of 'R' in equation

$$g \text{ may be taken as } 1.3 \exp \left[-\frac{62.5 - (-18)}{62} \right] = 0.35$$

which gives

$$\frac{\partial \ln(-\Delta v)}{\partial T} = \frac{\partial \ln v}{\partial T} \left\{ 1.36 - 0.26 \right\} = 1.10 \frac{\partial \ln v}{\partial T}, \quad (9b)$$

thus indicating that, for the temperature variation of the viscosity depression in allyl phenol, an equation of the form

$$\ln(-\Delta v) = K^1 + 1.10 \ln v \quad (9c)$$

should hold. The value 1.10 calculated here for the coefficient of $\ln v$ bears satisfactory comparison with the value 1.17 ± 0.03 determined experimentally.⁵ It is believed that the remaining discrepancy can be explained by inclusion of the third term $(\partial K/\partial T)/(\partial \ln v/\partial T)$ of equation (8), and

it is hoped to investigate this aspect further when experimental data at low temperatures is available on allyl phenol and bhilawanol.

Acknowledgements

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