

# ANOMALOUS BEHAVIOUR OF SOLUTIONS OF SIMPLE AROMATIC COMPOUNDS IN STRAIGHT-CHAIN HYDROCARBONS AND MINERAL OILS

## Part II.—Viscosity Depression Measurements in the Binary Systems: Toluene-Heptane and Phenol-Light Mineral Oil

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As a sequel to previous measurements of viscosity depression in the benzene-heptane and heptane-cyclohexane systems, similar experiments have now been carried out on toluene-heptane from 5° to 40°C. and on phenol in light mineral oil from 60°C. to 120°C. Viscosity depressions of 6% and 20% respectively are obtained in the two systems at 40°C., corresponding to excess free energies  $\Delta G$  of mixing of 87 and 295 cal./mole, respectively. In each system,  $\Delta G$  apparently shows the step-wise behaviour previously observed with benzene, a rapid drop in  $\Delta G$  being noticeable at 15 to 25°C. for toluene and 75° to 90°C. for phenol.

The phenol-oil system, being partially miscible below 77°C., exhibits a large anomalous increase in viscosity in the neighbourhood of 70 mole % phenol, which is similar to that observed previously with allylcatechol.

### 1. Introduction

Viscosity depression measurements on the benzene-heptane and heptane-cyclohexane systems were given in Part I of this series,<sup>1</sup> and the data were used to estimate the excess free energy of mixing for benzene, which was found to be of the order of a third of that observed with most polar compounds, and showed an unexpected type of temperature variation. In order to study this phenomenon further, similar measurements have now been carried out with two related systems, namely, toluene-heptane and phenol-light mineral oil. The latter system has the added interest of possessing a critical solution temperature of about 80°C., so that below this temperature, there is only partial miscibility of the two components, as in the allylcatechol and oil system that was studied some time earlier.<sup>2</sup>

The experimental technique was the same as in the previously described measurements<sup>1</sup> on benzene-heptane and cyclohexane-heptane, and the readings for toluene-heptane were taken from 5°C. to 30°C. in steps of 5°C. and then at 40°C. Because of the added complication of partial miscibility for the phenol-oil system, the measurements were in this case first taken from 80°C. to 120°C. at 10°C. intervals and were later extended to below 80°C. using some selected compositions. Viscometer No. 0 (B.S.S.) was used and the flow times ranged from 10 to 20 minutes, measured to an accuracy of  $\pm 0.2$  secs. giving a final reproducibility of about  $\pm 0.000,6$  centistokes, i.e.,  $\pm 0.1\%$  from the mean of three to five readings at each temperature.

### 2. Experiments with Toluene in Heptane

The kinematic viscosity of heptane is 10% to 15% lower than that of toluene as shown in

TABLE I(a).—COMPARISON OF VISCOSITIES OF *n*-HEPTANE, TOLUENE, AND THE HEPTANE-OIL BLEND.

Temperature (°C.)	Viscosity of <i>n</i> -heptane (c.s.)	Viscosity of toluene (c.s.)		Viscosity of heptane plus 15% oil (c.s.)	
		Standard	Measured	Initial	Final
5	—	—	.8055	.7934	.7936
10	—	—	.7612	.7578	.7582
15	.628	.715	.7137	.7094	.7100
20	.600	—	.6729	.6698	.6706
25	.570	.639	.6347	.6358	.6360
30	.542	.613	.6127	.6144	.6150
40	.500	—	.5500	.5518	.5518

Note:—The experimental errors are of the order of  $\pm 0.1\%$  corresponding to  $\pm 0.000,6$  c.s.

Table I(a), second and third columns. In order to obtain a clear picture of the viscosity depression phenomena, it was considered desirable to arrange the viscosities of the two components to be more nearly equal in the middle of the temperature range (5°C. to 40°C.) used. Therefore, heptane was replaced by a blend of pure heptane (E. Merck) with about 15% of (kerosene) mineral oil, and the viscosities of this blend, measured before and after the main experiment, are compared with toluene in Table I(a). At 25°C. the two are equal to within 0.001 c.s., and the maximum divergence between the two over the whole temperature range is only 1.5%. It follows that use of either the linear or logarithmic interpolation formula for ideal will give results agreeing to better than 0.1%, which is within the limit of the present experimental accuracy.

Mixtures were prepared containing various percentages of pure toluene (B. D. H. Analar) in the heptane-oil blend, and the viscosity measurements for the full range of toluene concentrations are

TABLE I (b).—VISCOSITY DATA FOR TOLUENE IN HEPTANE-OIL BLEND, TOGETHER WITH DEDUCED DEPRESSION (ACTUAL MEASUREMENTS TAKEN BY VOLUME CONCENTRATION).

Volume % of oil blend in toluene	$\nu_{\text{expt}}$ (c.s.)	$\nu_{\text{id}}$ (c.s.)	$\Delta\nu$ (c.s.)	$\frac{10\Delta\nu}{\nu_{\text{id}}}$	Volume % of oil blend in toluene	$\nu_{\text{expt}}$ (c.s.)	$\nu_{\text{id}}$ (c.s.)	$\Delta\nu$ (c.s.)	$\frac{10\Delta\nu}{\nu_{\text{id}}}$
Temperature = 5.0°C.					Temperature = 10.0°C.				
0.0	.8055	.8055	.000	0.00	0.0	.7612	.7612	.000	0.00
5.0	.7942	.8049	.011	0.13	5.0	.7454	.7610	.016	0.21
10.0	.7829	.8043	.021	0.27	10.0	.7361	.7609	.025	0.33
20.0	.7673	.8031	.036	0.45	20.0	.7204	.7606	.040	0.53
30.0	.7537	.8019	.048	0.60	30.0	.7093	.7602	.051	0.67
40.0	.7465	.8007	.054	0.67	40.0	.7036	.7599	.056	0.74
50.0	.7436	.7995	.056	0.70	50.0	.6988	.7596	.061	0.80
60.0	.7421	.7983	.056	0.70	60.0	.6996	.7593	.060	0.79
70.0	.7464	.7971	.051	0.64	70.0	.7044	.7589	.054	0.72
80.0	.7560	.7959	.040	0.50	80.0	.7131	.7586	.046	0.60
90.0	.7726	.7947	.022	0.28	90.0	.7289	.7583	.029	0.39
95.0	.7846	.7941	.010	0.12	95.0	.7421	.7582	.016	0.21
100.0	.7935	.7935	.000	0.00	100.0	.7580	.7580	.000	0.00
Temperature = 15.0°C.					Temperature = 20.0°C.				
0.0	.7137	.7137	.000	0.00	0.0	.6729	.6729	.000	0.00
5.0	.7032	.7135	.010	0.14	5.0	.6624	.6728	.010	0.15
10.0	.6939	.7133	.019	0.27	10.0	.6548	.6726	.018	0.26
20.0	.6816	.7129	.031	0.44	20.0	.6433	.6724	.029	0.43
30.0	.6694	.7125	.043	0.60	30.0	.6340	.6721	.038	0.57
40.0	.6647	.7121	.047	0.67	40.0	.6290	.6718	.043	0.64
50.0	.6612	.7117	.051	0.71	50.0	.6267	.6716	.045	0.67
60.0	.6615	.7113	.050	0.70	60.0	.6288	.6713	.043	0.63
70.0	.6674	.7109	.044	0.61	70.0	.6326	.6710	.038	0.57
80.0	.6750	.7105	.036	0.50	80.0	.6399	.6707	.031	0.46
90.0	.6890	.7101	.021	0.30	90.0	.6536	.6705	.017	0.25
95.0	.6995	.7099	.010	0.15	95.0	.6640	.6703	.006	0.09
100.0	.7097	.7097	.000	0.00	100.0	.6702	.6702	.000	0.00
Temperature = 25.0°C.					Temperature = 30.0°C.				
0.0	.6347	.6347	.000	0.00	0.0	.6127	.6127	.000	0.00
5.0	.6267	.6348	.008	0.13	5.0	.6049	.6128	.008	0.13
10.0	.6205	.6348	.014	0.23	10.0	.5993	.6129	.014	0.22
20.0	.6104	.6349	.024	0.39	20.0	.5910	.6131	.022	0.36
30.0	.6034	.6351	.032	0.50	30.0	.5840	.6133	.029	0.48
40.0	.5985	.6352	.037	0.58	40.0	.5805	.6135	0.33	0.54
50.0	.5970	.6353	.038	0.60	50.0	.5791	.6137	.035	0.56
60.0	.5981	.6354	.037	0.59	60.0	.5801	.6139	.034	0.55
70.0	.6017	.6355	.034	0.53	70.0	.5838	.6141	.030	0.49
80.0	.6088	.6357	.027	0.42	80.0	.5910	.6143	.023	0.38
90.0	.6213	.6358	.014	0.23	90.0	.6016	.6145	.013	0.21
95.0	.6303	.6358	.006	0.09	95.0	.6075	.6146	.007	0.12
100.0	.6359	.6359	.000	0.00	100.0	.6147	.6147	.000	0.00
Temperature = 40.0°C.					Temperature = 40.0°C. (Contd.)				
0.0	.5500	.5500	.000	0.00	80.0	.5307	.5514	.021	0.38
5.0	.5417	.5501	.008	0.15	90.0	.5380	.5516	.014	0.25
10.0	.5354	.5502	.015	0.27	95.0	.5460	.5517	.006	0.10
20.0	.5278	.5504	.023	0.41	100.0	.5518	.5518	.000	0.00
30.0	.5220	.5505	.028	0.52					
40.0	.5188	.5507	.032	0.58					
50.0	.5179	.5509	.033	0.60					
60.0	.5196	.5511	.032	0.57					
70.0	.5226	.5513	.029	0.52					

given in Table (1)b for the seven temperatures from 5°C. to 40°C. This table also shows the values of  $v_{ideal}$  calculated by linear interpolation between  $v_{toluene}$  and  $v_{heptane-oil\ blend}$ , together with the values of viscosity depression  $\Delta v$  calculated as

$$-\Delta v = v_{expt} - v_{ideal} \quad (1)$$

The values of  $\Delta v$  are plotted for the seven temperatures in Fig. 1(a), while Fig. 1(b) shows

the corresponding graphs for  $10\Delta v/v_{ideal} = 10(1 - v_{expt}/v_{ideal})$ . These graphs are in general similar to those for the benzene-heptane system, but the maximum values of  $10(\Delta v/v_{ideal})$  are about  $2/3$  of these for benzene-heptane. The inset to Fig. 1(b) shows a plot of these maximum values  $10(\Delta v/v)_{max}$  against temperature, and once again we find the anomaly previously noted with benzene, namely, that between two regions of near constancy,  $(\Delta v/v)_{max}$  drops rapidly

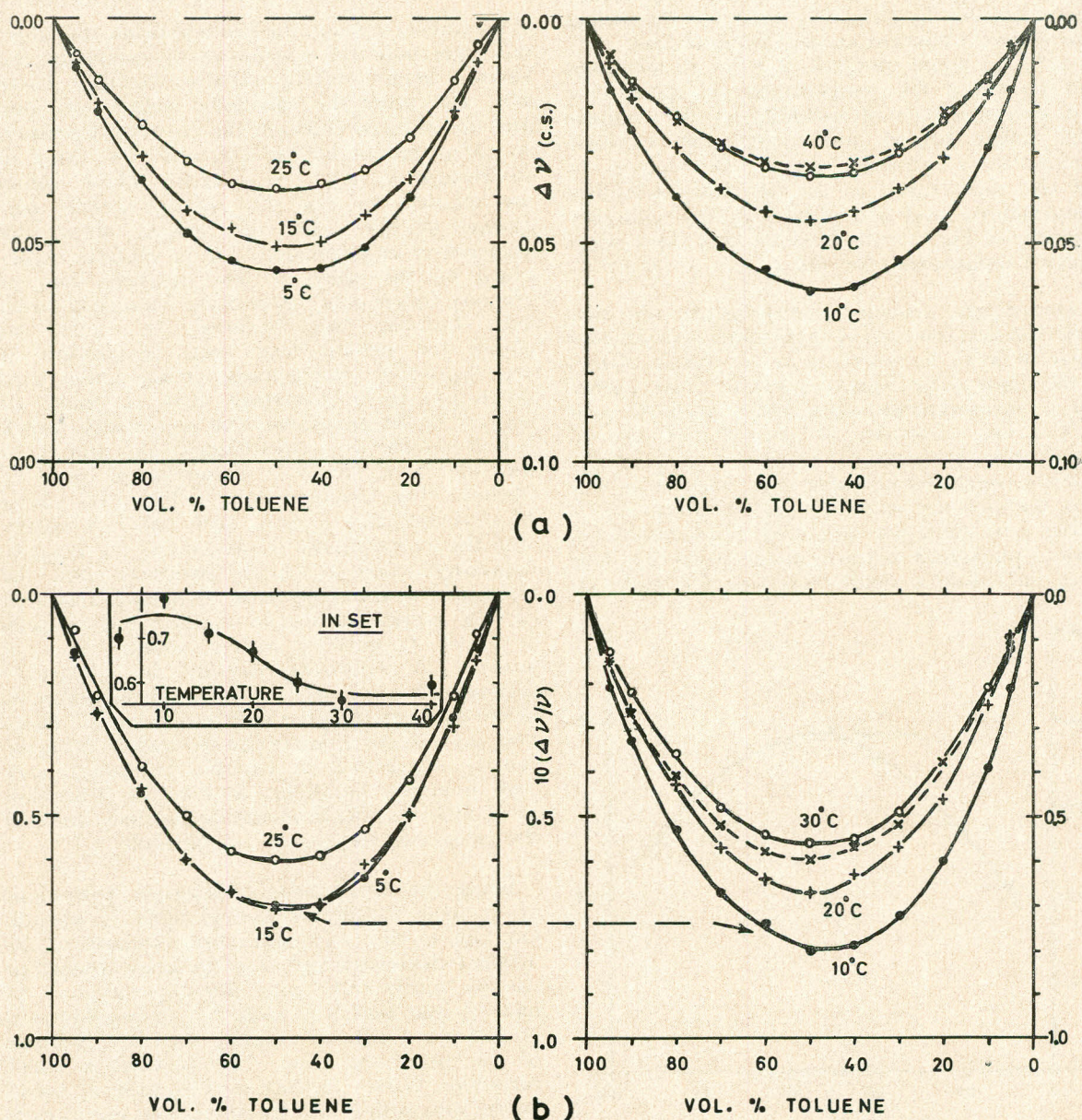


Fig. 1—Graphs showing the dependence of (a) viscosity depression  $\Delta v$  and (b)  $10 \Delta v/v_{ideal}$  on the concentration of toluene in the heptane oil-blend at a series of temperatures from 5°C. to 40°C. The inset to Fig. 1 (b) left shows the temperature dependence of  $10(\Delta v/v)_{max}$ .

from one value to the next. Moreover, the temperatures over which this drop occurs, viz. 15°C. to 25°C., generally agree with those in the case of the benzene-heptane system, viz. 18°C. to 30°C.

### 3. Results with Phenol-Mineral Oil System

After preparing a suitable oil blend from high-speed diesel oil, the first step was to determine the solubility curve for phenol in this blend. This was done by preparing mixtures containing nine different concentrations of phenol from 10% to 90% (at equal intervals of 10%) in test tubes and observing the temperatures of appearance and disappearance of turbidity as the samples were slowly heated and cooled with constant stirring in a glycerine bath. The means of the two were taken as the boundary solubility temperatures, and are plotted in the solubility diagram of Fig. 2, which shows that the critical solution temperature for this system is  $77 \pm 1^\circ\text{C}$ .

Accordingly, viscosity measurements were first undertaken at intervals of  $10^\circ\text{C}$ . in the temperature range of  $80^\circ\text{C}$ . to  $120^\circ\text{C}$ . so as to remain always in the single-phase region, and later two partial sets of measurements were taken at  $60^\circ\text{C}$ . and  $70^\circ\text{C}$ . The viscosities of phenol and the oil blend were first measured at several temperatures and are compared in Table 2(a), where it is seen that the two are exactly equal at about  $95^\circ\text{C}$ . Table 2(b) gives the measured viscosities of the various phenol-oil mixtures at the seven temperatures, including a small correction for oxidation

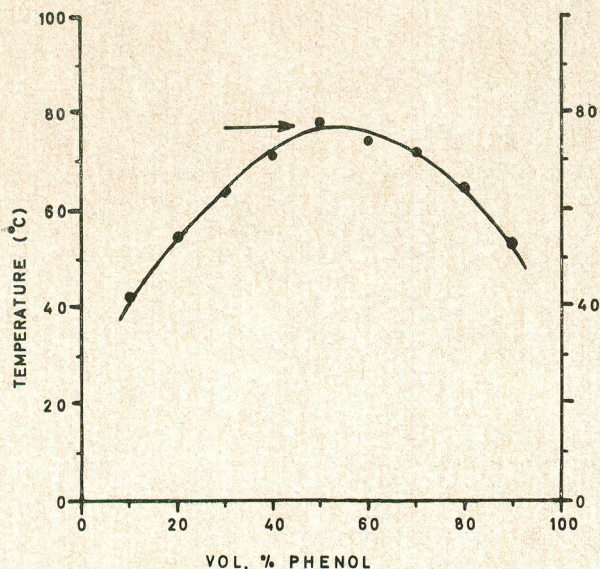


Fig. 2.—Plot of the measured miscibility temperatures for phenol in high-speed diesel oil, showing a consolution temperature of  $77^\circ\text{C}$ .

TABLE 2(a).—COMPARISON OF VISCOSITIES OF PHENOL AND THE OIL BLEND.

Temperature (°C.)	60	70	80	90	100	120	140	
Viscosity in centistokes	Phenol	2.362	1.894	1.546	1.293	1.103	0.849	0.679
	Oil blend	1.904	1.639	1.427	1.264	1.130	0.926	0.777

of the phenol given in the footnote below the table; this correction was determined by measuring the viscosity before heating and after cooling. Table 2(b) also gives the calculated values of  $v_{\text{ideal}}$  and the deduced values of the viscosity depression  $\Delta v$  calculated as before, and also the value of  $10 \Delta v/v_{\text{ideal}} = 10(1 - v_{\text{expt}}/v_{\text{ideal}})$ . These values are plotted in Fig. 3(a) against weight percentage phenol, and the graphs show the existence of an anomalous rise in viscosity superposed on the more or less parabolic type of viscosity depression previously observed with both benzene and toluene. In order to obtain the precise form and magnitude of this depression, particularly at the lower temperatures, it is necessary first to make an analysis of the anomalous rise in viscosity, which is best studied by recalculating  $v_{\text{ideal}}$  and plotting the  $(\Delta v/v)$  values as a function of mole % phenol. This has been done in Fig. 3(b), (using  $M_{\text{oil}} = 210$  and  $\rho_{\text{oil}} = .828$ ) and it is readily seen that (i) at higher temperatures, the viscosity depression curve is closely parabolic with the minimum at about 52 mole % phenol, and that (ii) the anomalous rise in viscosity has its peak at nearly 72 mole % phenol, so that it is not possible to determine directly the "normal" depression for 52 mole % at the lower temperatures where the anomalous rise is extremely large. However, an indirect estimate can be made by using the fact (i) above that the viscosity depression curve itself is closely parabolic, so that the depression at 15 mole % phenol should be precisely one-half the maximum depression (at 52 mole %).

Using the experimentally observed depressions at 15 mole % phenol and 72 mole % phenol, one can in this way get a first estimate of the 'normal' depression and then the peak anomalous rise by subtracting twice the depression at 15 mole % from that at 72 mole %. Using a process of successive approximations, the first estimate of the peak anomalous rise provides a small correction to the depression at 15 mole % based on the assumption that the anomalous rise at each concentration is a function of the temperature excess above the miscibility limit. The convergence to the ultimate values is rapid, stability being obtained in two or three cycles. This

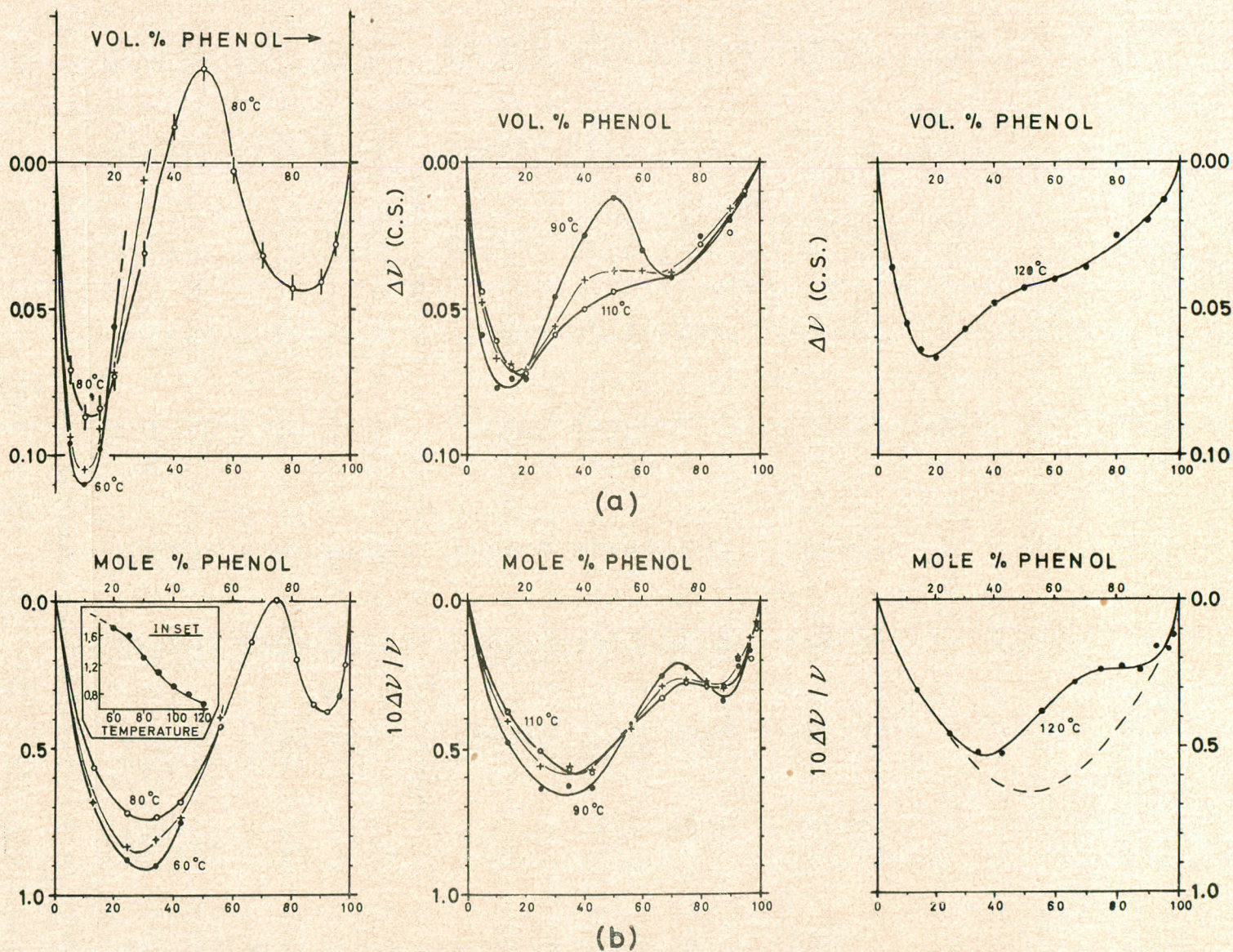


Fig. 3.—(a) Graphs showing the variation of viscosity depression  $\Delta\nu$  with Vol. % of phenol in mineral oil, the large anomalous rise in the middle being prominent below 100°C. The short vertical lines for 80°C. indicate the differences between two sets of measurements. (b) The depression data recalculated and  $10\Delta\nu/\nu$  ideal plotted in terms of mole % phenol, the broken line showing the estimated normal depression curve at 120°C. The inset is the temperature variation of  $10(\Delta\nu/\nu)_{\max}$ , showing the relatively steep drop from 75° to 90°C.

TABLE 2(b).—VALUES OF MEASURED VISCOSITY AND  $\Delta v$  OF PHENOL-H. S. D. SYSTEM ON VOLUME % BASIS FROM  $60 \pm 0.1^\circ\text{C}$ ., TO  $120 \pm 0.1^\circ\text{C}$ ., TO GETHER WITH  $10\Delta v/v_{id}$  ON MOLE % BASIS.

Volume % of phenol in H. S. D.	$v_{\text{expt.}}$ (c.s.)	$v_{id}$ (c.s.)	$v\Delta$ (c.s.)	$\frac{10\Delta v}{v_{id}}$	Volume % of phenol in H. S. D.	$v_{\text{expt.}}$ (c.s.)	$v_{id}$ (c.s.)	$\Delta v$ (c.s.)	$\frac{10\Delta v}{v_{id}}$
Temperature = $60.0^\circ\text{C}$ .					Temperature = $80.0^\circ\text{C}$ .				
0.0	1.904	1.904	0.000	0.00	0.0	1.428	1.428	0.000	0.00
5.0	1.831	1.927	0.096	0.69	5.0	1.363	1.434	0.071	0.57
10.0	1.840	1.950	0.110	0.88	10.0	1.354	1.441	0.087	0.72
15.0	1.875	1.973	0.098	0.90	15.0	1.363	1.447	0.084	0.73
20.0	1.940	1.996	0.056	0.75					
					20.0	1.380	1.453	0.073	0.68
					30.0	1.434	1.465	0.031	0.43
					40.0	1.490	1.478	- 0.012	0.14
					50.0	1.522	1.490	- 0.032	0.01
Temperature = $70.0^\circ\text{C}$ .					Temperature = $100.0^\circ\text{C}$ .				
0.0	1.639	1.639	0.000	0.00	60.0	1.500	1.503	0.003	0.20
5.0	1.558	1.652	0.094	0.69	70.0	1.483	1.515	0.032	0.35
10.0	1.560	1.665	0.105	0.83	80.0	1.485	1.528	0.043	0.38
15.0	1.586	1.677	0.091	0.81	90.0	1.498	1.539	0.041	0.32
20.0	1.618	1.690	0.072	0.74	95.0	1.517	1.545	0.028	0.22
30.0	1.710	1.716	0.006	0.40	100.0	1.553	1.553	0.000	0.00
Temperature = $90.0^\circ\text{C}$ .					Temperature = $120.0^\circ\text{C}$ .				
0.0	1.259	1.259	0.000	0.00	0.0	0.920	0.920	0.000	0.00
5.0	1.202	1.261	0.059	0.48	5.0	0.879	0.915	0.036	0.31
10.0	1.185	1.262	0.077	0.64	10.0	0.856	0.911	0.055	0.46
15.0	1.189	1.263	0.074	0.63	15.0	0.842	0.906	0.064	0.52
20.0	1.191	1.265	0.074	0.64	20.0	0.834	0.901	0.067	0.52
30.0	1.222	1.268	0.046	0.42	30.0	0.835	0.892	0.057	0.38
40.0	1.246	1.271	0.025	0.26	40.0	0.834	0.882	0.048	0.28
50.0	1.252	1.274	0.012	0.23	50.0	0.830	0.873	0.043	0.24
60.0	1.247	1.277	0.030	0.28	60.0	0.824	0.864	0.040	0.23
70.0	1.241	1.280	0.039	0.34	70.0	0.818	0.854	0.036	0.24
80.0	1.258	1.283	0.025	0.23	80.0	0.820	0.845	0.025	0.16
90.0	1.266	1.286	0.020	0.17	90.0	0.815	0.835	0.020	0.17
95.0	1.278	1.288	0.010	0.08	95.0	0.818	0.831	0.013	0.12
100.0	1.289	1.289	0.000	0.00	100.0	0.826	0.826	0.000	0.00

Note:— Corrections used in  $v_{\text{expt}}$  for oxidation of phenol-oil mixtures during heating from  $80^\circ$  to  $120^\circ\text{C}$ .:—

Vol. % phenol:	0	60	90	100
Correction (c.s.)	0.000	0.000	0.000	0.000
{ $80^\circ\text{C}$ .	0.000	0.002	0.004	0.008
{ $100^\circ\text{C}$ .	0.000	0.004	0.008	0.018
{ $120^\circ\text{C}$ .	0.000	0.004	0.008	0.018

process gives the following values shown in Table 3(a) for  $(\Delta v_{1.5\%}/v)_{\text{observed}}$  and for the deduced estimates of  $(\Delta v/v)_{\text{max}}$ .

TABLE 3(a).—VALUES OF  $10(\Delta v/v)_{\text{MAX}}$ . ESTIMATED AT VARIOUS TEMPERATURES FOR PHENOL IN OIL.

Temperature (°C.)	60	70	80	90	100	110	120
$(\Delta v_{1.5\%}/v)_{\text{observed}}$	.072	.070	.059	.051	.043	.040	.033
Deduced $10(\Delta v/v)_{\text{max}}$	1.70	1.60	1.30	1.10	0.90	0.80	0.66

TABLE 3(b).—COMPARISON OF VALUES OF  $10(\Delta v/v)_{\text{MAX}}$  AND FREE ENERGY OF MIXING,  $\Delta G$ , FOR VARIOUS COMPOUNDS AT 40°C.

Compound	Benzene	Toluene	Allylbenzene	Phenol	Allylphenol	Allylcatechol
$10(\Delta v/v)_{\text{max}}$	0.99	0.57	0.54	$1.95 \pm 0.05$	0.99	$1.45 \pm .05$
$\Delta G(\text{cal./mole})$	151	87	82	$295 \pm 8$	151	$220 \pm 8$

Note.—  $\Delta G \approx 2.45 RT(\Delta v/v)_{\text{max}}$ .

#### 4. Discussion

Because of the errors involved in the above indirect estimation of  $(\Delta v)_{\text{max}}$  for phenol, it is not possible to expect a reliability of much better than 5%, and therefore no definite conclusions can be drawn in this case about the jump seen from 75° to 90°C. in the temperature variation of  $10(\Delta v/v)_{\text{max}}$  in the inset to Fig. 3(b). However, one can readily see that the estimated values of  $10(\Delta v/v)_{\text{max}}$  would extrapolate to about  $1.95 \pm 0.05$  at a temperature of 40°C., which is more than three times the value found for toluene and 95% greater than that for benzene at the same temperature, as shown in Table 3(b). Values of  $10(\Delta v/v)_{\text{max}}$  previously obtained<sup>2,3</sup> and the excess free energy of mixing  $\Delta G$  estimated<sup>1,4</sup> for allylbenzene, allylphenol and allylcatechol are also shown in the same table for comparison, and one can reasonably draw some general conclusions at this stage.

Firstly, if we take benzene as the standard material with  $\Delta G = 151$  cal./mole, then it is fairly clear that the effect of introducing the aliphatic side group in toluene and allylbenzene is to reduce  $\Delta G$  by about 45% from 151 to  $84 \pm 2$  cal./mole. Secondly, the introduction of the phenolic OH in simple phenol and allylphenol

apparently increases  $\Delta G$  by about  $100 \pm 30$  cal./mole. The estimated value of  $\Delta G$  for allyl catechol is higher by 40% ( $69 \pm 10$  cal./mole) than that for allylphenol, and so we may deduce that the addition of each phenolic group increases  $\Delta G$  on the average by 90 cal./mole, i.e. 60% of the  $\Delta G$  for benzene.

We may pause here to examine the empirical relationship proposed in the previous work from this laboratory between  $\Delta v$  and  $v$  for any one series of phenolic compounds at a fixed temperature, namely,

$$\ln (\Delta v)_m = A + 1.36 \ln v$$

where  $v$  is in stokes and  $A$  is a constant that apparently depends only slightly on the length of the aliphatic side chain; thus  $A = -1.6, -1.0,$  and  $-0.4$ , respectively, for the case of bhilawanol ( $C_{15}H_{27}$  side chain), allylphenol ( $C_3H_5$  side chain), and simple benzene series. It follows<sup>4</sup> that

$$\begin{aligned} \Delta G/2.45 RT &= \ln (\Delta v/v)_m = A + 0.36 \ln v, \\ \text{whence} \\ \Delta G &= (2.45 A + 0.88 \ln v) \times RT \quad (2) \\ &= 620 (2.45 A + 0.88 \ln v) \text{ cal./mole for } T \\ &= 313^\circ K \end{aligned}$$

If  $v$  is expressible as  $\exp (B + E/RT)$ , then we get from (2),

$$\Delta G = 0.88 E + (2.45 A + 0.88B) RT \quad (3)$$

Finally, we note that many of the systems examined so far seem to show a non-uniform temperature variation of  $(\Delta v/v)_m$  and therefore of  $\Delta G$ , and this phenomenon merits further study, especially because of the bearing it may have on the intermolecular structure within these binary systems. It may also be mentioned that the anomalous viscosity increase observed near the two-phase boundary in cases of partial miscibility is in general considerably greater than the normal viscosity depressions, and a detailed analysis of this in the case of phenol will be presented separately.

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