

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

Part I.—Viscosity Depression Measurements at Various Temperatures in the Binary Systems: Benzene-Heptane and Heptane-Cyclohexane

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In continuation of previous investigations on long-chain phenolic additives for oils, accurate measurements of viscosity depression have been made every 5°C. from 15°C. to 40°C. over the full range of concentrations in the binary system of benzene-heptane; for comparison, the heptane-cyclohexane system has been similarly measured. Viscosity depressions of the order of 12% of the ideally interpolated viscosity are observed in the benzene-heptane system, and the maximum relative viscosity depression ($\Delta v/v$) appears to show an anomalous variation with temperature. The heptane-cyclohexane control gives only 4% depression and does not show the temperature variation anomaly.

A quantitative estimate of the excess free energy of mixing is made at about 180 cal./mole for benzene-heptane, and the phenomena are consistent with the existence of an appreciable interaction between benzene molecules, which might be of the order of 1/4 of that in most polar molecules. Further investigations on benzene and on related binary systems are in hand.

1. Introduction

In previous communications from this laboratory^{1,2,3} dealing with long and short-chain phenolic compounds, it was shown that because the viscosity of these phenolic compounds is strongly dependent on both the length of the side chain and the number of active phenolic groups, the viscosity depression Δv produced by mixing them with a straight mineral oil (of the same viscosity) is better correlated with the actual viscosity rather than just the number of OH groups, and a relation of the form

$$\log(\Delta v) = A + 1.33 \log v = A + \log v^{1.33} \quad (1)$$

was found to fit the results for both the $C_{15}H_{27}$ side chain and the C_3H_5 allyl side chain (Figure 5 in ref. 3). Two most striking observations made in the course of this generalization were (i) the existence of a very appreciable viscosity depression with both allylbenzene³ and dimethoxy-bhilawanol,² neither of which has any active OH groups, and (ii) the occurrence of an actual increase in viscosity near the 2-phase boundary for allylcatechol and mineral oil.^{3,4}

The discovery of these phenomena has prompted a study of similar compounds without a side chain, viz. benzene, phenol, toluene, and cyclohexane, etc., leading to an analysis of the viscosity effects (at various temperatures) when mixed with straight hydrocarbons. The present communication describes the results obtained on the benzene-heptane system in the range of 15°C. to 40°C., together with comparative measurements on the heptane-cyclohexane system. Further measurements, on oil

solutions of phenol and toluene, will be reported in later papers in this series.

2. Experimental Procedure

Ideally, for best sensitivity, the straight-chain hydrocarbons or oils chosen for mixing with the compounds under study should have the same viscosity and nearly the same molecular size as the compound itself, but in practice a compromise is often necessary. Thus, normal heptane ($M=100$, $v_{25}=0.570$ c.s.) was selected for mixing with benzene ($M=78$, $v_{25}=0.686$ c.s.) because it gives a good balance between equality of molecular weight and equality of viscosity at 25°C. Also, there is not much difference between their volatilities, the boiling points being 98°C. and 80°C., respectively. In the case of heptane-cyclohexane system, the heptane was blended with 20% of kerosene oil so that the viscosities of the two component liquids of the system are equal at about 25°C.

The mixtures in concentration steps of 10% (with extra ones at 5% and 95%) were prepared at room temperature and shaken in a stoppered flask to prevent differential evaporation losses. The viscosity measurements were carried out according to standard procedures, using calibrated B.S.S. No. 0 viscometer (constant=0.000,734) suspended vertically with drying tubes attached in a cylindrical Gallenkamp thermostat, the temperature of which was controlled to within 0.1°C. The flow-time measurements were first made below room temperature (26°C.) and then above room temperature so as to minimize the possible effects of fractional evaporation from

the test solutions, the whole series of measurements for any one concentration being completed in one working day. The flow times ranged from 10 to 20 minutes, measured to 0.2 sec., so that a reproducibility of ± 0.0006 centistoke i.e. $\pm 0.1\%$ was easily obtained with four or five readings at each temperature. This would correspond to a temperature uncertainty of about $\pm 0.08^\circ\text{C}$.

3. Results with the Benzene-Heptane System from 15°C . to 40°C .

Table 1(a) shows the values of kinematic viscosity obtained for pure dry benzene and pure heptane (Merck) at the various temperatures, compared with the standard (Timmermans,⁵ Int. Critical and Landolt-Boernstein⁶ Tables) values. The agreement is satisfactory, the root-mean-square difference being 0.002,5 c.s. for benzene and 0.001,8 c.s. for heptane, both of which are less than 0.5% of the actual viscosities.

The measurements for the full range of concentrations of benzene in heptane are given in Table 1(b) for the six temperatures from 15.4°C . to 40°C ., together with the values of ν_{ideal} , calculated by linear interpolation between ν_{benzene} and ν_{heptane} , and the viscosity depression $\Delta \nu$ obtained from

$$-\Delta \nu = \nu_{\text{expt}} - \nu_{\text{ideal}}. \quad (2)$$

It should be noted here that (i) the values of ν_{expt} and ν_{ideal} are given to the fourth place to avoid cumulative errors in evaluating $\Delta \nu$, and (ii) because the difference between ν_{benzene} and ν_{heptane} is about 17% on the average, the use of linear interpolation (in place of the Kendall logarithmic form) will produce a (consistent) discrepancy of about 0.5% i.e. 0.003 c.s. near the middle of the concentration range (cf. ref. 2 and 3). This is only slightly greater than the experimental

errors in ν and very much less than the calculated values of $\Delta \nu$.

The values of $\Delta \nu$ are plotted for the six temperatures in Fig. 1(a), while the corresponding graphs for $\Delta \nu/\nu_{\text{ideal}} = (1 - \nu_{\text{expt}}/\nu_{\text{ideal}})$ are shown in Figure 1(b). These graphs bear witness to the accuracy of about ± 0.001 centistoke estimated for the results, and indicate that the benzene heptane system shows a maximum viscosity depression of 10 to 14% at a concentration of 54% to 58% benzene by weight. This may be compared directly with the corresponding figures (12% and 10%) previously obtained for allylbenzene and dimethoxybhillawanol in mineral oil at 40°C ., thus showing the consistent nature of the effect, in agreement with equation (1).

Finally, a graph is also plotted in the inset to the right-hand half of Fig. 1(b) showing the temperature variation of $10(\Delta \nu/\nu)_{\text{m}}$, which gives a measure of the change ΔG_{m} in the free energy on mixing (cf. discussion). This graph exhibits a more or less definite singularity in the region of 30° to 35°C ., with some suggestion of another one below 15°C . However, it must be noted that the magnitudes of the deviations from a smoothly decreasing curve are only 3 to 5 times the experimental errors.

4. Results with Cyclohexane in a Heptane-Oil Blend

In an effort to throw further light on the nature of these phenomena, it was considered necessary first to make a comparative study of a simple cyclic saturated compound showing a very small degree of residual valence or polar effect. Cyclohexane was selected for this purpose, having $M=84$ and $\nu_{25}=1.14$ c.s. For mixing with it, a blend of four parts of heptane with one part of kerosene oil was prepared, and its viscosity is

TABLE 1(a).—COMPARISON OF MEASURED VISCOSITIES (CENTISTOKES) OF BENZENE AND HEPTANE WITH STANDARD DATA.

| Temperature ($^\circ\text{C}$.) | Benzene | | <i>n</i> -Heptane | |
|--------------------------------------|--|---------------|--|---------------|
| | Observed | Standard | Observed | Standard |
| 15.4 | 0.784 ₆ | 0.784 \pm 1 | 0.628 ₉ | 0.625 \pm 3 |
| 20.0 | 0.736 ₇ | 0.740 \pm 1 | 0.600 ₆ | 0.600 \pm 1 |
| 25.0 | 0.686 ₃ | 0.685 \pm 3 | 0.571 ₃ | 0.570 \pm 2 |
| 30.0 | 0.642 ₄ | 0.649 \pm 4 | 0.542 ₂ | 0.542 \pm 3 |
| 35.0 | 0.605 ₈ | 0.606 \pm 3 | 0.521 ₁ | — |
| 40.0 | 0.568 ₀ | 0.569 \pm 5 | 0.499 ₀ | 0.501 \pm 1 |
| | Root-mean-square difference=0.002,5 | | Root-mean-square difference=0.001,8 | |

compared with that of the cyclohexane (Merck) at various temperatures in Table 2(a). The values for viscosity of the heptane blend were also determined at the end of the main experiment as a check on reproducibility, and are seen to be consistently higher than the first set by about

0.001 c.s. Table 2(a) also gives the values of kinematic viscosity of cyclohexane as calculated from the standard values given in the compilation by Timmermans⁵ and in the Landolt-Boernstein Tables.⁶ Our measured values are seen to agree well with these.

TABLE I (b).— VISCOSITY MEASUREMENTS ON BENZENE-HEPTANE SYSTEM, WITH DEDUCED DEPRESSIONS, Δv AND $10\Delta v/v_{id}$.

| % Benzene | v_{expt} (c.s.) | v_{id} (c.s.) | Δv (c.s.) | $10\Delta v/v_{id}$ | % Benzene | v_{expt} (c.s.) | v_{id} (c.s.) | Δv (c.s.) | $10\Delta v/v_{id}$ |
|---------------------|--------------------------|-----------------|-------------------|---------------------|---------------------|--------------------------|-----------------|-------------------|---------------------|
| Temperature=15.4°C. | | | | | Temperature=20.0°C. | | | | |
| 0.0 | .6289 | .6289 | .000 | 0.00 | 0.0 | .6006 | .6006 | .000 | 0.00 |
| 5.0 | .6208 | .6367 | .016 | 0.25 | 5.0 | .5933 | .6074 | .014 | 0.23 |
| 10.0 | .6153 | .6445 | .029 | 0.45 | 10.0 | .5881 | .6142 | .026 | 0.42 |
| 20.0 | .6072 | .6601 | .053 | 0.80 | 20.0 | .5790 | .6278 | .049 | 0.78 |
| 30.0 | .6036 | .6756 | .072 | 1.07 | 30.0 | .5772 | .6414 | .064 | 1.00 |
| 40.0 | .6028 | .6912 | .088 | 1.27 | 40.0 | .5757 | .6549 | .079 | 1.21 |
| 50.0 | .6109 | .7068 | .096 | 1.36 | 50.0 | .5816 | .6686 | .087 | 1.30 |
| 60.0 | .6233 | .7222 | .099 | 1.37 | 60.0 | .5923 | .6822 | .090 | 1.32 |
| 70.0 | .6447 | .7379 | .093 | 1.26 | 70.0 | .6109 | .6959 | .085 | 1.22 |
| 80.0 | .6762 | .7534 | .077 | 1.02 | 80.0 | .6388 | .7095 | .071 | 1.00 |
| 90.0 | .7199 | .7690 | .049 | 0.64 | 90.0 | .6792 | .7231 | .044 | 0.61 |
| 95.0 | .7474 | .7768 | .029 | 0.37 | 95.0 | .7034 | .7299 | .026 | 0.36 |
| 100.0 | .7846 | .7846 | .000 | 0.00 | 100.0 | .7367 | .7367 | .000 | 0.00 |
| Temperature=25.0°C. | | | | | Temperature=30.0°C. | | | | |
| 0.0 | .5713 | .5713 | .000 | 0.00 | 0.0 | .5422 | .5422 | .000 | 0.00 |
| 5.0 | .5654 | .5771 | .012 | 0.21 | 5.0 | .5378 | .5472 | .009 | 0.16 |
| 10.0 | .5602 | .5828 | .023 | 0.39 | 10.0 | .5354 | .5522 | .017 | 0.31 |
| 20.0 | .5514 | .5943 | .043 | 0.72 | 20.0 | .5286 | .5622 | .033 | 0.59 |
| 30.0 | .5502 | .6058 | .056 | 0.92 | 30.0 | .5253 | .5722 | .047 | 0.82 |
| 40.0 | .5485 | .6173 | .069 | 1.12 | 40.0 | .5242 | .5823 | .058 | 1.00 |
| 50.0 | .5529 | .6288 | .076 | 1.21 | 50.0 | .5287 | .5923 | .064 | 1.08 |
| 60.0 | .5630 | .6403 | .077 | 1.20 | 60.0 | .5374 | .6023 | .065 | 1.08 |
| 70.0 | .5794 | .6518 | .072 | 1.10 | 70.0 | .5502 | .6123 | .062 | 1.01 |
| 80.0 | .6087 | .6633 | .055 | 0.83 | 80.0 | .5745 | .6224 | .048 | 0.77 |
| 90.0 | .6424 | .6748 | .032 | 0.47 | 90.0 | .6061 | .6324 | .026 | 0.41 |
| 95.0 | .6608 | .6806 | .020 | 0.29 | 95.0 | .6229 | .6374 | .015 | 0.24 |
| 100.0 | .6863 | .6863 | .000 | 0.00 | 100.0 | .6424 | .6424 | .000 | 0.00 |
| Temperature=35.0°C. | | | | | Temperature=40.0°C. | | | | |
| 0.0 | .5211 | .5211 | .000 | 0.00 | 0.0 | .4990 | .4990 | .000 | 0.00 |
| 5.0 | .5163 | .5253 | .009 | 0.17 | 5.0 | .4952 | .5024 | .007 | 0.14 |
| 10.0 | .5112 | .5296 | .018 | 0.34 | 10.0 | .4900 | .5059 | .016 | 0.32 |
| 20.0 | .5045 | .5380 | .034 | 0.63 | 20.0 | .4839 | .5128 | .029 | 0.57 |
| 30.0 | .5021 | .5465 | .044 | 0.81 | 30.0 | .4788 | .5197 | .041 | 0.79 |
| 40.0 | .4997 | .5550 | .055 | 1.00 | 40.0 | .4780 | .5266 | .049 | 0.93 |
| 50.0 | .5026 | .5634 | .061 | 1.08 | 50.0 | .4810 | .5335 | .052 | 0.98 |
| 60.0 | .5111 | .5720 | .061 | 1.06 | 60.0 | .4870 | .5404 | .053 | 0.98 |
| 70.0 | .5231 | .5804 | .057 | 0.98 | 70.0 | .4979 | .5473 | .049 | 0.90 |
| 80.0 | .5456 | .5889 | .043 | 0.73 | 80.0 | .5152 | .5542 | .039 | 0.71 |
| 90.0 | .5721 | .5973 | .025 | 0.42 | 90.0 | .5380 | .5611 | .023 | 0.41 |
| 95.0 | .5867 | .6016 | .015 | 0.25 | 95.0 | .5544 | .5645 | .010 | 0.18 |
| 100.0 | .6058 | .6058 | .000 | 0.00 | 100.0 | .5680 | .5680 | .000 | 0.00 |

Note.—The fourth figures in the values of v_{expt} and v_{ideal} are given merely to avoid cumulative errors in calculating Δv which is given only to three places.

TABLE 2(a).—COMPARISON OF VISCOSITIES (IN CENTISTOKES) OF (I) HEPTANE-OIL BLEND, (II) CYCLOHEXANE AS OBSERVED, AND (III) CYCLOHEXANE FROM STANDARD DATA.

| Temperature (°C.) | Heptane-oil blend | | Cyclohexane | |
|----------------------|-------------------------------------|--------|---|----------|
| | Initial | Final | Observed | Standard |
| 15.4 | 1.2527 | 1.2546 | 1.344 | 1.340±2 |
| 20.0 | 1.1702 | 1.1709 | 1.245 | 1.250±2 |
| 25.0 | 1.0935 | 1.0944 | 1.147 | — |
| 30.0 | 1.0249 | 1.0255 | 1.060 | 1.066±2 |
| 40.0 | 0.9058 | 0.9066 | 0.915 | — |
| | Average increase of 0.001,0 c.s. | | Root-mean-square difference=0.005 c.s. | |

 TABLE 2(b).—MEASURED VISCOSITIES FOR CYCLOHEXANE-HEPTANE (BLEND) SYSTEM, WITH DEDUCED DEPRESSIONS, Δv AND $10(\Delta v/v_{id})$.

| Wt. % Cyc. hex. | v_{expt} (c.s.) | v_{id} (c.s.) | Δv (c.s.) | $10\Delta v/v_{id}$ | Wt. % cyc. hex. | v_{expt} (c.s.) | v_{id} (c.s.) | Δv (c.s.) | $10\Delta v/v_{id}$ |
|---------------------|-----------------------------|--------------------|----------------------|---------------------|---------------------|-----------------------------|--------------------|----------------------|---------------------|
| Temperature=15.4°C. | | | | | Temperature=20.0°C. | | | | |
| 0.0 | 1.254 | 1.254 | .000 | 0.00 | 0.0 | 1.171 | 1.171 | .000 | 0.00 |
| 5.0 | 1.241 | 1.258 | .017 | 0.14 | 5.0 | 1.163 | 1.175 | .012 | 0.10 |
| 10.0 | 1.237 | 1.263 | .026 | 0.21 | 10.0 | 1.159 | 1.178 | .019 | 0.16 |
| 20.0 | 1.231 | 1.272 | .041 | 0.32 | 20.0 | 1.153 | 1.186 | .033 | 0.28 |
| 30.0 | 1.231 | 1.281 | .050 | 0.39 | 30.0 | 1.152 | 1.193 | .041 | 0.34 |
| 40.0 | 1.230 | 1.290 | .060 | 0.46 | 40.0 | 1.150 | 1.201 | .051 | 0.42 |
| 50.0 | 1.233 | 1.299 | .066 | 0.51 | 50.0 | 1.153 | 1.208 | .055 | 0.46 |
| 60.0 | 1.239 | 1.308 | .069 | 0.53 | 60.0 | 1.157 | 1.215 | .058 | 0.48 |
| 70.0 | 1.255 | 1.317 | .062 | 0.47 | 70.0 | 1.170 | 1.223 | .053 | 0.43 |
| 80.0 | 1.277 | 1.326 | .049 | 0.37 | 80.0 | 1.188 | 1.230 | .042 | 0.34 |
| 90.0 | 1.304 | 1.335 | .031 | 0.23 | 90.0 | 1.213 | 1.238 | .025 | 0.20 |
| 95.0 | 1.323 | 1.340 | .017 | 0.13 | 95.0 | 1.227 | 1.241 | .014 | 0.11 |
| 100.0 | 1.344 | 1.344 | .000 | 0.00 | 100.0 | 1.245 | 1.245 | .000 | 0.00 |
| Temperature=25.0°C. | | | | | Temperature=30.0°C. | | | | |
| 0.0 | 1.094 | 1.094 | .000 | 0.00 | 0.0 | 1.025 | 1.025 | .000 | 0.00 |
| 5.0 | 1.088 | 1.097 | .009 | 0.08 | 5.0 | 1.018 | 1.027 | .009 | 0.09 |
| 10.0 | 1.084 | 1.099 | .015 | 0.14 | 10.0 | 1.014 | 1.029 | .015 | 0.15 |
| 20.0 | 1.080 | 1.105 | .025 | 0.23 | 20.0 | 1.009 | 1.032 | .023 | 0.22 |
| 30.0 | 1.075 | 1.110 | .035 | 0.32 | 30.0 | 1.005 | 1.036 | .031 | 0.30 |
| 40.0 | 1.075 | 1.115 | .040 | 0.36 | 40.0 | 1.004 | 1.039 | .035 | 0.34 |
| 50.0 | 1.074 | 1.120 | .046 | 0.41 | 50.0 | 1.003 | 1.043 | .040 | 0.38 |
| 60.0 | 1.077 | 1.126 | .049 | 0.44 | 60.0 | 1.005 | 1.047 | .042 | 0.40 |
| 70.0 | 1.086 | 1.131 | .045 | 0.40 | 70.0 | 1.012 | 1.050 | .038 | 0.36 |
| 80.0 | 1.101 | 1.136 | .035 | 0.31 | 80.0 | 1.023 | 1.054 | .031 | 0.29 |
| 90.0 | 1.121 | 1.142 | .021 | 0.18 | 90.0 | 1.039 | 1.057 | .018 | 0.17 |
| 95.0 | 1.133 | 1.144 | .011 | 0.10 | 95.0 | 1.049 | 1.059 | .010 | 0.09 |
| 100.0 | 1.147 | 1.147 | .000 | 0.00 | 100.0 | 1.061 | 1.061 | .000 | 0.00 |
| Temperature=40.0°C. | | | | | Temperature=40.0°C. | | | | |
| | | | | | 0.0 | 0.906 | 0.906 | .000 | 0.00 |
| | | | | | 5.0 | 0.901 | 0.906 | .005 | 0.06 |
| | | | | | 10.0 | 0.898 | 0.907 | .009 | 0.10 |
| | | | | | 20.0 | 0.892 | 0.908 | .016 | 0.18 |
| | | | | | 30.0 | 0.888 | 0.909 | .021 | 0.23 |
| | | | | | 40.0 | 0.884 | 0.909 | .025 | 0.28 |
| | | | | | 50.0 | 0.882 | 0.910 | .028 | 0.31 |
| | | | | | 60.0 | 0.880 | 0.911 | .031 | 0.34 |
| | | | | | 70.0 | 0.885 | 0.912 | .027 | 0.30 |
| | | | | | 80.0 | 0.891 | 0.913 | .022 | 0.24 |
| | | | | | 90.0 | 0.903 | 0.914 | .011 | 0.12 |
| | | | | | 95.0 | 0.908 | 0.915 | .007 | 0.08 |
| | | | | | 100.0 | 0.915 | 0.915 | .000 | 0.00 |

Note.—Measurements at 35°C. were omitted because of the relatively small changes with temperature in this region.

The measurements on the mixtures over the full range of concentrations were carried out as for benzene-heptane, but omitting the readings at 35°C. because of the smaller changes with

temperature in this case, and the results are shown in Table 2(b) together with the linearly interpolated values of ν_{ideal} and the values of viscosity depression deduced as before from

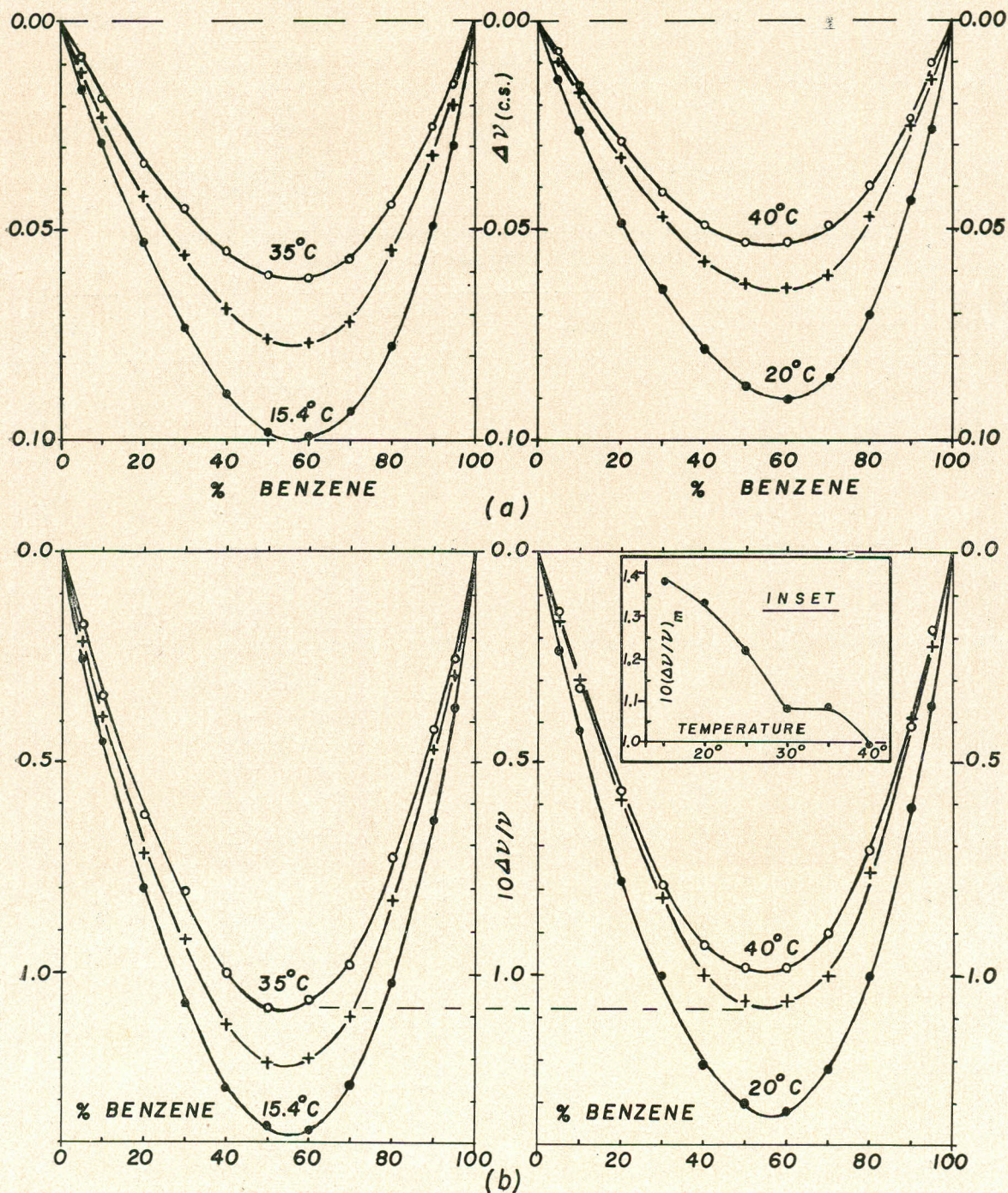


Fig. 1.—(a) Graphs for the measured viscosity depression $\Delta\nu$ (in centistokes) for the benzene-heptane system plotted against % benzene concentration at various temperatures from 15°C. to 40°C. (b) Corresponding graphs for $10\Delta\nu/\nu_{\text{id}}$, with the inset showing the anomalous temperature variation $10(\Delta\nu/\nu_{\text{id}})_{\text{max}}$.

$-\Delta v = v_{\text{expt}} - v_{\text{ideal}}$. Fig. 2(a) shows plots of Δv against weight% cyclohexane for the five temperatures, and Fig. 2(b) below shows those for $10\Delta v/v$. These graphs show that $\Delta v/v$ at the minima is about 0.04, so that the deviation from ideal behaviour is only $1/3$ of that in the case of benzene-heptane, which is in satisfactory agreement with the fact that the cyclohexane molecule, being fully saturated, exhibits a very small degree of residual interaction.

Also interesting is the plot of $10(\Delta v/v)_{\text{max}}$ against temperature in the inset to Fig. 2(b) which shows a smooth graph with a uniformly diminishing slope with increasing temperature, as would be expected in the absence of any

anomalous interactions between molecules. This is to be contrasted with the corresponding graph for the benzene-heptane system (inset to Fig. 1(b)).

5. Conclusions and Discussion

Thus, we may, by comparison with the cyclohexane-heptane system, conclude that benzene in heptane exhibits a significant anomalous behaviour, showing a viscosity depression with $(\Delta v/v)_{\text{max}}$ of the order of 0.12, which is comparable with that observed earlier in mixtures of allylbenzene and dimethoxybhitlanol with mineral oils^{2,3} of appropriate viscosity. In addition, the present measurements on the benzene-heptane system

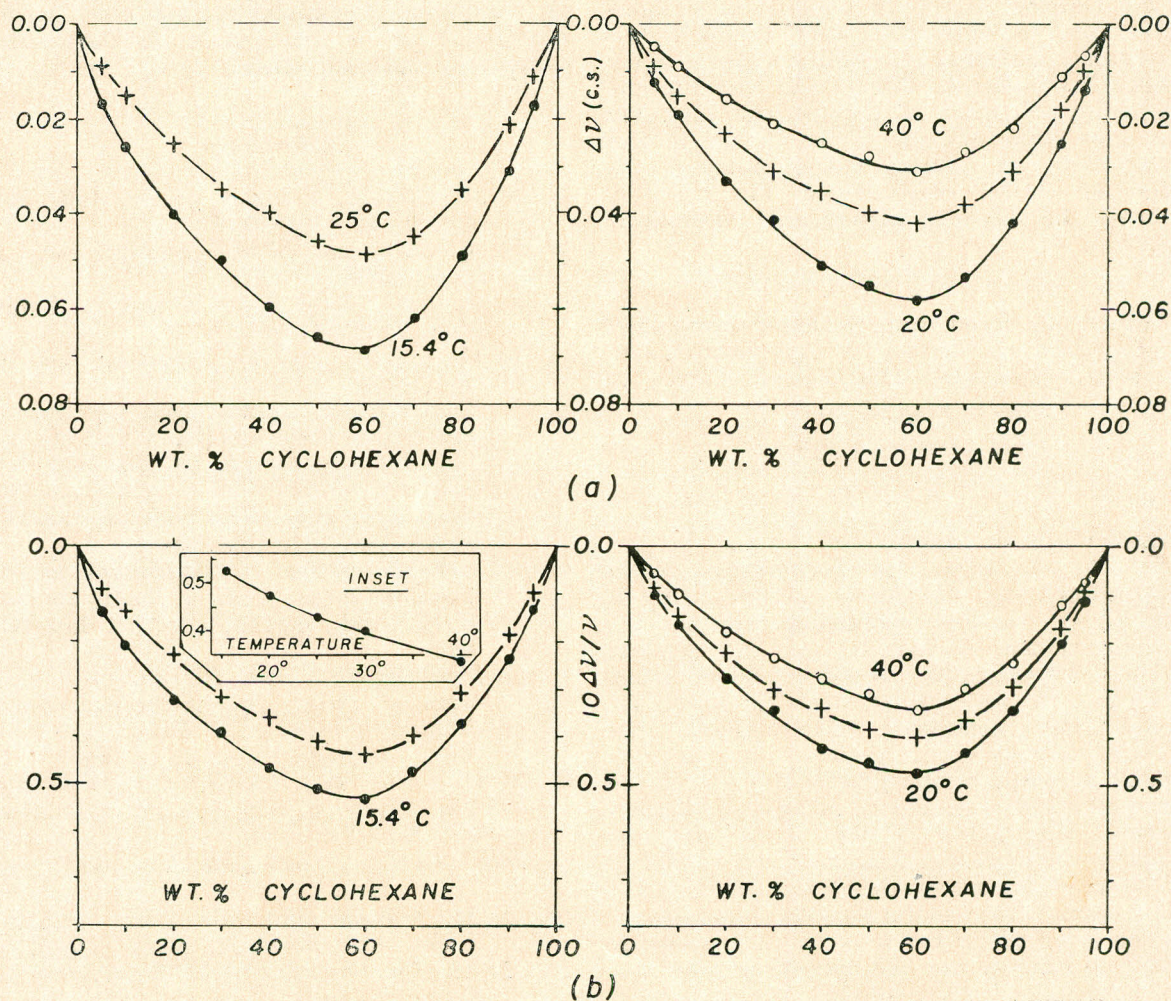


Fig. 2.—(a) Graph showing the viscosity depression Δv (in centistokes) measured for cyclohexane in heptane-oil blend, plotted against weight % cyclohexane at various temperatures from 15°C. to 40°C. (b) Corresponding curves for $10\Delta v/v_{\text{id}}$, with the inset showing the normal character of the temperature variation for $10(\Delta v/v_{\text{id}})_{\text{max}}$.

have brought to light the existence of a further anomaly in the temperature variation of the maximum relative viscosity depression, $(\Delta v/v)_{\max}$. As seen in the inset to Fig. 1(b), this quantity does not show the expected smooth drop with rising temperature, but instead presents the appearance of a rapid drop between two regions of near constancy. While a viscosity depression of 5% is noticeable in earlier reported data on hexane-benzene,⁷ the above-mentioned type of temperature variation of $(\Delta v/v)$ does not appear to have been observed previously and its study should therefore be of some importance.

It is interesting to examine the origin of the above behaviour, because the large viscosity depression points to a significant polar interaction of the benzene nucleus in solutions of straight-chain oils, in agreement with equation (1). Presumably, the effect is to be connected with the residual intermolecular forces emanating from the resonating π -electrons of the benzene ring. We can make some estimate of the change in free energy ΔG_m on mixing, corresponding to the values of $(\Delta v/v)$ observed in Fig. 1(b), by utilizing the following approximate theoretical⁸ equation:

$$\eta_{\text{expt.}}/\eta_{\text{ideal}} \simeq \text{expt}[-\Delta G_m/2.45RT] \quad (3)$$

in which the factor 2.45 is found empirically to give good agreement with experimental data on several systems.⁹ This equation leads to

$$\begin{aligned} \Delta G_m &= 2.45 RT \ln (\eta_i/\eta_e) \\ &= 2.45RT (\Delta\eta/\eta) \simeq 2.45RT (\Delta v/v) \quad (4) \end{aligned}$$

because $\frac{\Delta v}{v} \simeq \frac{\Delta\eta}{\eta} \ll 1$. This shows that over a small range of temperatures, ΔG_m is proportional to $+(\Delta v/v)$; for $T \simeq 300^\circ\text{K}$. (room temperature), the constant of proportionality is nearly 1,500 cal./mole. It follows that for the benzene-heptane interaction, at the greatest viscosity depression, G_m is nearly 180 cal./mole, which is of the order of 1/4 to 1/2 the figures for several polar molecules.⁹ This suggests that viscosity depression is probably to be explained in terms of the greater strength of the benzene-benzene interactions as against benzene-heptane. The shape of the curves for Δv against concentration of benzene is very similar to that observed for allylbenzene³ and allylphenol,³ and it appears likely that a theoretical formulation can be given along the lines of that previously used¹⁰ to connect the hydrogen-bond concentration (determined from infrared measurements)

with the viscosity depressions observed for allylphenol in oil. It is hoped to publish a detailed account after analyzing measurements with toluene, phenol, etc.

As regards the anomaly in the temperature variation of the relative viscosity depression (inset to Fig. 1(b), since $(\Delta v/v)$ is proportional to ΔG_m by equation (4), it follows that this excess free energy of mixing apparently varies in a periodic manner with temperature, showing successive regions of constant value and a rapid drop from one to the next. This is rather similar to the segments and steps already observed in the activation energy of several pure associated liquids e.g. glycerol, ethylene glycol, water,¹¹ and the present experiments thus suggest that it would be worthwhile to examine various other binary mixtures as well as pure benzene for the possible existence of such an effect.

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