

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

Part III.—Further Viscosity Measurements in Some Binary Systems, and Development of a Formula for Predicting the Free Energy of Mixing for Aromatic Compounds

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The previously reported measurements of viscosity depression and free energy of mixing have been repeated in case of benzene and toluene, now mixed with nonane and octane, respectively, in place of octane and heptane previously used. The previous results are generally confirmed, and mean values of 171 ± 20 and 102 ± 15 cal/mole for ΔG_m are obtained for benzene and toluene, respectively.

The data for nine aromatic compounds so far studied are analyzed, and a least-squares treatment gives the following relation as a first approximation:

$$\Delta G_m = 180 + 70 \times (\text{No. of phenolic groups}) - [95] \text{ for side chain.}$$

This fits the observed values of ΔG_m to within ± 18 cal/mole r.m.s., except in case of phenol, for which the observed value of ΔG_m is 295, i.e. 45 cal/mole higher than that predicted by the formula. Further studies on xylenes and similar compounds are in hand for elucidation of the remaining second-order effects.

1. Introduction

For ideal behaviour of the viscosity of mixtures of two constituents A and B in molar proportions X_A and X_B two theoretical relations have been proposed, viz.

$$\ln \eta_{\text{ideal}} = X_A \ln \eta_A + X_B \ln \eta_B \quad (1a)$$

$$\text{and } \phi_{\text{ideal}} = X_A \phi_A + X_B \phi_B \quad (1b)$$

where $\phi = 1/\eta$ is the fluidity, i.e. the reciprocal of dynamic viscosity. It is readily shown that these two relations can be approximated to by

$$\eta_{\text{ideal}} = X_A \eta_A + X_B \eta_B \quad (2a)$$

provided η_A and η_B are not appreciably different, and this is approximately equivalent to

$$\nu_{\text{ideal}} = X_A \nu_A + X_B \nu_B \quad (2b)$$

since the changes in density are generally much smaller than those in η . (Also, X_A and X_B can often be replaced by proportions by weight or volume of the components A and B, provided that molecular weights and densities of the two liquids are not very much different.) Departures from these linear relationships are measured as the viscosity depression $\Delta\eta$ or $\Delta\nu$.

In the previous communications^{1,2} relating to viscosity measurements of long-chain phenolic compounds mixed with appropriate mineral oils, it was shown that the fractional viscosity depression ($\Delta\nu/\nu_{\text{id}}$) is correlated as much with the

actual viscosity of the mixture, as with the number of active hydroxylic groups. This prompted the investigation of similar compounds *without* a long side-chain, such as allylphenol and allylbenzene,³ and cyclohexane and benzene,⁴ when mixed with suitable straight-chain hydrocarbons or mineral oils, in Part I of this series.⁴ In Part II, viscosity measurements were undertaken on toluene-heptane and phenol-mineral-oil systems⁵ from 5°C to 40°C and 60°C to 120°C respectively, and fractional viscosity depressions of the order of 6% and 20% respectively, were found in these two systems at 40°C. This corresponds to free energy of mixing, ΔG_m , of the magnitude of 87 and 295 cal/mole, respectively, using the semiempirical formula

$$\Delta G_m = 2.45 RT \ln (\eta_{\text{ideal}}/\eta_{\text{expt}}) \simeq 2.45 RT (\Delta\eta/\eta) \simeq 2.45 RT (\Delta\nu/\nu) \quad (3)$$

In Part I of this series, the measurements on the benzene heptane system⁴ from 15°C to 40°C at intervals of 5°C yielded the free energy of mixing as about 180 cal/mole, and the plot of maximum relative viscosity depression ($\Delta\nu/\nu_{\text{id}}$) showed an anomalous variation with temperature in the region of 30°C to 35°C. The experiments could not be taken to higher temperatures because of preferential loss of heptane. The large viscosity depression ($\Delta\nu/\nu_{\text{id}}$) of the order of 10% to 20% can be understood as being due to polar interaction of the benzene nucleus through residual intermolecular forces (emanating from the resonating electrons of its ring), and the temperature variation anomaly, though unexpected, is in consonance with the measurements on the flow activation

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energy,⁶ $E\eta$, which exhibited a cyclic variation, changing to stepwise pattern below 18°C.

To further examine and verify the phenomena underlying this peculiar temperature variation of ΔG_m for benzene and toluene, it was considered worthwhile to carry out similar experiments by mixing benzene with an aliphatic hydrocarbon of somewhat higher viscosity and density than those of benzene. Nonane was considered suitable, because it provides a fair balance of molecular weight, density, as well as viscosity. These experiments carried out at intervals of 2.5°C are reported in the present communication, which also includes similar duplicate measurements on the toluene-octane system and the cyclohexane-decane system in the range of 10°C–50°C at the thermal interval of 5°C. The data for nine aromatic compounds are analyzed to give a formula for predicting ΔG_m .

2. Experimental Procedure

Various mixtures were prepared, as before, in a stoppered-flask at concentration increments of 10%, with extra ones at 5% and 95%, by adding calculated volumes of the corresponding hydrocarbons to benzene, cyclohexane or toluene, and the viscosity measurements on each solution were completed within one working day. Viscosity measurements were carried out by recording 5 to 6 concordant readings of the flow-time with a calibrated stopwatch, graduated to ± 0.1 sec or better. The B.S.S. Viscometer No. 'o' (constant = 0.000736) was supported vertically in a Townson and Mercer thermostatic bath, which gives temperature stability to $\pm 0.005^\circ\text{C}$, and the temperatures were noted with a standardized mercury thermometer, reading to one-tenth of a degree, fitted with a magnifying thermometer-reader. In order to minimize the errors due to losses by fractional evaporation of one component from the solutions, the viscosity measurements were performed first at low temperatures, going downwards below room temperature (30°C), and then working upwards. The selective evaporation of the more volatile component of the solution is further counteracted at the higher temperatures by attaching a ballast bottle (containing the test solution) well immersed in the bath; this arrangement controls the concentration changes by maintaining dynamic vapour equilibrium. Drying tubes containing calcium chloride were attached to both limbs of the viscometer, so as to prevent entry of moisture from air. The viscosity is calculated by the formula

$$v = At + B/t^2$$

where t is the flow time, and A and B are the two previously determined viscometer constants.

3. Results with the Benzene-Nonane System from 10°C to 50°C at Intervals of 2.5°C

In the previous viscosity data on benzene-heptane system,⁴ the viscosity and density of n-heptane at 25°C are both lower (by 0.1 c.s. and 0.174 units) than those of benzene, the molecular weight of which is 78, as against 100 for heptane. In the case of nonane, both the density and viscosity are correspondingly higher than those of benzene. Table 1a shows the measured values of density and kinematic viscosity for our samples of nonane (B.D.H., Analar) and benzene (Merck) at various temperatures, together with the standard values (Timmerman,^{7a} I.C.T.,^{7b} and Kaye and Labye^{7c}). The agreement between the observed and standard values is satisfactory, showing a root-mean-square difference of ± 0.006 c.s. and ± 0.005 c.s. for benzene and nonane, respectively, thus providing a check on the purity of the samples.

The experimental values of viscosities for various mixtures in the benzene-nonane system at seventeen temperatures from 10°C to 50°C are given in Table 1b. This table also contains the corresponding ideal viscosities v_{id} (obtained by linear interpolation between the viscosity values of nonane and benzene), together with the values of the viscosity depression,

$$-\Delta v = v_{\text{expt}} - v_{id}$$

The viscosity of nonane is about 20% higher than that of benzene, so that this linear interpolation is liable to errors that may go up to a possible maximum of about 2% near the middle of the range, i.e. about 0.02 in $\Delta v/v_{id}$

TABLE 1a.—COMPARISON OF MEASURED AND STANDARD VISCOSITIES OF BENZENE AND NONANE.

Temp (°C)	Viscosities for benzene (c.s.)		Viscosities for nonane (c.s.)	
	Observed	Standard	Observed	Standard
10.0	0.863	0.851	1.140	1.141
12.5	0.823	—	1.091	—
15.0	0.793	0.787	1.064	—
17.5	0.753	—	1.035	—
20.0	0.734	0.739	0.998	0.991
22.5	0.712	—	0.965	—
25.0	0.690	0.686	0.932	0.927
27.5	0.670	—	0.909	—
30.0	0.648	0.647	0.877	0.872
32.5	0.626	—	0.857	—
35.5	0.610	0.606	0.833	—
37.5	0.590	—	0.810	—
40.0	0.573	0.569	0.780	0.781
42.5	0.557	—	0.762	—
45.0	0.544	—	0.744	—
47.5	0.530	—	0.726	—
50.0	0.514	0.517	0.710	—

root-mean-square difference = ± 0.006 c.s. root-mean-square difference = ± 0.005 c.s.

TABLE 1b.—VISCOSITY MEASUREMENTS ON BENZENE-NONANE SYSTEM, TOGETHER WITH DEPRESSION, Δv AND $10(\Delta v/v_{id})$ VALUES FROM 10°C TO 50°C AT THE INTERVAL OF 2.5°C.

Benzene %	v_{expt}	v_{id}	Δv	$10(\Delta v/v_{id})$
60.0	0.741	0.866	0.125	1.443
70.0	0.732	0.838	0.106	1.264
80.0	0.736	0.809	0.073	0.902
90.0	0.732	0.781	0.047	0.603
95.0	0.752	0.767	0.015	0.196
100.0	0.753	0.753	0.000	0.000

Benzene %	v_{expt}	v_{id}	Δv	$10(\Delta v/v_{id})$
<i>Temperature 10.0°C</i>				
0.0	1.140	1.140	0.000	0.000
5.0	1.081	1.126	0.045	0.400
10.0	1.042	1.112	0.070	0.629
20.0	0.967	1.085	0.118	1.088
30.0	0.911	1.057	0.146	1.381
40.0	0.869	1.029	0.160	1.554
50.0	0.843	1.002	0.159	1.587
60.0	0.821	0.974	0.153	1.571
70.0	0.816	0.946	0.130	1.374
80.0	0.813	0.918	0.105	1.437
90.0	0.839	0.891	0.052	0.584
95.0	0.847	0.877	0.030	0.342
100.0	0.863	0.863	0.000	0.000
<i>Temperature 12.5°C</i>				
0.0	1.091	1.091	0.000	0.000
5.0	1.046	1.078	0.032	0.297
10.0	1.005	1.064	0.059	0.554
20.0	0.931	1.037	0.106	1.022
30.0	0.877	1.011	0.134	1.325
40.0	0.838	0.984	0.146	1.483
50.0	0.817	0.957	0.140	1.463
60.0	0.801	0.930	0.129	1.387
70.0	0.795	0.903	0.108	1.196
80.0	0.798	0.877	0.079	0.901
90.0	0.809	0.850	0.041	0.482
95.0	0.811	0.836	0.025	0.299
100.0	0.823	0.823	0.000	0.000
<i>Temperature 15.0°C</i>				
0.0	1.064	1.064	0.000	0.000
5.0	1.002	1.050	0.048	0.457
10.0	0.973	1.037	0.064	0.617
20.0	0.903	1.009	0.106	1.051
30.0	0.852	0.982	0.130	1.323
40.0	0.812	0.954	0.142	1.488
50.0	0.792	0.927	0.135	1.456
60.0	0.774	0.900	0.126	1.400
70.0	0.768	0.872	0.104	1.192
80.0	0.767	0.845	0.078	0.923
90.0	0.779	0.817	0.038	0.465
95.0	0.787	0.804	0.017	0.211
100.0	0.790	0.790	0.000	0.000
<i>Temperature 17.5°C</i>				
0.0	1.035	1.035	0.000	0.000
5.0	0.974	1.021	0.047	0.460
10.0	0.934	1.007	0.073	0.725
20.0	0.859	0.979	0.120	1.226
30.0	0.810	0.950	0.140	1.473
40.0	0.784	0.922	0.138	1.497
50.0	0.758	0.894	0.136	1.521

Benzene %	v_{expt}	v_{id}	Δv	$10(\Delta v/v_{id})$
<i>Temperature 20.0°C</i>				
0.0	0.998	0.998	0.000	0.000
5.0	0.945	0.985	0.040	0.406
10.0	0.920	0.972	0.052	0.535
20.0	0.855	0.945	0.090	1.058
30.0	0.808	0.919	0.111	1.288
40.0	0.768	0.892	0.124	1.390
50.0	0.748	0.866	0.118	1.363
60.0	0.735	0.840	0.105	1.250
70.0	0.732	0.813	0.082	1.009
80.0	0.730	0.787	0.057	0.724
90.0	0.739	0.760	0.021	0.276
95.0	0.733	0.747	0.014	0.187
100.0	0.734	0.734	0.000	0.000
<i>Temperature 22.5°C</i>				
0.0	0.965	0.965	0.000	0.000
5.0	0.920	0.952	0.032	0.336
10.0	0.880	0.940	0.060	0.638
20.0	0.809	0.914	0.105	1.148
30.0	0.772	0.889	0.117	1.316
40.0	0.740	0.864	0.123	1.423
50.0	0.718	0.839	0.118	1.406
60.0	0.702	0.813	0.111	1.365
70.0	0.700	0.788	0.088	1.117
80.0	0.697	0.763	0.066	0.865
90.0	0.706	0.737	0.031	0.021
95.0	0.714	0.725	0.011	0.152
100.0	0.712	0.712	0.000	0.000
<i>Temperature 25.0°C</i>				
0.0	0.932	0.931	0.000	0.000
5.0	0.880	0.920	0.031	0.337
10.0	0.855	0.908	0.053	0.584
20.0	0.795	0.884	0.089	1.006
30.0	0.749	0.859	0.110	1.281
40.0	0.719	0.835	0.116	1.389
50.0	0.698	0.811	0.113	1.393
60.0	0.684	0.787	0.103	1.308
70.0	0.679	0.763	0.084	1.101
80.0	0.677	0.738	0.061	0.826
90.0	0.684	0.714	0.030	0.420
95.0	0.687	0.702	0.015	0.214
100.0	0.690	0.690	0.000	0.000
<i>Temperature 27.5°C</i>				
0.0	0.909	0.909	0.000	0.000
5.0	0.856	0.897	0.041	0.457
10.0	0.822	0.885	0.063	0.712
20.0	0.768	0.862	0.094	1.090
30.0	0.729	0.838	0.109	1.300

Benzene %	v_{expt}	v_{id}	Δv	$10(\Delta v/v_{\text{id}})$	Benzene %	v_{expt}	v_{id}	Δv	$10(\Delta v/v)$
40.0	0.699	0.814	0.115	1.412	10.0	0.747	0.786	0.039	0.496
50.0	0.679	0.790	0.111	1.405	20.0	0.701	0.764	0.063	0.825
60.0	0.665	0.766	0.101	1.318	30.0	0.663	0.742	0.079	1.065
70.0	0.658	0.742	0.084	1.132	40.0	0.632	0.720	0.088	1.222
80.0	0.660	0.718	0.058	0.807	50.0	0.609	0.698	0.089	1.275
90.0	0.666	0.694	0.028	0.403	60.0	0.596	0.676	0.080	1.183
95.0	0.672	0.682	0.010	0.147	70.0	0.590	0.654	0.064	0.978
100.0	0.670	0.670	0.000	0.000	80.0	0.586	0.632	0.046	0.728
<i>Temperature 30.0°C</i>					90.0	0.589	0.610	0.021	0.344
0.0	0.877	0.877	0.000	0.000	95.0	0.590	0.601	0.011	0.166
5.0	0.834	0.866	0.032	0.369	100.0	0.590	0.590	0.000	0.000
10.0	0.803	0.854	0.051	0.597	<i>Temperature 40.0°C</i>				
20.0	0.741	0.832	0.091	1.093	0.0	0.783	0.783	0.000	0.000
30.0	0.706	0.809	0.103	1.273	5.0	0.754	0.773	0.019	0.246
40.0	0.675	0.785	0.111	1.412	10.0	0.718	0.762	0.044	0.577
50.0	0.656	0.763	0.107	1.402	20.0	0.678	0.741	0.063	0.850
60.0	0.638	0.740	0.102	1.378	30.0	0.646	0.720	0.074	1.027
70.0	0.632	0.717	0.085	1.185	40.0	0.615	0.699	0.084	1.202
80.0	0.633	0.694	0.061	0.878	50.0	0.593	0.678	0.085	1.254
90.0	0.633	0.671	0.038	0.566	60.0	0.582	0.657	0.075	1.142
95.0	0.637	0.659	0.022	0.334	70.0	0.575	0.636	0.061	1.959
100.0	0.648	0.648	0.000	0.000	80.0	0.569	0.615	0.046	0.748
<i>Temperature 32.5°C</i>					90.0	0.570	0.594	0.024	0.404
0.0	0.857	0.857	0.000	0.000	95.0	0.574	0.584	0.010	0.171
5.0	0.826	0.846	0.020	0.236	100.0	0.573	0.573	0.000	0.000
10.0	0.794	0.834	0.040	0.480	<i>Temperature 42.5°C</i>				
20.0	0.748	0.810	0.062	0.765	0.0	0.762	0.762	0.000	0.000
30.0	0.704	0.787	0.083	1.055	5.0	0.740	0.752	0.012	0.160
40.0	0.665	0.764	0.093	1.217	10.0	0.701	0.741	0.031	0.418
50.0	0.656	0.741	0.085	1.147	20.0	0.665	0.721	0.056	0.777
60.0	0.639	0.718	0.079	1.002	30.0	0.630	0.700	0.070	1.000
70.0	0.626	0.965	0.069	0.993	40.0	0.602	0.680	0.078	1.147
80.0	0.623	0.672	0.049	0.729	50.0	0.580	0.659	0.079	1.199
90.0	0.623	0.649	0.026	0.401	60.0	0.572	0.639	0.067	1.049
95.0	0.629	0.638	0.009	0.158	70.0	0.563	0.618	0.055	0.889
100.0	0.626	0.626	0.000	0.000	80.0	0.557	0.598	0.041	0.686
<i>Temperature 35.0°C</i>					90.0	0.558	0.578	0.020	0.346
0.0	0.833	0.833	0.000	0.000	95.0	0.561	0.568	0.007	0.123
5.0	0.807	0.822	0.015	0.182	100.0	0.557	0.557	0.000	0.000
10.0	0.788	0.811	0.023	0.284	<i>Temperature 45.0°C</i>				
20.0	0.735	0.788	0.053	0.673	0.0	0.744	0.744	0.000	0.000
30.0	0.694	0.766	0.072	0.940	5.0	0.718	0.734	0.016	0.218
40.0	0.663	0.744	0.081	1.089	10.0	0.691	0.724	0.033	0.455
50.0	0.642	0.722	0.080	1.108	20.0	0.648	0.704	0.056	0.795
60.0	0.627	0.699	0.072	1.030	30.0	0.618	0.684	0.066	0.965
70.0	0.610	0.677	0.067	0.970	40.0	0.590	0.664	0.074	0.114
80.0	0.598	0.655	0.057	0.774	50.0	0.568	0.644	0.076	1.180
90.0	0.607	0.632	0.025	0.402	60.0	0.559	0.624	0.065	1.042
95.0	0.608	0.622	0.014	0.225	70.0	0.547	0.604	0.057	0.944
100.0	0.610	0.610	0.000	0.000	80.0	0.543	0.584	0.041	0.702
<i>Temperature 37.5°C</i>					90.0	0.535	0.564	0.029	0.514
0.0	0.810	0.810	0.000	0.000	95.0	0.545	0.554	0.009	0.162
5.0	0.797	0.797	0.020	0.251	100.0	0.544	0.544	0.000	0.000

Benzene %	ν_{expt}	ν_{id}	$\Delta\nu$	$10(\Delta\nu/\nu_{\text{id}})$	Benzene %	ν_{expt}	ν_{id}	$\Delta\nu$	$10(\Delta\nu/\nu_{\text{id}})$
<i>Temperature 47.5°C</i>					<i>Temperature 50.0°C</i>				
0.0	0.726	0.726	0.000	0.000	0.0	0.710	0.710	0.000	0.000
5.0	0.703	0.716	0.013	0.182	5.0	0.680	0.700	0.020	0.286
10.0	0.672	0.706	0.034	0.481	10.0	0.665	0.690	0.025	0.507
20.0	0.537	0.686	0.049	0.714	20.0	0.616	0.670	0.054	0.806
30.0	0.600	0.667	0.067	1.044	30.0	0.579	0.651	0.072	1.105
40.0	0.580	0.647	0.067	1.036	40.0	0.560	0.631	0.071	1.125
50.0	0.562	0.628	0.066	1.051	50.0	0.539	0.612	0.073	1.193
60.0	0.547	0.608	0.061	1.003	60.0	0.528	0.592	0.064	1.081
70.0	0.538	0.589	0.051	0.866	70.0	0.519	0.573	0.054	0.942
80.0	0.533	0.569	0.036	0.632	80.0	0.515	0.553	0.038	0.687
90.0	0.535	0.550	0.015	0.273	90.0	0.519	0.534	0.015	0.281
95.0	0.533	0.540	0.007	0.130	95.0	0.516	0.524	0.008	0.153
100.0	0.530	0.530	0.000	0.000	100.0	0.514	0.514	0.000	0.000

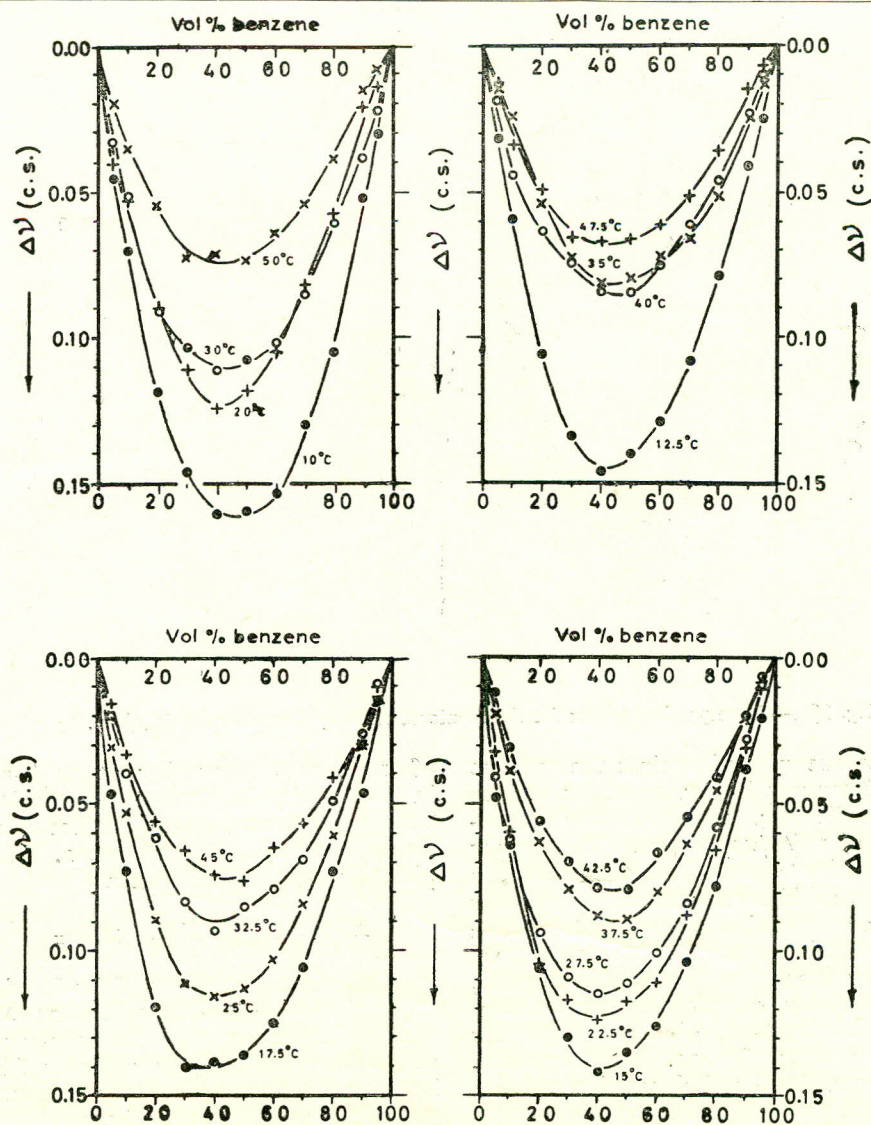


Fig. 1(a).—Graphs for the viscosity depression, $\Delta\nu$, against benzene concentration, as observed with mixture of benzene and nonane at seventeen temperatures from 10° to 50°C.

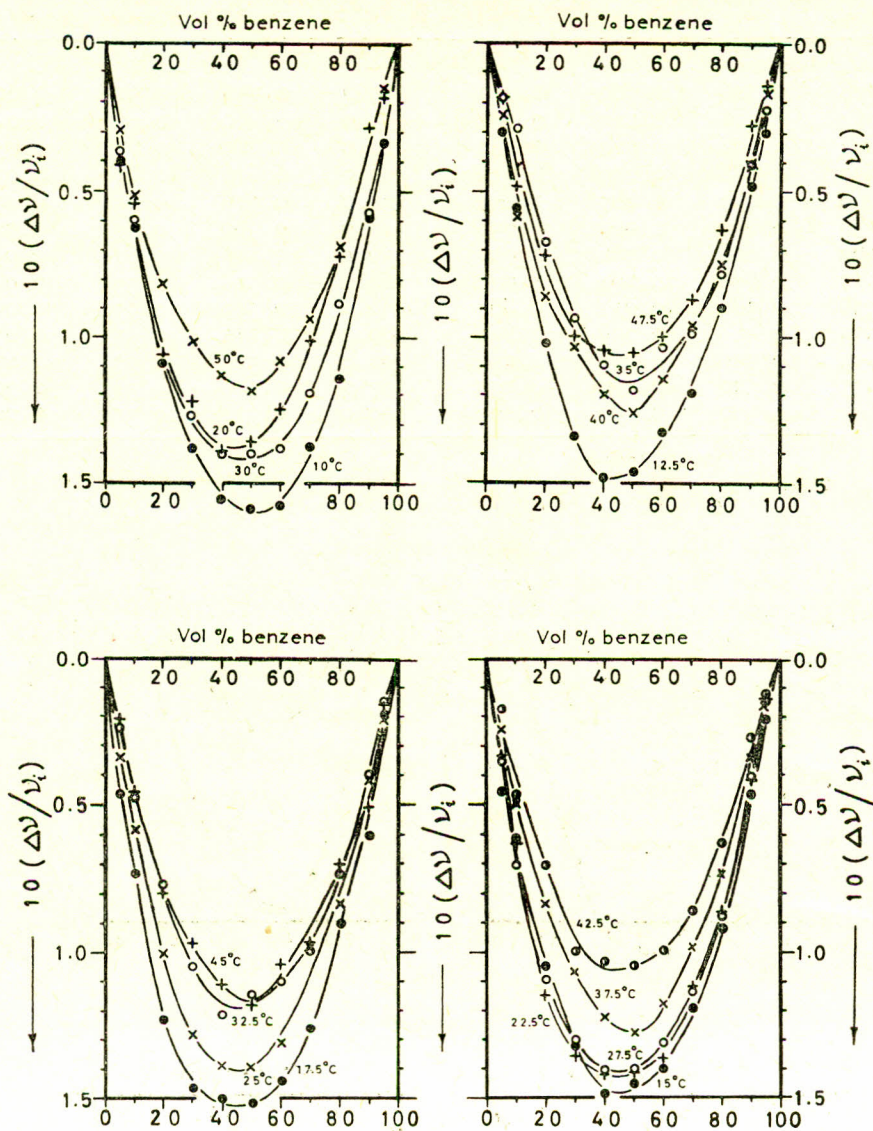


Fig. 1(b).—Corresponding graphs for the fractional viscosity depression, $10 (\Delta v/v_i)$.

The Δv values are plotted against the volume concentration of benzene in Fig. 1a at the various temperatures, while Fig. 1b shows the corresponding graphs of $10(\Delta v/v_i)$ values. The graphs of viscosity depression Δv , show that the maximum depression at the middle temperature of 30°C is 0.11 c.s., which corresponds to a value of $(\Delta v/v_i)_{\text{max}}$ of 0.14 units. This is to be compared with the corresponding depression of 0.08 c.s. at 30°C , found in the previous experiments on benzene when mixed with heptane, giving a value for $(\Delta v/v_i)_{\text{max}}$ of the order of 0.12. In the present case, the maximum fractional depression (of the order of 14%) occurs at 45% volume concentration of benzene, which bears comparison with the figures

of 10%–14% occurring at 54%–58% benzene in the benzene–heptane system studied previously. This agreement further justifies the use of the linear interpolation formulae 2. Using the empirically established formula

$$\Delta G_m = 2.45 RT (\Delta v/v_i)_{\text{max}}$$

it follows from the values of the fractional viscosity depression $(\Delta v/v_i)_{\text{max}}$ at 40°C that ΔG_m is nearly 191 cal/mole for the benzene–nonane system at 40°C , as against 151 cal/mole for benzene in heptane at the same temperature. These two provide a mean figure of 171 ± 20 cal/mole, the large r.m.s. deviation being a consequence of the

different anomalous temperature variations in the two systems, as discussed below.

The maximum values of $10(\Delta v/v_{id})$ for the benzene-nonane system are plotted against temperature in Fig 2a as hollow circles, wherein for comparison, the broken-line graph through the crosses is reproduced from our previously published data on the benzene-heptane system. It is clear from Fig. 2a, that there exists an anomalous step-like variation from 10°C to 32°C, followed by a cyclic behaviour above 32°C, and the discontinuities seen in the lower curve of benzene mixed with heptane become more clear in the upper curve through the hollow circles. This is partly due to the use of a greater range of temperatures in the present experiments, and partly to the use of nonane and a smaller thermal interval. The two horizontal portions extend over intervals of 5°C–10°C, while the sharp jumps extend over just about 2.5°C, which is the experimental interval in the present case. The depths of the jumps are more than 5 times the r.m.s. deviation in the present experiments.

4. Results on Toluene-Octane System

After studying the nature of temperature variation of $(\Delta v/v_{id})_{max}$ for benzene, it was thought desirable to extend the observations to another related compound, toluene, which had previously been studied as mixtures with n-heptane. Accordingly, the next series of experiments deals with the measurements on toluene mixed with n-octane at steps of 10% concentration, and the resulting values of $10(\Delta v/v_{id})_{max}$ are compared together.

Mixing with n-octane (B.D.H., Analar) was considered to be of interest for the present investigations, since it provides a satisfactory balance of density and viscosity, as well as for its unusual type of behaviour in respect of activation energy of viscous flow, $E\eta$, which remains remarkably constant⁸ over a considerable range of temperatures (in contrast to most other liquids studied). The flow measurements were carried out from 10°C to 50°C at 5°C intervals, to an accuracy of ± 0.1 sec, and the actually determined viscosities of toluene and octane are first compared with the standard values in Table 2a.

Here again, the agreement between the two sets of values is satisfactory, with r.m.s. difference of the order of ± 0.003 c.s. for the values of toluene, and ± 0.005 c.s. for those of octane.

The Δv values for different temperatures, together with their corresponding $10(\Delta v/v_{id})$ values are given in Table 2b, and represented graphically in Fig 3a and Fig. 3b, respectively. The minima of these curves are observed to lie between 25% and 45% volume of toluene, while in the previously studied system of toluene in heptane-oil blend it was found to occur around

50% concentration. However, the maximum values of $10(\Delta v/v_{id})$ are comparable with the previous ones.

The temperature variation of $10(\Delta v/v_{id})$ for the toluene-octane system is shown by the upper curve through the solid circles in Fig. 2b, wherein for comparison, the lower one (through the crosses) represents the previously reported results for the mixtures of toluene with heptane. Instead of the gradual drop, with an indication of constant ΔG_m from 5°C to 15°C and 30°C to 40°C, notice-

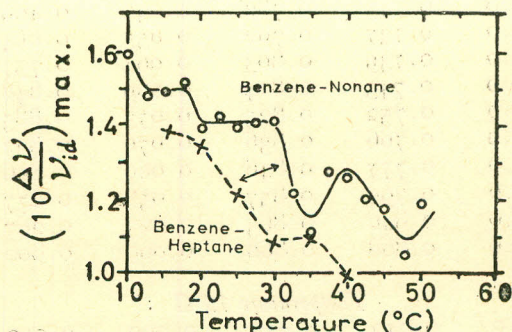


Fig. 2(a).—Comparative plots of $10(\Delta v/v_{id})_{max}$ as a function of temperature for benzene-nonane (hollow circles) and benzene-heptane (crosses), showing two clear steps, going over into oscillatory behaviour above 32°C in case of benzene-nonane.

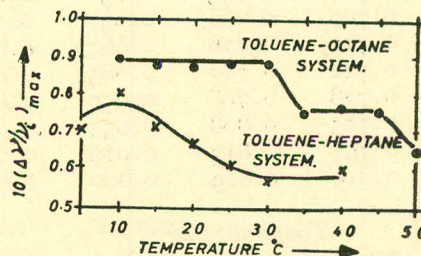


Fig. 2(b).—Similar plots of $10(\Delta v/v_{id})_{max}$ against temperature for toluene-octane (solid circles) compared with toluene-heptane (crosses).

TABLE 2(a).—COMPARISON OF THE MEASURED VISCOSITIES OF TOLUENE AND OCTANE WITH THE STANDARD VALUES.

Temp °C	Viscosities (c.s.) of toluene		Viscosities (c.s.) of n-octane	
	Standard	Measured	Standard	Measured
10.0	0.762±2	0.760	0.869±2	0.874
15.0	0.715±2	0.712	0.819±3	0.814
20.0	0.678±3	0.675	0.773±2	0.772
25.0	0.639±1	0.638	0.727±1	0.730
30.0	0.611±3	0.610	0.688±1	0.692
35.0		0.575		0.656
40.0	0.550±5	0.547	0.634±3	0.635
45.0		0.520		0.603
50.0	0.499±1	0.496	0.581	0.572
	r.m.s. deviation = ±0.003 c.s.		r.m.s. deviation = ±0.005 c.s.	

TABLE 2(b).—VISCOSITY DATA FOR TOLUENE-OCTANE SYSTEM, TOGETHER WITH DEDUCED DEPRESSION Δv AND FRACTIONAL DEPRESSION IN VISCOSITY $\Delta v/v_{id}$.

% Volume of octane	v_{expt}	v_{id}	Δv	$IO(\Delta v/v_{id})$	% Volume of octane	v_{expt}	v_{id}	Δv	$IO(\Delta v/v_{id})$
					50.0	0.631	0.684	0.053	0.775
					60.0	0.639	0.693	0.054	0.779
					70.0	0.644	0.702	0.058	0.826
					80.0	0.648	0.711	0.063	0.881
					90.0	0.675	0.721	0.046	0.638
					95.0	0.704	0.726	0.022	0.303
					100.0	0.730	0.730	0.000	0.000
<i>Temperature 10°C</i>					<i>Temperature 30°C</i>				
0.0	0.760	0.760	0.000	0.000	0.0	0.610	0.610	0.000	0.000
5.0	0.750	0.765	0.015	0.196	5.0	0.597	0.614	0.007	0.114
10.0	0.748	0.777	0.029	0.373	10.0	0.594	0.618	0.024	0.388
20.0	0.743	0.782	0.039	0.499	20.0	0.594	0.627	0.033	0.526
30.0	0.737	0.792	0.055	0.694	30.0	0.592	0.635	0.043	0.678
40.0	0.739	0.803	0.064	0.797	40.0	0.593	0.643	0.050	0.778
50.0	0.745	0.814	0.069	0.848	50.0	0.602	0.651	0.049	0.753
60.0	0.752	0.825	0.073	0.885	60.0	0.606	0.659	0.053	0.804
70.0	0.766	0.836	0.070	0.837	70.0	0.609	0.668	0.059	0.883
80.0	0.777	0.846	0.069	0.816	80.0	0.625	0.676	0.051	0.754
90.0	0.799	0.857	0.058	0.677	90.0	0.641	0.685	0.044	0.642
95.0	0.840	0.863	0.023	0.267	95.0	0.669	0.689	0.020	0.290
100.0	0.868	0.868	0.000	0.000	100.0	0.693	0.693	0.000	0.000
<i>Temperature 15°C</i>					<i>Temperature 35°C</i>				
0.0	0.712	0.712	0.000	0.000	0.0	0.575	0.575	0.000	0.000
5.0	0.703	0.717	0.014	0.195	5.0	0.573	0.579	0.006	0.104
10.0	0.700	0.723	0.023	0.318	10.0	0.566	0.583	0.017	0.292
20.0	0.701	0.734	0.031	0.422	20.0	0.567	0.591	0.024	0.466
30.0	0.697	0.744	0.047	0.632	30.0	0.563	0.599	0.036	0.601
40.0	0.704	0.755	0.051	0.675	40.0	0.562	0.605	0.043	0.711
50.0	0.709	0.766	0.057	0.744	50.0	0.573	0.616	0.043	0.698
60.0	0.713	0.776	0.063	0.812	60.0	0.579	0.624	0.045	0.721
70.0	0.722	0.787	0.065	0.826	70.0	0.585	0.632	0.047	0.744
80.0	0.728	0.798	0.070	0.877	80.0	0.592	0.640	0.048	0.750
90.0	0.755	0.808	0.053	0.656	90.0	0.611	0.648	0.037	0.571
95.0	0.794	0.813	0.019	0.234	95.0	0.633	0.652	0.019	0.291
100.0	0.819	0.819	0.000	0.000	100.0	0.656	0.656	0.000	0.000
<i>Temperature 20°C</i>					<i>Temperature 40°C</i>				
0.0	0.672	0.672	0.000	0.000	0.0	0.547	0.547	0.000	0.000
5.0	0.665	0.677	0.012	0.177	5.0	0.545	0.551	0.006	0.109
10.0	0.659	0.682	0.023	0.377	10.0	0.543	0.556	0.013	0.234
20.0	0.661	0.692	0.031	0.448	20.0	0.545	0.565	0.020	0.354
30.0	0.657	0.702	0.045	0.641	30.0	0.544	0.573	0.029	0.506
40.0	0.661	0.712	0.051	0.716	40.0	0.546	0.582	0.036	0.619
50.0	0.667	0.722	0.055	0.762	50.0	0.549	0.591	0.042	0.711
60.0	0.671	0.732	0.061	0.833	60.0	0.556	0.600	0.044	0.733
70.0	0.677	0.742	0.065	0.876	70.0	0.567	0.609	0.042	0.690
80.0	0.695	0.752	0.057	0.758	80.0	0.574	0.617	0.043	0.697
90.0	0.712	0.762	0.050	0.665	90.0	0.593	0.626	0.033	0.527
95.0	0.746	0.767	0.021	0.274	95.0	0.614	0.631	0.017	0.269
100.0	0.772	0.772	0.000	0.000	100.0	0.635	0.635	0.000	0.000
<i>Temperature 25°C</i>					<i>Temperature 45°C</i>				
0.0	0.638	0.638	0.000	0.000	0.0	0.520	0.520	0.000	0.000
5.0	0.634	0.643	0.009	0.140	5.0	0.517	0.524	0.007	0.134
10.0	0.626	0.647	0.021	0.325	10.0	0.514	0.528	0.014	0.265
20.0	0.626	0.656	0.030	0.457					
30.0	0.627	0.666	0.039	0.586					
40.0	0.627	0.675	0.045	0.711					

% Volume of octane	v_{expt}	v_{id}	Δ_v	$10(\Delta_v/v_{\text{id}})$
20.0	0.516	0.537	0.021	0.391
30.0	0.516	0.545	0.029	0.532
40.0	0.518	0.553	0.035	0.633
50.0	0.526	0.562	0.036	0.641
60.0	0.531	0.570	0.039	0.684
70.0	0.534	0.578	0.044	0.761
80.0	0.550	0.586	0.036	0.614
90.0	0.563	0.595	0.032	0.538
95.0	0.585	0.599	0.014	0.200
100.0	0.603	0.603	0.000	0.000
Temperature 50°C				
0.0	0.497	0.497	0.000	0.000
5.0	0.496	0.501	0.005	0.100
10.0	0.498	0.505	0.007	0.139
20.0	0.498	0.514	0.016	0.311
30.0	0.500	0.522	0.022	0.421
40.0	0.498	0.530	0.032	0.604
50.0	0.506	0.539	0.033	0.612
60.0	0.512	0.547	0.035	0.640
70.0	0.519	0.555	0.036	0.649
80.0	0.532	0.563	0.031	0.551
90.0	0.547	0.572	0.025	0.437
95.0	0.563	0.576	0.013	0.226
100.0	0.580	0.580	0.000	0.000

able in the toluene-heptane system, now two sharp jumps at 32.5°C and 47°C are clearly observable in the upper graph of Fig. 2b for toluene in octane. Here again, the jumps are extending over 105°C which is twice the measuring interval used during this particular series of experiments. These results are in conformity with the findings on benzene, and yield the free energy of mixing at 40°C as 117 cal/mole, in contrast to 87 cal/mole, for the toluene-heptane system. This provides a mean figure of 102 ± 15 cal/mole for these systems, the large r.m.s. difference being partly a consequence of the different temperature variation anomalies in the two cases.

5. Results with Cyclohexane-Decane System

In the previous experiments undertaken on mixtures of cyclohexane and heptane from 10°C to 40°C, it was observed that the temperature variation for the maximum values of $10(\Delta v/v_{\text{id}})$ followed a smooth curve, with no clear indication of any singularity. This could of course be a consequence of the use of a relatively small experimental range of temperatures, and it was therefore considered desirable to repeat the measurements on cyclohexane over a comparatively greater range of temperatures, and with a different aliphatic hydrocarbon. For the present investigation, n-decane (B.D.H., Analar) was used as the other component of the binary mixture

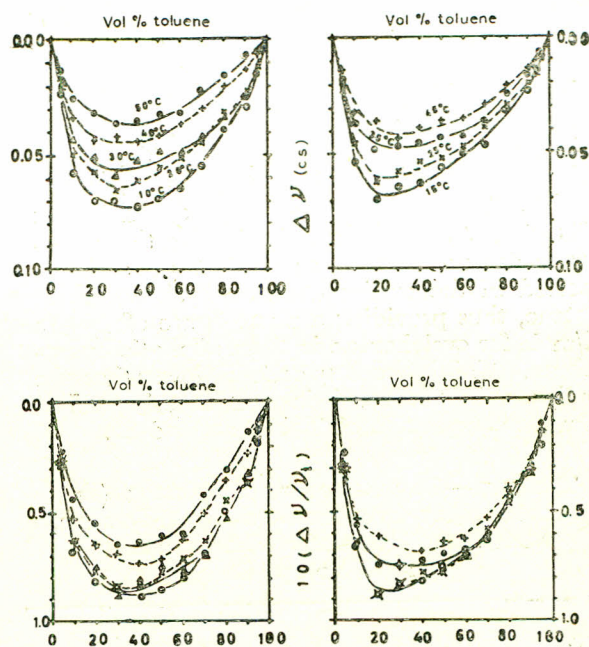


Fig. 3.—Graphs showing the dependence of (a) viscosity depression, Δv , and (b) $10(\Delta v/v_{\text{id}})$ on the concentration of toluene in octane at various temperatures from 10°C to 50°C.

for the nearly equal values of density (0.722 for decane and 0.769 for cyclohexane) at 25°C as well as viscosities in the temperature range of 10°C–50°C.

The viscosities of the two liquids were determined to an accuracy of ± 0.001 c.s. from 10°C to 50°C at intervals of 50°C, using viscometer No. 'o' BSS/188 (constant = 0.000398) and stopwatch calibrated to 0.1 sec. Table 3 shows a comparison of the actually measured values of viscosities of cyclohexane and decane with the standard data.

These values agree well with each other, giving root-mean-square deviations of the order of ± 0.002 to ± 0.003 c.s. The measured values of viscosity depressions Δv for the nine temperatures used in the main experiment from 10°C to 50°C, together with their $10(\Delta v/v_{\text{id}})$ values are plotted against the corresponding concentrations in Fig. 4a and Fig. 4b, respectively. For the cyclohexane-decane system, the minima of these curves fall near 50% of cyclohexane concentration, and the Δv values are about 35% higher than those found in the cyclohexane-heptane system. This could in part be attributed to the comparatively stronger interaction of the cyclohexane molecule with decane, as compared with that of heptane.

The temperature variation of maximum values of $10(\Delta v/v_{\text{id}})$ for the mixtures of cyclohexane and decane are plotted in Fig. 4c as solid circles, while those for cyclohexane and heptane (reproduced from the earlier work) are shown by the crosses

in the lower curve. It is seen that, although the curve through the crosses runs uniformly with temperature, the one for cyclohexane and decane (through the circles) shows some anomalous variation similar to that observed for the mixtures of benzene in Fig. 2a. At least the horizontal region, from 30°C to 40°C, between the jumps indicated by the arrows in Fig. 4c appears to be genuine. The maximum viscosity depression at 40°C gives ΔG_m as 82 cal/mole for the cyclohexane-decane system, as against 52 cal/mole reported in the earlier work on cyclohexane in heptane, thus providing a mean figure of 67 ± 15 cal/mole for cyclohexane in these aliphatic hydrocarbons. This is about 15 cal/mole lower than the smallest value recorded in our experiments on aromatic compounds, cf. Tables 4a and 4b.

TABLE 3.—COMPARISON OF VISCOSITIES (IN CENTISTOKES) OF CYCLOHEXANE AND n-DECANE, WITH THEIR STANDARD VALUES, FROM 10°C TO 50°C.

Temp. °C	Viscosities (c.s.) of cyclohexane		Viscosities (c.s.) of n-decane	
	Measured	Standard	Measured	Standard
10.0	1.473		1.472	1.465 ± 3
15.0	1.356		1.365	
20.0	1.246	1.250 ± 2	1.264	1.260 ± 2
25.0	1.149		1.178	
30.0	1.064	1.066 ± 1	1.103	1.102 ± 2
35.0	0.985		1.037	
40.0	0.916	0.915 ± 1	0.974	0.975 ± 3
45.0	0.855		0.914	
50.0	0.802		0.868	0.870 ± 3
	r.m.s. deviation ±0.003 c.s.		r.m.s. deviation ±0.003 c.s.	

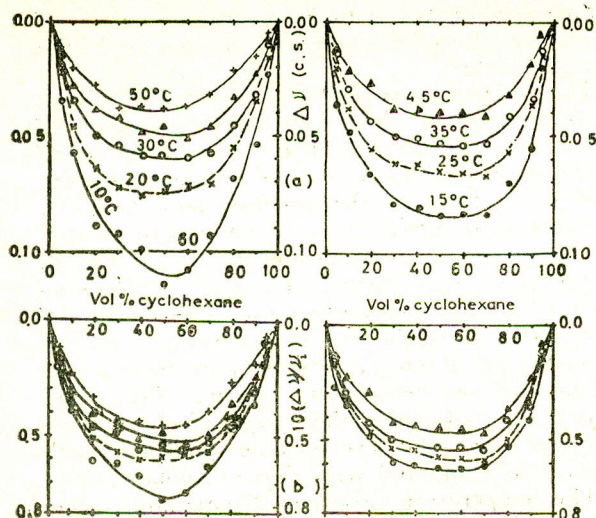


Fig. 4(a) and (b).—Graphs of viscosity depression, Δv , and of $10(\Delta v/v)_d$ for various mixtures of cyclohexane in decane at a series of temperatures from 10°C to 50°C.

6. Synopsis of Data, and Development of a Structure-dependent Formula for ΔG_m

The experimental results described above provide ample confirmation of our previously reported data, and indicate that an accuracy and reliability of the order of ± 15 cal/mole can be claimed for the values of the free energy of mixing, ΔG_m , deduced from the observed viscosity depressions. It is now possible to make a synopsis of the data on ΔG_m for the various compounds so far studied and to examine it for possible quantitative correlation of ΔG_m with the structure, i.e. number of OH groups and the side-chains.

Accordingly, Table 4a presents a collection of the values of fractional viscosity depression and the free energy of mixing at 40°C for benzene, toluene and phenol, along with the three compounds of the allyl series, viz. allylbenzene, allylphenol and allylcatechol. A temperature of 40°C has been fixed for this comparison, because the phenol-oil system, which is only partially miscible below 80°C, exhibits an anomalous increase in the viscosity near 70% phenol concentration,⁵ in a manner similar to that of allylcatechol reported sometime earlier,³ and accurate extrapolation of the data on $(\Delta v/v)_d$ is only possible down to 40°C. It had already been surmised in Part II that the addition of each phenolic group increases ΔG_m on the average by 90 cal/mole. Taking into consideration also the fact that ΔG_m for toluene and allylbenzene are *not* very different from each other, the mean being 92 ± 10 cal/mole, we may first assume that ΔG_m is independent of the nature of the side-chain, and would be given to a first approximation by a simple formula, such as $\Delta G_m = A + B \times (\text{No. of phenolic groups}) - [C]$ for the side-chain. (4)

Accordingly, a least-squares fitting of equation 4 to the experimental values of ΔG_m for these five compounds was attempted, giving half weightage to the data for phenol and allylcatechol, which are subject to larger uncertainties than the rest. This gives us $A = 181$, $B = 72$, $C = 97$ cal/mole, for the allyl side-chain, with a probable error of ± 8 cal, so that in round figures we may write

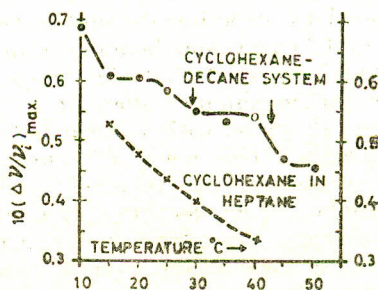


Fig. 4(c).—Comparative graphs of $10(\Delta v/v)_d$ max against temperature for cyclohexane in decane (solid circles) and cyclohexane in a heptane and mineral oil blend (crosses).

TABLE 4(a).—COMPARATIVE TABLE OF VALUES OF $10(\Delta v/v_{id})_{\max}$ AND FREE ENERGY OF MIXING ΔG_m , FOR VARIOUS SIMPLE COMPOUNDS AT 40°C.

Compound	Benzene	Toluene	Allylbenzene	Phenol	Allylphenol	Allylcatechol
$10(\Delta v/v_{id})_{\max}$	1.13	0.67	0.54	1.95 ± 0.15	0.99	1.45 ± 0.15
ΔG_m (cal/mole)	171	102	82	295 ± 23	151	220 ± 23
ΔG_m (calc)	180	85	85	250	155	225
Difference	+9	-17	+3	-45	+4	+5
						(r.m.s.=20)

TABLE 4(b).—COMPARISON OF THE OBSERVED VALUES OF ΔG_m WITH THOSE CALCULATED FROM FORMULA 5 FOR TOLUENE, ALLYL BENZENE AND THREE BHILAWANOL COMPOUNDS.

Compound	Toluene	Allylbenzene	Dimethoxybhilawanol	Monomethoxybhilawanol	Bhilawanol
ΔG_m (observed)	102	82	91	190	192
ΔG_m (calculated)	85	85	85	155	225
Difference	-17	+3	-6	-35	+33

$$\Delta G_m = 180 + 70 \times (\text{No. of phenolic groups}) - [95] \text{ for side chain.} \quad (5)$$

A comparison of these calculated values is made in the last two rows of Table 4a with the experimentally observed values for the five compounds and it is seen that the agreement is excellent in case of allylbenzene, allylphenol and allylcatechol, and also good in case of benzene. The calculated value for phenol is 45 cal/mole lower than the experimentally observed one, this difference being twice the estimated experimental errors. This is not altogether unexpected, because phenol owes its properties to the remarkable electronic behaviour of the lone OH attached to the benzene ring, and this would be reflected in an abnormally high free energy of mixing, ΔG_m . Of course, it is worth noting here that the major contribution (180 cal/mole) to ΔG_m comes from the benzene nucleus itself.

We can now attempt to apply formula 5 to toluene and to the three compounds of the bhilawanol series so far studied. Bhilawanol has a $C_{15}H_{27}$ side-chain, while toluene has only a CH_3 so that this comparison can throw further light on the effect of various lengths of the side-chain. Accordingly, Table 4b shows a comparison between the calculated and observed ΔG_m for these four compounds, together with allylbenzene, which has an intermediate length of side-chain, viz., $CH_2CH.CH_2$. The first three compounds in this table, which have a benzene nucleus without any free or exposed OH groups, and side-chains of three different lengths, have a mean ΔG_m of 92 ± 5 cal/mole. This is in good agreement with the value of 85 cal/mole deduced above on the basis

of the allyl series, and provides further justification for trying formula 5 in the present case. The first three differences in the last row of Table 4b are -17, +3 and -6, with a mean value of -7 ± 5 , and do not show any significant correlation with the length of side-chain, so that we may conclude that the value of C is substantially independent (within ± 5 cal/mole) of the length and structure of the side-chain.

Coming now to the three compounds of the bhilawanol series, we find that, although the mean deviation between calculated and observed is ± 25 cal/mole, yet on the average, the calculated values are only 3 cal/mole lower than those observed. This may perhaps indicate that the value of C should be a little smaller, but is, however, offset by the fact that the experimental values of ΔG_m for bhilawanol and monomethoxybhilawanol are both nearly equal, and show rather large deviations (± 34 cal/mole) from the values calculated by formula 5.

We can justifiably conclude at this stage that equation 5 fits the data for all the studied compounds, except phenol, to ± 18 cal/mole (r.m.s.) and that $C = 95 \pm 5$ cal/mole for all lengths of side-chain, to a first approximation. Nevertheless, in view of the above-mentioned discrepancies, it is equally clear that there is scope for further careful experimental and theoretical study of the second-order effects due to the length of the side-chain as well as the relative positions (i.e. *o, p, m*) where two or more groups are attached to the benzene nucleus. For this purpose, some measurements are being undertaken on xylenes and some other compounds.

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