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Transport Properties of Nonelectrolyte Liquid Mixtures— VI. Viscosimetric Study of Binary Mixtures of Hexafluorobenzene with Aromatic Hydrocarbons

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Viscosity coefficients for binary mixtures of hexafluorobenzene with benzene, toluene, para-xylene, and mesitylene have been measured along the saturation line at temperatures from 15 to 120°C using specially designed capillary viscometers. Densities were measured using a pyknometer and volume-change apparatus. Deviations of the viscosities from a rectilinear dependence on mole fraction are consistent with enhanced interactions between unlike species, which increase with increasing number of methyl groups on the aromatic hydrocarbon and decrease with increasing temperature. The application of the Grunberg and Nissan equation, the Hildebrand equation, and energy of activation theories to these results is examined.

KEY WORDS: aromatic hydrocarbons; density; excess free energy of activation; Grunberg and Nissan equation; hexafluorobenzene; viscosity coefficient.

1. INTRODUCTION

Since the observation by Patrick and Prosser [1] of a 1:1 intermolecular complex between hexafluorobenzene and benzene in the solid state, there have been many reports of the formation of crystalline complexes between hexafluorobenzene and a wide range of aromatic hydrocarbons. These include complexes with toluene, para-xylene, and mesitylene [2], naphthalene and biphenyl [3], anthracene, pyrene, and perylene [4], durene [5], and hexamethylbenzene [6]. X-ray and wide-line nuclear magnetic resonance

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studies have confirmed that the molecules adopt an alternate stacked plane structure in these complexes but are aligned perpendicularly in the pure compounds [7, 8].

Although the existence of such complexes does not prove that complex formation occurs in the liquid state, there is evidence [9–11] that there are enhanced intermolecular interactions between the unlike molecular species. Vrbancich and Ritchie [12] have measured the quadrupole moments of benzene and hexafluorobenzene at 25°C and found that they are of approximately equal magnitude but of opposite signs. These measurements are consistent with other results [10, 13, 14] which can be interpreted as evidence for oriented pairs of dissimilar species in the liquid, although the ordering of pairs is short-lived.

We have previously reported [15] the viscosity coefficients of benzene, hexafluorobenzene, and an equimolar mixture of benzene + hexafluorobenzene from 25 to 100°C and at pressures up to the point of onset of solidification or 400 MPa. Subsequently, we reported [16] density measurements for benzene, hexafluorobenzene, and five binary mixtures over the same ranges of temperature and pressure and determined the temperature and pressure dependence of the molar excess volume. This paper continues the study by presenting the viscosity coefficients for binary mixtures of hexafluorobenzene with benzene, toluene, para-xylene, and mesitylene at temperatures from 15 to 120°C. Specially designed sealed capillary viscometers were used to allow measurements to be made along the saturation line, even above the normal boiling point.

2. EXPERIMENTAL

2.1. Measurement of Viscosity

The viscometers have been fully described elsewhere [17]. Scrupulous cleanliness was observed and each viscometer was thoroughly cleaned before use with hot chromic acid and rinsed with distilled water followed by distilled acetone. Liquids were carefully filtered into the dried viscometers through a Millipore filter having a pore size of 0.5 μm. The liquid was frozen by placing the viscometer in liquid nitrogen or a mixture of dry ice and acetone, the air removed by pumping, and the viscometer sealed by a Rotaflo tap.

Temperature control to better than 0.02°C was achieved by immersing the viscometers in a bridge-controlled constant-temperature bath (Model E270, Series III) manufactured by Townson and Mercer Ltd. Water was used as the constant temperature liquid for temperatures up to 90°C, while Shell Risella oil was used for higher temperatures.

Each liquid was used to fill at least two viscometers having different dimensions in order to obtain an estimate of the precision of the measurements. The equation used to calculate kinematic viscosity was

$$\eta/\rho = M(1-\rho_v/\rho)[1+\alpha(T-T_r)]t - N/t \qquad (1)$$

where η is the dynamic viscosity coefficient, ρ is the density of the liquid, ρ_v is the density of the vapor, t is the time for the liquid to flow through the capillary, and M and N are constants for a particular viscometer. The term $[1+\alpha(T-T_r)]$, where α is the temperature coefficient of linear expansion of glass, takes account of expansion of the viscometer between the reference temperature T_r (taken as 25°C) and the experimental temperature T, while the term $(1-\rho_v/\rho)$ takes account of the buoyant effect of the vapor. Calibration of the viscometers was carried out using benzene and toluene for which kinematic viscosity coefficients had been measured in a master viscometer [17]. Equation (1) was able to reproduce the kinematic viscosity coefficient to well within 0.2%. However, the equation takes no account of surface tension effects, which may lead to errors of a parts of a percent [18].

2.2. Measurement of Density

Densities at 25°C were measured using a glass pyknometer of approximately 19-cm^3 capacity. Evaporation losses were minimized by ground-glass caps which fitted the ends of the capillaries. The calibration liquids were distilled degassed water and toluene, for which the densities are accurately known [19, 20]. Standard corrections [21] were applied to take account of the buoyant effect of the air and the effect of the vapor in the enclosed gas space of the pyknometer.

Densities at temperatures other than 25°C were measured using a volume-change apparatus [17] which was basically a glass bulb of capacity 2.7 cm^3 fitted to a length of Veridia precision-bore (0.85-mm) capillary tubing. The density at temperature T was determined from the density at 25°C and the ratio of the liquid volume at 25°C to that at temperature T. The calibration liquids were benzene and toluene. Corrections were applied to account for evaporation of the liquid and for volume changes in the apparatus arising from changes of temperature. It is estimated that experimental densities will be accurate to $\pm 0.1\ \mathrm{kg \cdot m^{-3}}$ in the range 25 to 50°C, increasing to $\pm 0.3\ \mathrm{kg \cdot m^{-3}}$ at 90°C.

Densities were measured for all the pure liquids and for at least one composition of each binary mixture. Values of the molar excess volume V^E were used to calculate densities at other mole fractions. The V^E value at mole fraction x and temperature T, $V^E(x, T)$, was determined from the measured value $V^E(x_A, T)$ at mole fraction x_A by

$$V^E(x, T) = V^E(x_A, T) \times V^E(x, 40°C)/V^E(x_A, 40°C) \qquad (2)$$

where $V^E(x, 40°C)$ and $V^E(x_A, 40°C)$ are the V^E values of Duncan et al. [22] at 40°C and at mole fractions x and x_A. A variation of 0.1 $cm^3 \cdot mol^{-1}$ in the excess volume leads to a typical uncertainty of 0.1% in the calculated density of the mixture. At temperatures above 90°C, densities were obtained by linear extrapolation of density with temperature.

3. MATERIALS

Hexafluorobenzene was purchased from Fluorochem Ltd., Glossop, Derbyshire, and had a stated purity of 99%. Toluene and cyclohexane (Aristar and AnalaR) were purchased from B.D.H. Chemicals Ltd., Poole, who stated the purities to be 99.95 and 99.5%, respectively. The benzene, para-xylene, and mesitylene had stated purities of not less than 99% and were purchased from Hopkin and Williams Ltd., Chadwell Heath, Aldrich Chemical Co. Ltd., Gillingham, and Aldrich Chemical Co. Inc., Milwaukee. The hexafluorobenzene was used as received but the cyclohexane, benzene, toluene, para-xylene, and mesitylene were distilled before use by passing through a 35-cm distillation column. Analysis of the freezing curves of benzene and hexafluorobenzene indicated purities of 99.7 and 99.6 mol %, respectively.

Table I compares the measured densities and refractive indices with literature values. Refractive index was measured using a high-accuracy 60/ED Abbé refractometer (Bellingham and Stanley Ltd.) illuminated by a sodium lamp and maintained at 25.0°C by water circulation.

4. RESULTS

The viscosity coefficients, densities, and kinematic viscosities for hexafluorobenzene, benzene, toluene, para-xylene, and mesitylene are listed as a function of temperature in Tables II to VI. Viscosity coefficients are estimated to be accurate to 0.5%. Literature values [9, 20, 24, 34–40] are included for comparison.

For hexafluorobenzene, there is good agreement with the results of Bedsole and Taylor [9] at 25 and 40°C, but the results of Nissema and Kuvaja [34] are rather low. The A.P.I. Tables [20] give good agreement for toluene and there is excellent agreement with the value of Timmermans [38]. Table V shows that the viscosity coefficients of para-xylene reported by the

Table I. Liquids Used

Liquid	Density at 25°C (kg·m^{-3})		Refractive index at 25°C (n_{25}^{D})	
	This work	Literature	This work	Literature
Hexafluorobenzene	1606.42	1607.32 [23] 1606.34 [24] 1606.94 [25]	1.37502	
Benzene	873.61	873.60 [26] 873.59 [27] 873.63 [28]	1.49797	1.49792 [28] 1.49800 [29]
Toluene	862.21	862.19 [26] 862.26 [27] 862.29 [25]	1.49414	1.49413 [28] 1.49414 [20]
Para-xylene	856.83	856.70 [27] 856.69 [28]	1.49319	1.49320 [29]
Mesitylene	860.64	861.08 [20] 861.11 [30]	1.49610	1.49684 [30] 1.49610 [31]
Cyclohexane	773.8 [17]	773.92 [33]	1.42374	1.42369 [32] 1.4233 [28]

A.P.I. Tables [20] are very slightly higher (up to 0.5%) than the present ones at temperatures up to 80°C and 1.5% lower at 120°C. The values of Timmermans [38] are scattered around the present values. There is good agreement with the results of Nissema and Kokkonen [39] for mesitylene, but the present results are higher than those of Kokkonen and Nissema [40] by 1.2% at 40°C.

Table II. Viscosity Coefficients and Densities of Hexafluorobenzene^{a}

			η (mPa·s)	
T (°C)	ρ (kg·m^{-3})	η/ρ (m^{2}·s^{-1} × 10^{-6})	This work	Literature [Ref. No.]
15.00	1629.0	0.636	1.036	
25.00	1606.4	0.544	0.8735	0.869 [24], 0.867^{i} [34], 0.871 [9]
40.00	1572.2	0.441	0.6942	0.714^{i} [24], 0.664 [34], 0.695^{i} [9]
60.00	1525.4	0.348	0.5317	
80.00	1477.0	0.284	0.420	
100.00	1428.3^{e}	0.240	0.342	
120.00	1380.0^{e}	0.206	0.284	

[a] Superscript e, extrapolated value; superscript i, interpolated value.

Table III. Viscosity Coefficients and Densities of Benzene[a]

T (°C)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1} × 10^{-6})	η (mPa·s) This work	η (mPa·s) Literature [Ref. No.]
25.00	873.61	0.690	0.602	0.601 [20], 0.603 [35]
40.00	857.5	0.574	0.492	0.490 [20], 0.492 [36]
60.00	836.0	0.466	0.390	0.388 [20]
80.00	813.7	0.391	0.318	0.317 [20], 0.317 [37]
100.00	791.3^{e}	0.334	0.265	0.262 [37]

[a] Superscript e, extrapolated value.

Table IV. Viscosity Coefficients and Densities of Toluene[a]

T (°C)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})	η (mPa·s) This work	η (mPa·s) Literature [Ref. No.]
15.00	871.5	0.717	0.625	0.625^{i} [38]
25.00	862.2	0.640	0.552	0.552 [20], 0.552^{i} [38]
40.00	848.3	0.550	0.466	0.465 [20], 0.466^{i} [38]
60.00	829.4	0.461	0.382	0.386 [20]
80.00	810.0	0.394	0.319	0.317 [20]
100.00	791.0^{e}	0.343	0.271	0.269 [20]
120.00	771.6^{e}	0.303	0.234	

[a] Superscript e, extrapolated value; superscript i, interpolated value.

Table V. Viscosity Coefficients and Density of Para-xylene[a]

T (°C)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})	η (mPa·s) This work	η (mPa·s) Literature [Ref. No.]
25.00	856.8	0.704	0.603	0.605 [20]
40.00	843.7	0.600	0.507	0.508 [20], 0.496^{i} [38]
60.00	826.1	0.500	0.413	0.415 [20], 0.420^{i} [38]
80.00	808.3	0.427	0.345	0.346 [20], 0.343^{i} [38]
100.00	790.6^{e}	0.371	0.293	0.293 [20], 0.292^{i} [38]
120.00	772.8^{e}	0.328	0.254	0.250 [20], 0.251^{i} [38]

[a] Superscript e, extrapolated value; superscript i, interpolated value.

Table VI. Viscosity Coefficients and Densities of Mesitylene[a]

T (°C)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})	η (mPa·s) This work	η (mPa·s) Literature [Ref. No.]
25.00	860.6	0.765	0.659	0.653^i [39]
40.00	848.4	0.650	0.552	0.552 [39], 0.545 [40]
60.00	831.4	0.540	0.449	
80.00	815.0	0.461	0.375	
100.00	797.7^e	0.400	0.319	
120.00	780.5^e	0.350	0.277	

[a] Superscript e, extrapolated value; superscript i, interpolated value.

Tables VII to X report the viscosity coefficients, densities, and kinematic viscosities for the binary mixtures of hexafluorobenzene + benzene, hexafluorobenzene + toluene, hexafluorobenzene + para-xylene, and hexafluorobenzene + mesitylene. Account has been taken of changes in mole fraction in the viscometers caused by greater evaporation of the more volatile component of the mixtures. Figures 1 to 4 show viscosity coefficients

Table VII. Viscosity Coefficients and Densities of Hexafluorobenzene(1) + Benzene(2) Mixtures

$x(1)$	T (°C)	η (mPa·s)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})
0.105 7	25.00	0.582	966.2	0.602
	40.00	0.478	947.9	0.504
	60.00	0.379	923.5	0.410
	80.00	0.311	898.0	0.346
	100.00	0.259	872.4	0.297
0.251 9	25.00	0.597	1 087.3	0.549
	40.00	0.489	1 066.2	0.458
	60.00	0.386	1 037.9	0.372
	80.00	0.315	1 008.7	0.312
	100.00	0.262	979.4	0.268
0.598 8	25.00	0.729	1 347.3	0.541
	40.00	0.582	1 320.0	0.441
	60.00	0.451	1 282.7	0.352
	80.00	0.359	1 244.1	0.289
	100.00	0.294	1 205.5	0.244

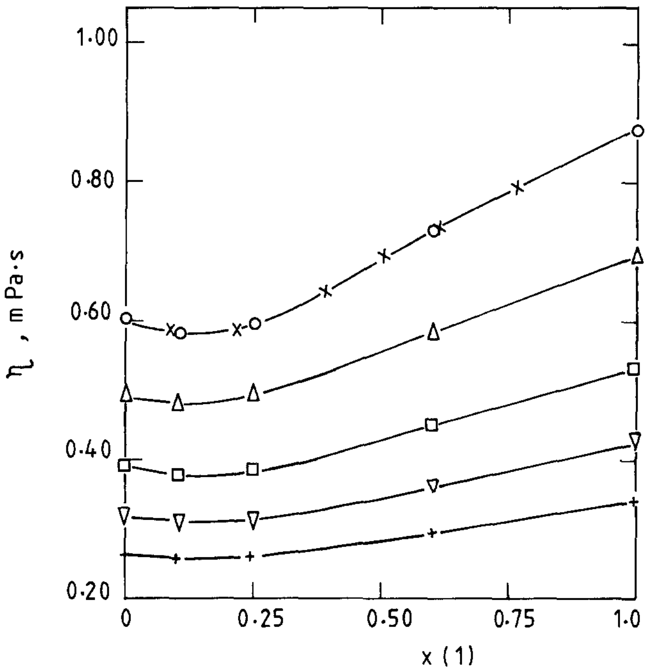

Fig. 1. Composition dependence of the viscosity for hexafluorobenzene(1) + benzene(2) at different temperatures: (○) 25.0°C; (×) 25.0°C, Ref. 9; (△) 40.0°C; (□) 60.0°C; (▽) 80.0°C; (+) 100.0°C.

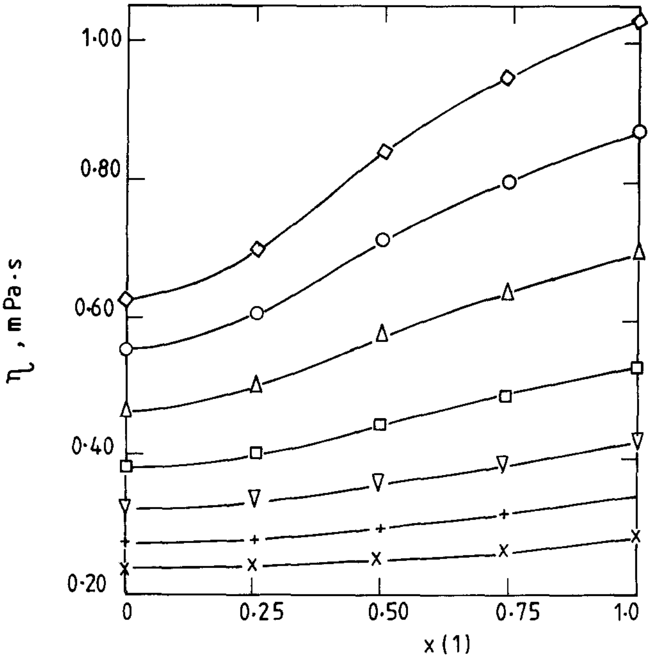

Fig. 2. Composition dependence of the viscosity for hexafluorobenzene(1) + toluene(2). (◇) 15.0°C; (○) 25.0°C; (△) 40.0°C; (□) 60.0°C; (▽) 80.0°C; (+) 100.0°C; (×) 120.0°C.

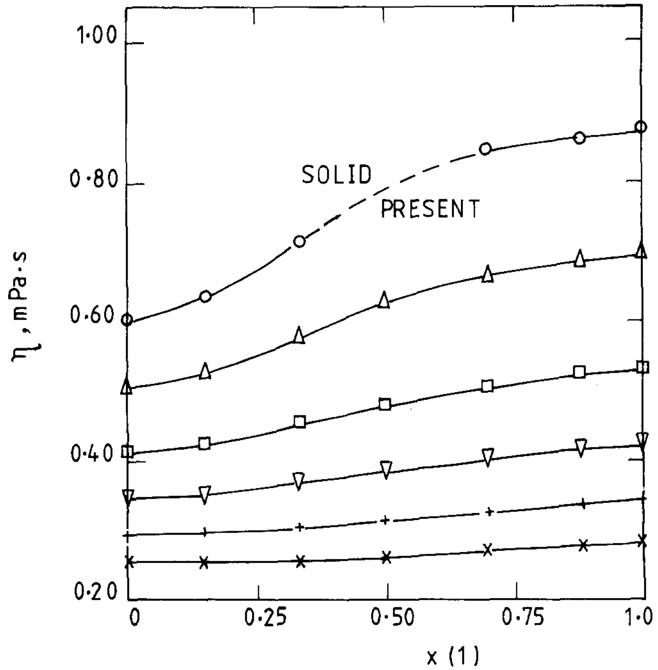

Fig. 3. Composition dependence of the viscosity for hexafluorobenzene(1) + *p*-xylene(2). Key as in the legend to Fig. 2.

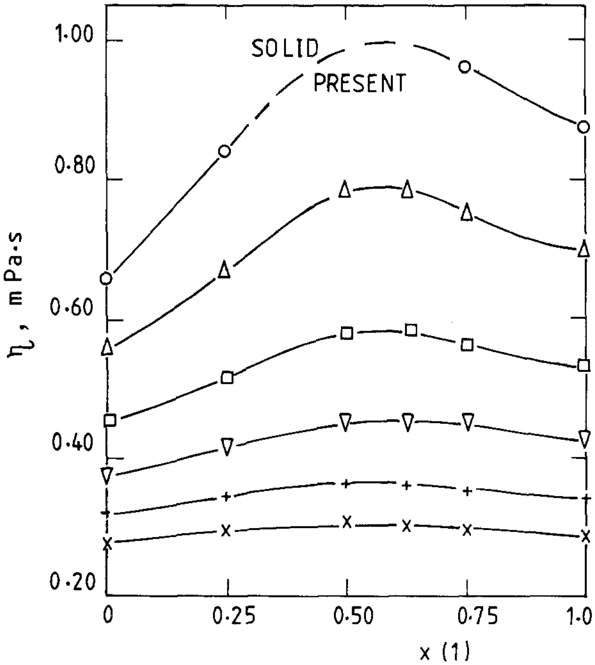

Fig. 4. Composition dependence of the viscosity for hexafluorobenzene(1) + mesitylene(2). Key as in the legend to Fig. 2.

Table VIII. Viscosity Coefficients and Densities of Hexafluorobenzene(1) + Toluene(2) Mixtures

$x(1)$	T (°C)	η (mPa·s)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})
0.256 5	15.00	0.701	1 072.5	0.653
	25.00	0.607	1 060.3	0.572
	40.00	0.502	1 041.8	0.482
	60.00	0.400	1 016.6	0.394
	80.00	0.332	990.7	0.335
	100.00	0.278	965.0	0.288
	120.00	0.240	938.9	0.256
0.501 9	15.00	0.843	1 260.7	0.669
	25.00	0.714	1 245.3	0.573
	40.00	0.572	1 222.0	0.468
	60.00	0.445	1 190.2	0.374
	80.00	0.359	1 157.2	0.310
	100.00	0.296	1 124.5	0.264
	120.00	0.250	1 091.5	0.229
0.743 1	15.00	0.951	1 440.8	0.660
	25.00	0.802	1 422.1	0.564
	40.00	0.637	1 393.8	0.457
	60.00	0.489	1 355.2	0.361
	80.00	0.388	1 315.1	0.295
	100.00	0.317	1 275.0	0.249
	120.00	0.262	1 234.9	0.212

plotted against the mole fraction of hexafluorobenzene for the four systems. Figure 1 also includes the results of Bedsole and Taylor [9] for the system hexafluorobenzene + benzene at 25°C. Their results fall below the present values up to about 0.7 mole fraction of hexafluorobenzene, after which they become higher than the present results. The maximum difference is 0.006 mPa · s at about 0.6 mole fraction of hexafluorobenzene.

The hexafluorobenzene + benzene system is the only system to show minima. These occur at about 0.12 mole fraction of hexafluorobenzene, with a slight shift to higher mole fractions at higher temperatures. The section between mole fractions of 0.25 and 1.0 shows a slight positive deviation at 25°C which decreases with increasing temperature and becomes negative at about 40°C. There are no minima for the system hexafluorobenzene + toluene but there are dips in the graph at low mole fractions of hexafluorobenzene. The peaking at higher mole fractions is more obvious this time but again it becomes less as the temperature increases.

Table IX. Viscosity Coefficients and Densities of Hexafluorobenzene(1) + *p*-Xylene(2) Mixtures

$x(1)$	T (°C)	η (mPa·s)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}$\times10^{-6}$)
0.149 5	25.00	0.634	960.3	0.660
	40.00	0.526	945.0	0.557
	60.00	0.423	924.4	0.458
	80.00	0.348	903.4	0.385
	100.00	0.295	882.4	0.334
	120.00	0.255	861.3	0.296
0.335 5	25.00	0.714	1 094.5	0.653
	40.00	0.578	1 075.9	0.537
	60.00	0.453	1 050.7	0.431
	80.00	0.367	1 024.8	0.358
	100.00	0.302	998.9	0.302
	120.00	0.255	972.9	0.262
0.504 5	25.00		Solid present	
	40.00	0.628	1 198.0	0.524
	60.00	0.481	1 168.1	0.411
	80.00	0.382	1 137.3	0.336
	100.00	0.314	1 106.4	0.284
	120.00	0.262	1 075.5	0.243
0.700 1	25.00	0.843	1 369.3	0.616
	40.00	0.665	1 343.0	0.495
	60.00	0.506	1 307.0	0.387
	80.00	0.399	1 269.8	0.314
	100.00	0.324	1 232.4	0.263
	120.00	0.269	1 195.1	0.225
0.875 2	25.00	0.861	1 506.7	0.572
	40.00	0.682	1 475.9	0.462
	60.00	0.523	1 433.7	0.364
	80.00	0.413	1 390.1	0.297
	100.00	0.338	1 346.3	0.251
	120.00	0.278	1 302.8	0.214

Similar characteristics are seen for the hexafluorobenzene + para-xylene system. The peaking disappears above 80°C in this instance and part of the 25°C isotherm is missing because some solid phase is present. The isotherms for the hexafluorobenzene + mesitylene system show maxima at about 0.55 mole fraction hexafluorobenzene, and although the maxima become smaller with increasing temperature, there is still a peak at 120°C.

The positive deviations from a rectilinear dependence on mole fraction observed in these systems provide evidence for enhanced interactions between the unlike species.

Table X. Viscosity Coefficients and Densities of Hexafluorobenzene(1) + Mesitylene(2) Mixtures

$x(1)$	T (°C)	η (mPa·s)	ρ (kg·m^{-3})	η/ρ (m^2·s^{-1}×10^{-6})
0.253 1	25.00	0.841	1 024.7	0.820
	40.00	0.670	1 009.0	0.664
	60.00	0.518	987.6	0.525
	80.00	0.417	966.4	0.431
	100.00	0.344	943.7	0.365
	120.00	0.294	921.3	0.320
0.506 7	25.00		Solid present	
	40.00	0.782	1 184.6	0.660
	60.00	0.579	1 157.0	0.500
	80.00	0.450	1 129.1	0.398
	100.00	0.365	1 099.3	0.332
	120.00	0.305	1 070.0	0.285
0.622 6	25.00		Solid present	
	40.00	0.784	1 269.8	0.617
	60.00	0.582	1 238.8	0.470
	80.00	0.452	1 207.0	0.374
	100.00	0.363	1 173.7	0.309
	120.00	0.299	1 140.7	0.262
0.751 4	25.00	0.959	1 394.4	0.688
	40.00	0.748	1 368.5	0.547
	60.00	0.562	1 332.5	0.422
	80.00	0.443	1 295.6	0.342
	100.00	0.354	1 258.7	0.281
	120.00	0.295	1 221.6	0.242

The measured values of molar excess volume are plotted as a function of temperature in Fig. 5, with literature values [22, 25, 41] for comparison. The accuracy of the present values is estimated to be ±0.04 cm^3 · mol^{-1}. There is excellent agreement with the literature values [22, 41] for hexafluorobenzene + benzene. The plots for each of the toluene mixtures lie below the results of Chen and Zwolinski [25] at 25°C and above the results of Duncan et al. [22] at 40°C. The present results for the para-xylene and mesitylene mixtures at 40°C are higher than those of Duncan et al. by 0.17 and 0.11 cm^3 · mol^{-1}, respectively.

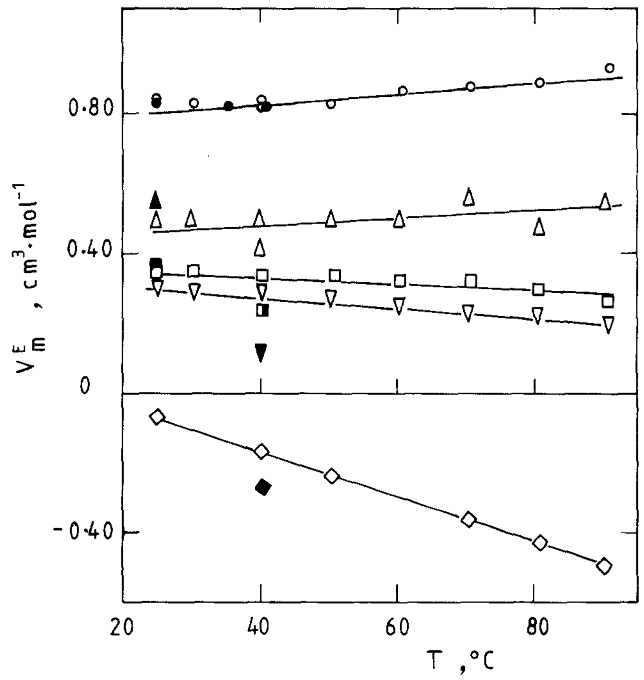

Fig. 5. Comparison of measured molar excess volumes with literature values for mixtures containing hexafluorobenzene. (○) + benzene(2) with $x_1 = 0.499$; (●) Ref. 41; (○) Ref. 22. (△) + Toluene(2) with $x_1 = 0.502$; (▲) Ref. 25; (◭) Ref. 22. (□) + Toluene(2) with $x_1 = 0.743$; (■) Ref. 25; (◨) Ref. 22. (▽) + p-Xylene(2) with $x_1 = 0.150$; (▼) Ref. 22. (◇) + Mesitylene with $x_1 = 0.702$; (◆) Ref. 22.

5. EXCESS FREE ENERGY OF ACTIVATION FOR VISCOUS FLOW

On the basis of the theory of absolute reaction rates [42], the excess free energy of activation for viscous flow $\Delta^* G^E$ may be calculated from

$$\Delta^* G^E = RT \left(\ln \eta V - \sum_i x_i \ln \eta_i V_i \right) \tag{3}$$

where η, V, η_i, and V_i are the viscosity coefficient and molar volume for the mixture and the viscosity coefficient and molar volume for pure component i, respectively.

The hexafluorobenzene + benzene system shows negative deviations from ideality at all mole fractions, the hexafluorobenzene + toluene and +

para-xylene systems show negative deviations at low mole fractions of hexafluorobenzene and positive deviations at higher mole fractions, and the hexafluorobenzene + mesitylene system shows positive deviations at all mole fractions. Typical graphs are shown in Figs. 6 and 7 for hexafluorobenzene + benzene and hexafluorobenzene + mesitylene. Δ^*G^E is estimated to be accurate to $\pm 25\ \mathrm{J \cdot mol^{-1}}$.

The well-defined peaks for the mesitylene system are symmetrical at about 0.5 mole fraction hexafluorobenzene, whereas for the toluene and para-xylene systems the peaks are shifted toward the higher mole fractions of hexafluorobenzene, the shifting increasing with increasing temperature.

Δ^*G^E appears to be strongly temperature dependent, but if Δ^*G^E is known to $\pm 50\ \mathrm{J \cdot mol^{-1}}$, then viscosity coefficients can be predicted to within 1%. Given these plots, the viscosity can be calculated at other temperatures and mole fractions with an accuracy approaching that of the actual measurements.

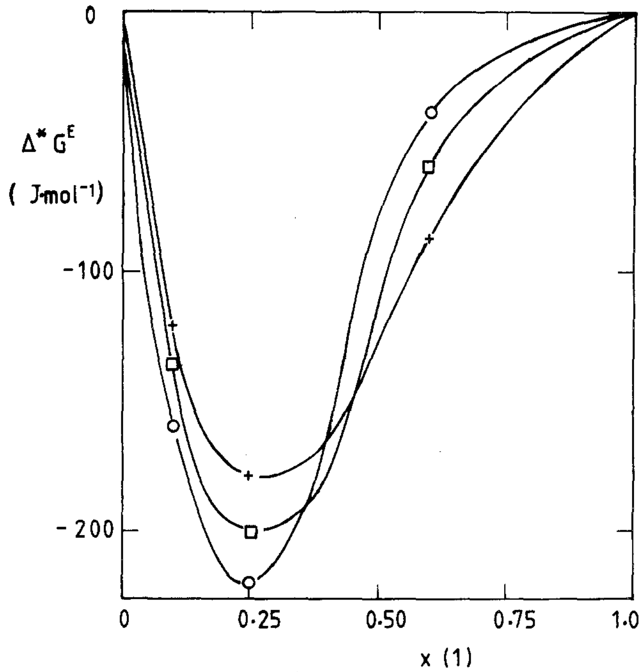

Fig. 6. Variation of Δ^*G^E with composition at different temperatures for hexafluorobenzene(1) + benzene(2). Key as in the legend to Fig. 1.

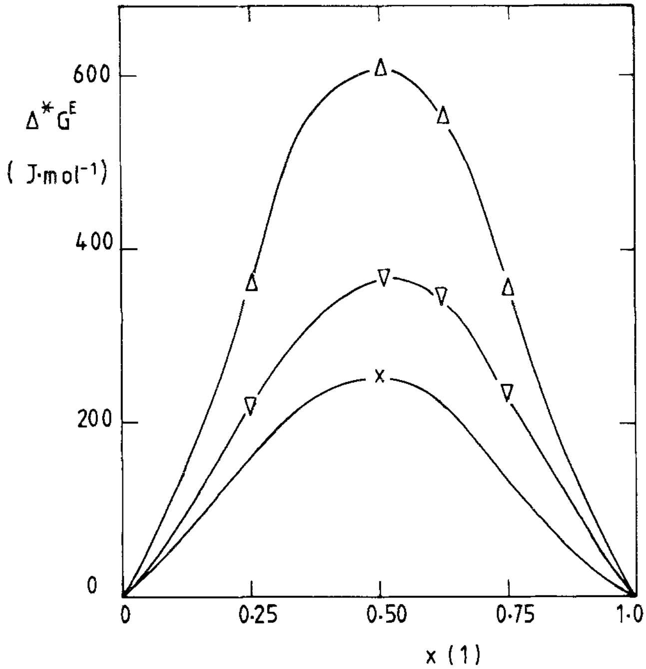

Fig. 7. Variation of Δ^*G^E with composition at different temperatures for hexafluorobenzene(1) + mesitylene(2). Key as in the legend to Fig. 2.

6. THE GRUNBERG AND NISSAN EQUATION

Irving [43] found that the Grunberg and Nissan equation [44]

$$\ln \eta = x_1 \ln \eta_1 + x_2 \ln \eta_2 + x_1 x_2 G \qquad (4)$$

gave the best overall fit of 25 equations tested for representing the viscosity coefficient of 318 binary mixtures at atmospheric pressure. The parameter G is plotted against the mole fraction of hexafluorobenzene for the systems hexafluorobenzene + mesitylene and hexafluorobenzene + toluene in Fig. 8 and for hexafluorobenzene + para-xylene and hexafluorobenzene + benzene in Fig. 9. G is estimated to be accurate to ±0.02 for equimolar mixtures, but the uncertainty increases to ±0.08 for mole fractions of 0.1. Figure 9 also includes approximate values of G for the system hexafluorobenzene + cyclohexane at 30°C which were calculated from the relative viscosities reported by Watkins and Brey [45].

G decreases in going from the mesitylene mixtures through the para-xylene and toluene mixtures to the benzene and cyclohexane mixtures,

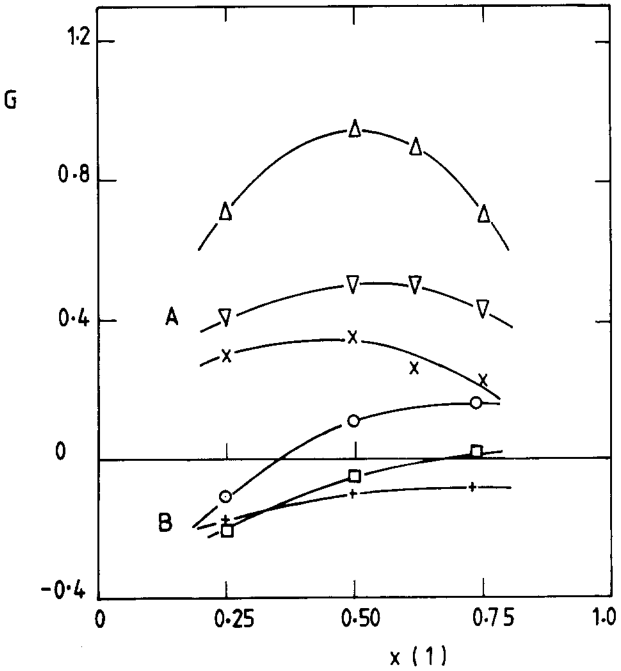

Fig. 8. Variation of Grunberg *G* with composition at different temperatures for hexafluorobenzene(1) + mesitylene (A) and +toluene (B). Key as in the lengend to Fig. 2.

although there is some overlap for para-xylene and toluene. For mesitylene, there is a peak in the graph which becomes less as the temperature increases. Para-xylene shows a smaller peak, and toluene smaller still. The peak disappears for both systems at higher temperatures. Benzene and cyclohexane show no peak. The temperature dependence of *G* is greatest for hexafluorobenzene + mesitylene and least for hexafluorobenzene + benzene.

The dependence of *G* on temperature and mole fraction must be taken into account for accurate prediction of viscosity for these systems.

7. THE EYRING EQUATION

One of the predictions of Eyring's theory of absolute reaction rates is that the logarithm of the viscosity coefficient should be a linear function of $1/T$. In practice, for these systems, graphs of $\ln \eta$ against $1/T$ are generally convex toward the $1/T$ axis but a linear equation fits the data to the accuracy shown in Table XI.

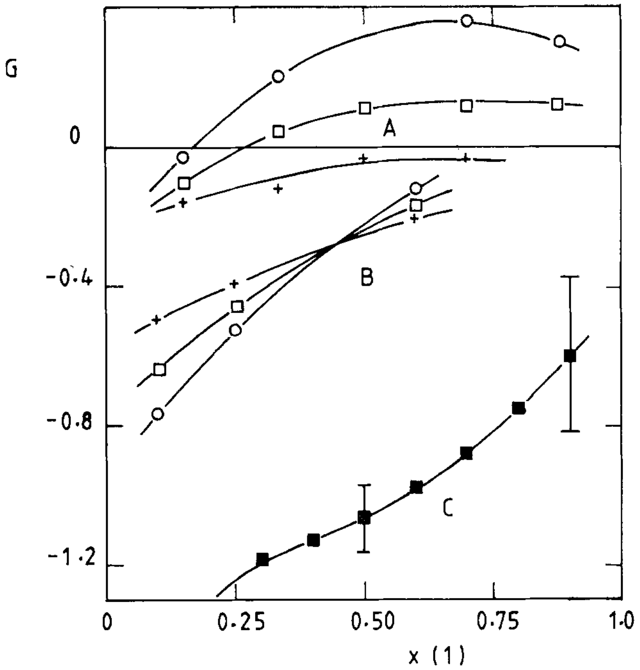

Fig. 9. Variation of Grunberg G with composition at different temperatures for hexafluorobenzene(1) + p-xylene (A), +benzene (B), and +cyclohexane (C) (■). Ref. 45. Key as in the legend to Fig. 2.

The coefficients of the equation in reciprocal temperature vary smoothly with the mole fraction for each system. However, the variation in the coefficients is not in accordance with the predictions of Eyring's theory, a fact which limits the usefulness of this type of two-parameter equation for summarizing data.

8. THE HILDEBRAND EQUATION

Following the work of Batschinski [46], Hildebrand [47] proposed that the fluidity φ of a fluid was given by

$$\varphi = 1/\eta = B(V - V_0)/V_0 \tag{5}$$

where $V \rightarrow V_0$ as $\varphi \rightarrow 0$ and B is a parameter related to the capacity of the molecule to absorb externally imposed momentum. Ertl and Dullien [48] showed that deviations normally occur at reduced temperatures below 0.46. Fluidity was fitted to an equation linear in molar volume for each pure liquid and each mixture. For the results presented here, which correspond to

Table XI. Effectiveness of the Eyring and Hildebrand Equations

Mole fraction of C_6F_6	Temperature range (°C)	Eyring equation % deviations		Hildebrand equation % deviations	
		rms	Max	rms	Max
		(a) Hexafluorobenzene + Benzene			
0.0	25–100	0.25	0.34	0.26	0.44
0.106	25–100	0.25	0.39	0.20	0.32
0.252	25–100	0.26	0.38	0.22	0.36
0.599	25–100	0.34	0.48	0.42	0.68
1.0	25–100	0.31	0.39	0.54	0.97
		(b) Hexafluorobenzene + toluene			
0.0	15–120	0.26	0.41	0.59	1.05
0.256	15–120	0.64	0.97	0.31	0.52
0.502	15–120	0.92	1.45	0.42	0.94
0.743	15–120	0.61	0.95	1.28	2.77
1.0	15–120	0.53	0.85	1.22	2.69
		(c) Hexafluorobenzene + para-xylene			
0.0	25–120	0.12	0.19	0.32	0.58
0.150	25–120	0.44	0.66	0.24	0.31
0.335	25–120	0.36	0.54	0.71	1.28
0.505	40–120	0.42	0.53	0.40	0.61
0.700	25–120	0.61	0.87	0.84	1.71
0.875	25–120	0.46	0.64	0.97	1.81
1.0	25–120	0.35	0.51	0.84	1.68
		(d) Hexafluorobenzene + mesitylene			
0.0	25–120	0.24	0.38	0.17	0.35
0.253	25–120	1.13	1.61	0.43	0.62
0.507	40–120	1.21	1.52	0.49	0.83
0.623	40–120	0.66	0.79	0.39	0.69
0.751	25–120	0.85	1.15	1.07	2.05
1.0	25–120	0.35	0.51	0.84	1.68

reduced temperatures above 0.46, Hildebrand's equation was generally able to reproduce the viscosities to well within 2% as shown in Table XI.

The composition dependence of B and V_0 for these systems can be represented by

$$V_0(x) = x_1 V_{01} + x_2 V_{02} + x_1 x_2 [a_0 + b_0(x_1 - x_2)] \tag{6}$$

and

$$B(x) = x_1 B_1 + x_2 B_2 + x_1 x_2 [c_0 + d_0(x_1 - x_2)] \tag{7}$$

Table XII. Values of the Constants in Eqs. (6) and (7)

Liquid	V_0 ($cm^3 \cdot mol^{-1}$)	B ($mPa^{-1} \cdot s^{-1}$)
Hexafluorobenzene	106.7	13.3
Benzene	82.2	18.7
Toluene	97.6	19.1
p-Xylene	114.2	19.4
Mesitylene	129.3	18.9

System	a_0 ($cm^3 \cdot mol^{-1}$)	b_0 ($cm^3 \cdot mol^{-1}$)	c_0 ($mPa^{-1} \cdot s^{-1}$)	d_0 ($mPa^{-1} \cdot s^{-1}$)
Hexafluorobenzene + benzene	2.5	3.9	1.9	1.2
Hexafluorobenzene + toluene	4.2	3.7	2.9	2.6
Hexafluorobenzene + *p*-xylene	5.7	0.7	4.6	−1.2
Hexafluorobenzene + mesitylene	10.8	0.1	5.6	−0.6

where V_{0i} and B_i are the values of V_0 and B for pure component i. The constants a_0, b_0, c_0, and d_0 are listed for each system in Table XII. Hexafluorobenzene is always taken as component 1. It is to be noted that V_0 shows increasing deviation from a linear dependence on mole fraction as the number of methyl groups on the aromatic hydrocarbon increases. Modifications [49] of Hildebrand's equation which assume that V_0 for a mixture is linearly related to the V_0 values for the pure components can result in viscosities which disagree with experimental values by over 11% for these systems.

9. CONCLUSIONS

Viscosity coefficients for binary mixtures of hexafluorobenzene with benzene, toluene, para-xylene, and mesitylene have been measured at temperatures from 15 to 120°C using specially designed capillary viscometers which enable measurements to be made along the saturation line, even above the normal boiling point. Densities were measured using a pyknometer and volume-change apparatus. Viscosity coefficients are estimated to be accurate to 0.5%; densities are estimated to be accurate to $\pm 0.1\ kg \cdot m^{-3}$ at temperatures up to 50°C, rising to $\pm 0.3\ kg \cdot m^{-3}$ at 120°C.

Values for the molar excess Gibbs free energy of activation for viscous flow are strongly temperature dependent in these systems, and values of the

Grunberg and Nissan parameter G depend on the temperature and mole fraction. The Eyring equation gives a reasonable fit to the temperature dependence of the viscosity coefficient for each liquid and mixture, but the variations of the coefficients of the equation in reciprocal temperature are not in accordance with the predictions of Eyring's theory. Hildebrand's equation generally fits the data for a liquid of given composition to well within 2%. The parameter V_0 varies approximately linearly with the mole fraction of hexafluorobenzene in the system hexafluorobenzene + benzene, but there are increasing positive deviations from linearity as the number of methyl groups on the aromatic hydrocarbon increases.

The composition dependence of these measured viscosity coefficients is consistent with enhanced interactions in these binary mixtures which increase in strength with increasing number of methyl groups on the aromatic hydrocarbon and which decrease in strength as the temperature is raised.

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