Journal of Fluorine Chemistry, 10 (1977) 507 - 521

Received: July 22, 1977

THE MIXING PROPERTIES OF HEXAFLUOROBENZENE WITH CARBON TETRACHLORIDE AND WITH PERFLUOROMETHYLCYCLOHEXANE

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SUMMARY

Excess thermodynamic functions (free energies, enthalpies and entropies of mixing) have been obtained from measurements of vapour pressures, together with excess volumes of mixing, for mixtures of hexafluorobenzene with carbon tetrachloride and with perfluoromethylcyclohexane (tetradecafluoromethylcyclohexane). Deviations from thermodynamic ideality are large, although the systems are completely miscible. Critical temperatures of the mixtures are also reported. A correlation between the data, anticipated from a simple model for mixtures of asymmetric molecules, does not obtain.

INTRODUCTION

Liquid mixtures of aliphatic perfluorocarbons have attracted considerable interest [1,2,3] on account of their large deviations from thermodynamic ideality, which in some cases of mixtures with essentially non-polar substances such as hydrocarbons, manifest themselves in limited miscibility. The development of convenient methods for the preparation of polyfluoroaromatic compounds, particularly by defluorination processes [4], made it possible to investigate the physical properties of polyfluoroaromatic compounds and their mixtures. The properties of liquid mixtures of hexafluorobenzene and cyclohexane have been studied [5,7], and special interest has been taken in the properties of mixtures of polyfluoroaromatic compounds with aromatic hydrocarbons [5,6,8,9], since solid complexes are formed between many such pairs of compounds, the simplest example being that formed from hexafluorobenzene and benzene [5,8].

The present paper presents some results of investigations of the liquid mixtures formed from hexafluorobenzene and carbon tetrachloride, and from hexafluorobenzene and perfluoromethylcyclohexane. The results comprise the excess free energies, excess heats, and excess entropies of mixing, obtained from measurements of the vapour pressures of the mixtures at temperatures between 20 °C and 50 °C, the volumes of mixing in the same range of temperature, and the critical temperatures of the mixtures. It is supposed that the critical temperatures give some information about intermolecular interactions. Relationships between the results are discussed in the context of mixtures of hexafluorobenzene on the basis of some theoretical models.

EXPERIMENTAL

The vapour pressures of the liquid mixtures, which will be presented in greater detail elsewhere [10], were measured using a static manometric system similar to that described by Waddington, Scott and others [11]. Hexafluorobenzene (supplied by Imperial Smelting Co.), perfluoromethylcyclohexane (prepared in this Department), and carbon tetrachloride (Analar B.D.H.), were purified carefully before use [17]. Vapour pressures of hexafluorobenzene and carbon tetrachloride agreed closely with the more precise of the respective available literature values [7,12,13]. Those for perfluoromethylcyclohexane agreed with values of Rowlinson and Thacker [16]. The vapour pressures of the mixtures were treated using the method of Barker [14] to obtain the excess free energy of mixing, as a function of composition, at each of the temperatures at which measurements were made. Allowance was made for virial coefficients, but the cross-virial coefficients were taken as arithmetic means of the virial coefficients of the pure components. From the variation of the excess free energy with temperature at any composition was calculated the excess entropy of mixing, and hence the excess heat of mixing.

The critical temperatures of mixing were measured in an apparatus based upon that of Ambrose and Grant [15]. Values of the critical temperatures of pure compounds measured with the apparatus accorded well with literature values.

The excess volumes of mixing close to room temperature were obtained from measurements of density.

RESULTS

Excess properties of liquid mixtures

The excess free energies (g^E), enthalpies (h^E), and entropies (s^E, reported as Ts^E), for the liquid mixtures are presented in Tables 1 and 2. The values given have been calculated from the Scatchard parameters

TABLE 1

Excess properties for mixture C_6F_6 - CCl_4

$x(C_6F_6)$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Temperature 25 °C									
g^E/J mol^{-1}	132	218	265	282	270	239	194	136	71
h^E/J mol^{-1}	282	517	627	702	690	613	481	353	183
Ts^E/J mol^{-1}	150	299	362	420	420	374	287	217	112
Temperature 50 °C									
g^E/J mol^{-1}	120	195	231	246	236	210	171	122	65
h^E/J mol^{-1}	282	520	623	782	690	616	482	352	187
Ts^E/J mol^{-1}	162	325	392	456	456	406	311	230	122

TABLE 2

Excess properties for mixture C_6F_6 - $C_6F_{11}CF_3$

$x(C_6F_6$	0.1	0.2	0.3	0.4	0.5	0.6	0.7	0.8	0.9
Temperature 25 °C									
g^E/J mol^{-1}	179	305	389	439	456	444	400	318	189
h^E/J mol^{-1}	601	903	1038	1125	1159	1147	1061	887	611
Ts^E/J mol^{-1}	422	598	649	686	703	703	661	569	422
Temperature 50 °C									
g^E/J mol^{-1}	138	250	333	385	405	183	345	264	149
h^E/J mol^{-1}	598	899	1036	1130	1166	944	1060	879	609
Ts^E/J mol^{-1}	460	649	703	744	761	761	715	615	460

A_g, B_g and C_g in the equations

$$g^E = x_1x_2[A_g + B_g(x_1 - x_2) + C_g(x_1 - x_2)^2]$$

where x_1 and x_2 are the mole fractions of components 1 and 2 respectively used to represent the excess free energies of mixing. These quantities will be presented fully in a forthcoming paper [17]. The entropies of mixing were derived from the smoothed variation of g^E with T, and h^E then obtained using the standard relationship

$$h^E = g^E + Ts^E$$

Both mixtures show azeotropic (low boiling) behaviour.

The volumes of mixing obtained from measured densities are presented in Tables 3 and 4. The precision of the measurements of density may be such as to cause errors of as much as ± 0.03 $cm^3\ mol^{-1}$ in these quantities.

TABLE 3

Volumes of mixing (v^E) for mixture C_6F_6 - CCl_4

$x(C_6F_6)$	0.256	0.478	0.737
$v^E/cm^3\ mol^{-1}$	0.81	0.89	0.63

TABLE 4

Volumes of mixing (v^E) for mixture C_6F_6 - $C_6F_{11}CF_3$

$x(C_6F_6)$	0.291	0.400	0.528	0.706	0.808
$v^E/cm^3\ mol^{-1}$	0.64	0.81	0.83	0.62	0.56

Critical temperatures

The critical temperatures of the mixtures are presented in Table 5. The critical temperatures measured in this study for the pure compounds are:

C_6F_6 T^c = 243.40 °C (best lit. value 243.57 °C [12])

CCl_4 T^c = 283.2 °C (best lit. value 283.2 °C [3])

$C_6F_{11}CF_3$ T^c = 213.3 °C (lit. values: 213.6 °C [16]; 213.4 [18])

TABLE 5

Critical temperatures of mixtures (Component 1 is C_6F_6)

x_1	$T^c/(°C)$	x_1	$T^c/(°C)$	x_1	$T^c/(°C)$
		Mixture:	C_6F_6 - CCl_4		
0.098	277.15	0.103	275.8	0.107	275.8
0.304	265.2	0.292	265.5	0.403	259.3
0.415	259.15	0.590	252.95	0.599	252.7
0.787	247.65	0.802	247.4		
		Mixture:	C_6F_6 - $C_6F_{11}CF_3$		
0.227	216.05	0.538	222.7	0.557	199.25
0.400	219.15	0.401	219.1	0.594	210.1
0.721	229.2	0.727	229.5	0.333	193.15
0.866	236.1				

The critical temperatures (T^c) measured (°C) can be represented by equations of the type

$$T^c = x_1T_1{}^c + x_2T_2{}^c + x_1x_2[A_c + B_c(x_1 - x_2) + C_c(x_1 - x_2)^2]$$

where $T_1{}^c$ and $T_2{}^c$ are the critical temperatures respectively of pure components 1 and 2, and the terms x are mole fractions. Values of A_c, B_c and C_c are given in Table 6.

TABLE 6

Values of coefficients in equation for critical temperatures of mixtures $T^c = x_1T_1^c + x_2T_2^c + x_1x_2[A_c + B_c(x_1 - x_2) + C_c(x_1 - x_2)^2]$

Mixture	A_c	B_c	C_c
C_6F_6 - CCl_4	-28.85	+7.08	+4.79
C_6F_6 - $C_6F_{11}CF_3$	-26.80	-4.40	+3.81

DISCUSSION

The excess free energies of mixtures of hexafluorobenzene with carbon tetrachloride show maximal values when the mole fraction of hexafluorobenzene is about 0.43. In this respect the mixtures are not regular in the sense (g^E proportional to x_1x_2) that the term is often used [3]. The maximal free energies for the system hexafluorobenzene-perfluoromethylcyclohexane occur in almost equimolar solutions. These mixtures are therefore more nearly regular in the accepted sense. The substances involved have significantly different molar volumes (V_m/cm^3 mol^{-1} at 25 °C: C_6F_6, 116; CCl_4, 97; $C_6F_{11}CF_3$, 196). Some theoretical models [2] suggest that for molecules that differ in size, the excess free energies for simple systems (having other attributes of so-called "regular" solutions) should be symmetrical functions of volume fractions, rather than mole fractions. It is striking, therefore, that of the cases studied here, the mixture whose components differ most in molar volume, namely C_6F_6 - $C_6F_{11}CF_3$, shows properties that are the more nearly symmetrical with respect to molarity.

Table 7 summarises the properties of equimolar mixtures of hexafluorobenzene (at 30 °C), including some not studied by ourselves, together with the properties of analogous mixtures. The deviations from ideal behaviour are greater for the system C_6F_6 - CCl_4 than for the system C_6H_6 - CCl_4. Those for the fluorocarbon aromatic-aliphatic system (C_6F_6 - c-$C_6F_{11}CF_3$), although large, are not overwhelmingly greater than those shown by the most nearly analogous hydrocarbon system (C_6H_6 - c-C_6H_{12}). The deviations shown by the aromatic fluorocarbon-aliphatic hydrocarbon system (C_6F_6 - c-C_6H_{12}), are greater than in the last-named system, but significantly smaller than are generally observed in aliphatic fluorocarbon-aliphatic hydrocarbon systems in which limited miscibility sometimes occurs [2]. Very notably the properties of the system C_6F_6 - C_6H_6 differ from the others reported. It is tempting to attribute the difference to the formation in the liquid mixture of a complex related to that which is formed as a solid at lower temperatures [6,8]. The negative heats of mixing (h^E) for this, and for other aromatic hydrocarbon-aromatic fluorocarbon systems [20,34] support the belief in formation of complexes. Gaw and Swinton [19] have made a plausible interpretation of g^E for this system to find the equilibrium constant for formation of the complex (see also [36]). That the volume of mixing of the C_6F_6 - C_6H_6 system is smaller than that for the C_6F_6 - c-C_6H_{12} system has also been used as evidence of complexing [23].

TABLE 7

Mixing properties of hexafluorobenzene and of related compounds (30 °C) in equimolar mixtures

Mixture	g^E/J mol^{-1}	h^E/J mol^{-1}	v^E/cm^3 mol^{-1}	References
C_6F_6 - CCl_4	260	650	0.90	This work
C_6H_6 - CCl_4	81	127	0.1	[3] (a)
C_6F_6 - $C_6F_{11}CF_3$	450	1160	0.80	This work
C_6H_6 - c-C_6H_{12}	300	800	0.66	[3] (a)
C_6F_6 - c-C_6H_{12}	801	1543	2.56 (c)	[7] (b)
C_6F_6 - C_6H_6	-60	-530 (b) (-540 (25 °C))	0.86 (c)	[19][6][23] [20]

(a) The values given are taken from, or interpolated from, values in work cited in this reference.

(b) Estimated (this work) from g^E as function of T given in ref.[19].

(c) The values given by the references cited ([6],[23]) are in good but not exact agreement.

The formation of a solid complex from two substances does not, of course, require the formation of a complex in solution, and, as we shall see, the formation of a complex in the liquid phase of the system C_6F_6 - C_6H_6 has been disputed [22].

Hildebrand's theory of solutions [2], despite its many successes, does not give good estimates of g^E for the mixtures investigated. For the system C_6F_6 - CCl_4 the Hildebrand estimate is too small (about 20 J mol^{-1}); for the system C_6F_6 - $C_6F_{11}CF_3$ it is too large (about 670 J mol^{-1}). These estimates do not correspond with the measured heats of mixing to which the arguments of the Hildebrand theory [2] might relate them more directly. The reasons for the discrepancies are easily understood. Scott has pointed out [25] that Hildebrand's theory is able to account well for systems if deviations from ideality are small (g^E less than about 250-400 J mol^{-1}). A critical assessment by McGlashan [26] suggests that even for such situations the predictive power of the theory is limited. More particularly the theory supposes that the excess entropy of mixing (s^E) should be small. (The criterion of relative smallness strictly applies to Ts^E, which is directly involved in g^E, rather than to s^E). In the solutions considered the contributions to g^E by s^E are significant.

It is customary to consider thermodynamic properties such as here presented in terms of more sophisticated theories of liquid mixtures. The theories most frequently used suppose that the substances involved share a common form of intermolecular potential. A necessary consequence is that the substances should obey a common equation of state. Pitzer [27,28] has defined a measure of the deviation of the thermodynamic properties of a substance from those predicted by the corresponding state formulation which represents closely the behaviour of the noble gases. Pitzer's analysis is essentially empirical, but follows forms suggested by treatments of molecules that do not possess spherically symmetrical intermolecular potentials. The measure used is the acentric factor, ω, which is the larger for substances which differ the more greatly from the inert gases. The acentric factors are notably greater for fluorocarbons than for analogous hydrocarbons. Examples of ω are c-C_6H_{12}, about 0.3; CCl_4, 0.19; C_6H_6, 0.22; $CF_3C_6F_{11}$, 0.45; C_6F_6, 0.40. (These values have been obtained from vapour pressures (extrapolated from or given in papers cited herein), critical temperatures and critical pressures, using Pitzer's elementary definition of ω. Critical constants not available in other references cited were obtained from ref.[29]).

In consequence it is unlikely that the simpler theories used will account well for the mixtures of present interest. The properties of the system C_6F_6 - c-C_6H_{12} have, however, been fitted [7] with some success to Prigogine's theory of conformal solutions [30]. We prefer here, for reasons given below, to treat the results on the basis of a theory for molecules which are not spherically symmetrical, that is having non-central intermolecular forces.

Rowlinson [3,31,32] has considered the properties of substances whose intermolecular potentials contain only a repulsive term (proportional to r^{-12}, where r is intermolecular distance) and one attractive term (proportional to r^{-6}), which is not spherically symmetrical. The deviations of the properties from those of analogous molecules with spherically symmetric intermolecular potentials (i.e. having Lennard-Jones, inverse 6-12 potentials), are measured by parameters δ, similar in character to Pitzer's ω. An explicit treatment of mixtures of molecules that possess such fields of force has been developed [33]. This treatment seems subsequently to have been applied only to simple molecules [35], but was applied recently [22] to some mixtures of hexafluorobenzene. For this reason we use it here.

We write [3] for the potential between a pair of molecules 1 and 2, at separation r,

$$u_{12}(r) = f_{12}\, u_{00}(r/g_{12})$$

where u_{00} is the intermolecular potential for a standard substance,

$$f_{12} = \varepsilon_{12}/\varepsilon_{00}$$
$$g_{12} = \sigma_{12}/\sigma_{00}$$

where the ε's and σ's are, respectively, the intermolecular energy parameters and molecular radii for the 1-2 and standard pairs.

The intermolecular potential for a pair of spherically symmetrical molecules is the starting point for the development of the treatment. If the attractive force is not spherically symmetrical, the effect (for small perturbations of symmetry) is (a) to reduce each of the "collision diameters", g_{11}, g_{12} and g_{22}, by a factor $[1 - \delta_{11}/3]$, $[1 - \delta_{12}/3]$, and $[1 - \delta_{22}/3]$, respectively, where the terms δ are the respective Rowlinson asymmetric factors, and (b) to increase the depths of the potentials for 1-1, 1-2, and 2-2, interactions by factors $(1 + 2\delta_{11})$, $(1 + 2\delta_{12})$ and $(1 + \delta_{22})$ respectively [3,31,33]. The properties of a mixture may be written in terms of the differences:

$$e_{12} = (2\varepsilon_{12} - \varepsilon_{11} - \varepsilon_{22})/\varepsilon_{oo}$$

$$s_{12} = (2\sigma_{12} - \sigma_{11} - \sigma_{22})/\sigma_{oo}$$

$$d_{12} = 2\delta_{12} - \delta_{11} - \delta_{22}$$

For the liquid mixtures we then have [33]

$$g^E/x_1x_2 = e_{12}[U]_o - 3s_{12}[RT]_o + d_{12}[2U + RT]_o$$

$$h^E/x_1x_2 = e_{12}[U - T(\partial U/\partial T)_p]_o$$

$$v^E/x_1x_2 = -e_{12}[T(\partial V/\partial T)_p]_o + 3s_{12}[V]_o - d_{12}[V + 2T(\partial V/\partial T)_p]_o$$

The subscripts o after the brackets refer to the standard substance, U, being the configurational energy, and V the volume. To the degree of approximation underlying these relationships, it makes no difference whether or not the standard substance is spherically symmetrical [33]. We have taken benzene as standard substance as in the original paper, and have used the values given in that paper for the several terms, (U, V, etc.), supplementing these with values interpolated or taken from standard sources (API Circular 44). The equations presented imply regularity of the solutions in the sense specified above. This is only approximately true for these mixtures, and is untrue for the system C_6H_6 - C_6F_6. No theories have attempted to predict terms d_{12} (or δ_{12} with respect to δ_{11} and δ_{22}). Other work has supposed $d_{12} \neq 0(e_{12}=0)$ or $e_{12} \neq 0(d_{12}=0)$ [3,33], that is, limiting cases. The terms δ are functions of temperature, being simply proportional to T^{-1} [3,33]. This is not always properly acknowledged. Pitzer's acentric factors, to which the terms δ are related, are not, from their definition and use, functions of temperature. We have calculated the terms e_{12}, s_{12} and d_{12} for the several mixtures listed in Table 7, using the relevant data, (g^E, h^E, v^E), at 25 °C. (The last procedure necessitated extrapolation of data in some cases, but was followed so as to make maximum use of information in ref.[33]). It is of interest to observe that, using the derived values of the parameters, it is possible to estimate well the measured values of g^E, h^E and v^E for the mixtures, except C_6F_6 - C_6H_6, at higher temperatures (50 °C or 70 °C) without taking account of any variation of d_{12} with temperature. (This success may result from the relative smallness of the range of temperature. The maximum change in d_{12} would amount only to about 10%). The fit for the case of C_6F_6 - C_6H_6 is, however, very poor. Even at the lowest temperature, g^E passes from positive values to negative values as $x(C_6F_6)$ is increased. The forms of Rowlinson's equations do not allow such changes with composition. The equations should not therefore be used to account for the behaviour of this system.

It is generally supposed that critical temperatures of substances are determined in large measure by intermolecular energies. The critical temperatures of mixtures have been used to give some information about the interactions between the molecules involved. Simple analysis [3] of critical temperatures of spherically symmetrical molecules leads to an expression of the form [3]

$$T^c(x_1,x_2) - x_1\,T_1{}^c - x_2\,T_2{}^c = x_1\,x_2\,t^E\,T_o{}^c$$

for the critical temperature $T^c(x_1,x_2)$ of a binary mixture containing respectively mole fractions x_1 and x_2 of components whose critical temperatures are $T_1{}^c$ and $T_2{}^c$. $T_o{}^c$ is the critical temperature of a standard substance, here, and often elsewhere [3,35,37], taken as the arithmetic mean of the critical temperatures of the two components.
In the simplest case, ignoring terms of higher order, which are however not always negligible and which may not be so [35] in this case, we may write

$$e_{12} = t_{12}{}^E$$

If the molecules are not spherically symmetrical, $t_{12}{}^E$ must involve the Rowlinson asymmetric factors δ, and, to the same order of approximation as just supposed, we may write

$$e'_{12} = t_{12}{}^E = e_{12} + 2d_{12}$$

(This follows from equations given in ref.[3]). Unless there is good reason to do so, the term in d_{12} should not be ignored as has been done [22].
We have calculated e'_{12}, by ignoring the terms in Table 6 that describe the slight asymmetry in the dependences of T^c on composition for the respective mixtures, and setting

$$e'_{12} = t_{12}{}^E = A_c/T_o{}^c$$

where $T_o{}^c = (T_1{}^c + T_2{}^c)/2$. We tabulate the values of e'_{12} for the mixtures we have studied, together with values reported for the other mixtures, in Table 8.

TABLE 8

Parameters derived from properties of mixtures

Mixture	From low temperature properties			From T^c
	e_{12}	s_{12}	d_{12}	e'_{12}
C_6F_6 - CCl_4	-0.00969	+0.004619	-0.01343	-0.0513
C_6H_6 - CCl_4	-0.01369	+0.00039	+0.00152	
C_6F_6 - $C_6F_{11}CF_3$	-0.07142	+0.00661	+0.05980	-0.0477
C_6H_6 - c-C_6H_{12}	-0.00315	-0.00263	-0.01911	-0.033 [21]
C_6F_6 - c-C_6H_{12}	-0.08757	+0.02111	-0.01092	-0.104 [22]
C_6F_6 - C_6H_6	-0.05970	+0.02404	+0.03208	-0.0776 [22]

There appears to be no simple correlation between the values of e'_{12} and the values of e_{12} which best fit the low temperature properties. Values of e'_{12} may not therefore be used directly with low temperature properties to test any hypothesis regarding the nature of intermolecular forces in cases that may show asymmetry, as was done recently, [22], in an analysis of data for mixtures of hexafluorobenzene. The analysis assumed that values obtained for e'_{12} from measurements of critical temperatures could be identified with e_{12} and used to correlate properties of the mixtures at low temperature, using Rowlinson's equations for molecules with non-central forces. It was concluded that the properties of the system C_6F_6 - C_6H_6 might be due to a combination of the imbalance in the intermolecular interactions and of the non-central components of these interactions, and it was suggested that the finding did away with the need to assume the involvement of complexes in this mixture. Although this last suggestion may yet prove to be correct, for reasons given in this paper it cannot be regarded as proved by the arguments offered in its favour.

We have attempted to calculate e_{12} from values of e'_{12} for the mixtures by assuming that

$$d_{12}(c)/d_{12}(303\ K) = T_o^c/303$$

where $d_{12}(303)$ is the value of d_{12} at 30 °C, and T_o^c, for the want of a better approximation, the value of temperature to which e'_{12} refers. This supposes the form of temperature-dependence usually ascribed to δ's and d_{12} [3]. The values of $d_{12}(c)$, (corresponding to T_0^c) have been used to estimate e_{12} (from $e'_{12} = e_{12} + 2d_{12}$). The values so obtained for e_{12} are inconsistent with the low-temperature values in Table 6. Further investigation might be of interest. Higher order terms [3,33,37] in the expression for e'_{12} or t_{12}^E might profitably be taken into account.

In conclusion we acknowledge that hexafluorobenzene mixes more readily with a wide range of substances, including aliphatic perfluorocarbons, although the solutions may show very significant deviations from ideality. The complexing which occurs between hexafluorobenzene and aromatic hydrocarbons to form solid complexes may also persist in solution. We are further persuaded that this might be so by the observation by Dantzler [36] of formation of a complex between hexafluorobenzene and benzene. Hexafluorobenzene may be regarded as an exceptional solvent amongst non-polar solvents [24]. It mixes readily with aliphatic hydrocarbons which are not always mutually miscible.

ACKNOWLEDGEMENTS

We thank the Imperial Smelting Company for a gift of hexafluorobenzene, and Dr A. E. Pedler, of this Department, for a supply of perfluoromethylcyclohexane. Dr G. S. Prosser made some early investigations of the mixtures studied. M.L.O. and F.T. acknowledge with gratitude maintenance awards received from the University funds.

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