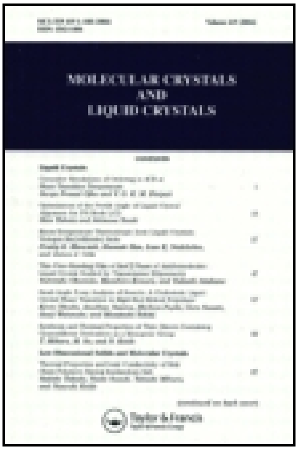

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Binary System Between Chlorobenzene and Hexafluorobenzene: Phase Diagram and Molecular Complex

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Binary System Between Chlorobenzene and Hexafluorobenzene: Phase Diagram and Molecular Complex

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Equilibrium phase diagram of the chlorobenzene-hexafluorobenzene binary system is experimentally determined by differential scanning calorimetry and X-ray diffraction analyses. This diagram is of the double eutectic type with a 1:1 crystalline molecular complex. The optimization of the complex thermodynamic quantities (melting temperature, melting enthalpy and first order polymorphic transition temperature) is carried out from the experimental data. The positive excess enthalpy of the melt resulting from repulsive interactions between C_6H_5Cl and C_6F_6 molecules is related to the low stability of the complex lattice.

Keywords: Molecular complexes; differential scanning calorimetry; X-ray diffraction; thermal analysis

INTRODUCTION

Binary systems based on organic compounds are known to give different types of structural alliances i.e. alloys and molecular complexes. It is well known that the syncrystallization is all the more extented as *i*) the degree of homeomorphism between the molecules of each component and *ii*) the degree of crystalline isomorphism between the pure components are high [1–4]: the resulting intermolecular interactions are more or less attractive. However, the formation of a molecular complex i.e. complexation results from specific interactions (charge-transfer between molecules of different type [5] or quadrupole-quadrupole interactions [6]) which stabilize the crystal lattice involving non isomorphous components. A special case lies with binary systems involving enantiomers: a racemate acts as a complex compound between the two non isomorphous enantiomers. In such a compound, compactness, symmetry and lattice energy should be the main factors explaining the racemate stability [7].

In order to determine criterions leading to these different types of complexes, we are looking into systems involving one highly fluorinated compound which may be enabled to give intermolecular bonds strengthened by charge-transfer mechanism or having an hydrogen-bonding character. In this way, the present work will give results on the chlorobenzene-hexafluorobenzene binary system: the phase diagram, estabilished by means of differential scanning calorimetry (DSC) and X-ray powder diffraction, shows the existence of a molecular complex 1:1 between chlorobenzene (Clbz) and hexafluorobenzene (6Fbz); the optimization of all experimental data enables the calculation of the liquidus lines and the determination of the Gibbs energy of the liquid phase; finally, a comparison with the homologous benzene-hexafluorobenzene binary phase diagram will be given.

EXPERIMENTAL

Clbz and 6Fbz are purchased from Aldrich (99. + and 99.5 + % grade respectively). Calorimetric measurements are made with a Perkin-Elmer DSC-7 differential scanning calorimeter. During the investigations, the following conditions are adopted:

- sample weight: 4 mg;
- heating and cooling rates: 2 K/mn;
- n independent measurements for each composition (generally $n = 6$).

Liquidus temperatures are determined from the DSC curves by using the shape-factor method [8]. The calibration procedure involved in these experiments is based on water, naphthalene and indium standards. The random part of the uncertainties during T-and enthalpy- measurements is estimated by the Student's method with 95% threshold of reliability. The systematic part is assumed to be ± 0.2 K for temperatures and 2% for enthalpies. Since the whole series of our experiments runs in the same conditions, the systematic parts are not reported in tables and diagrams. Experimental points given without uncertainty correspond to $n \leqslant 2$.

Crystallographic measurements concerning the pure components and mixed samples at selected regulated temperatures are made by means of

X-ray powder diffraction, using a Siemens D500 diffractometer. Diffraction measurements are also carried out versus continuous T variations with a Guinier-Simon camera (GS). In both cases, the wavelength of copper $K_{\alpha 1}$ radiation ($\lambda = 1.5406\,\text{Å}$) is used.

PURE COMPONENTS PROPERTIES

Clbz is known to crystallize with orthorhombic symmetry ($Pbcn$, $Z = 8$): the cell parameters measured at 208 K by [9] are $a = 13.66\,\text{Å}$, $b = 11.14\,\text{Å}$, $c = 7.20\,\text{Å}$. The temperature and enthalpy of melting are $T_{fus} = (228.0 \pm 0.6)$ K and $\Delta_{fus}H = (10380 \pm 160)$ J/mol respectively [10]; liquid vaporization is due to the high vapour pressure p^o which varies with temperature according to the following equation $\log p^o = 5.367 - 2141/T(hPa)$ [11].

6Fbz is of monoclinic symmetry ($P2_1/n$, $Z = 6$): its cell parameters at 120 K are $a = 16.82\,\text{Å}$, $b = 9.17\,\text{Å}$, $c = 5.76\,\text{Å}$, $\beta = 95.8°$ [12]). It melts at $T_{fus} = 278.2$ K [13] with the melting enthalpy $\Delta_{fus}H = (11490 \pm 103)$ J/mol [14]; 6Fbz is more volatile than Clbz ($\log p^o = 19.975 - 2525/T - 5.035 \log T$ (hPa) [15]): at 298.15 K, the vapour pressure values for Clbz and 6Fbz are respectively 0.015 hPa and 0.11 hPa.

For Clbz, our calorimetric results are very similar to the ones of [10]: $T_{fus} = (228.2 \pm 0.5)$ K, $\Delta_{fus}H = (10640 \pm 140)$ J/mol. Our 6Fbz results are also in good agreement with [13, 14]: $T_{fus} = (277.5 \pm 0.5)$ K, $\Delta_{fus}H = (11200 \pm 170)$ J/mol.

EXPERIMENTAL EQUILIBRIUM PHASE DIAGRAM

The experimental diagram has been established by combining DSC and X-ray diffraction X approaches.

The X-ray analysis by the GS technic (Fig. 1) clearly shows the existence of a complex with the 1:1 ratio, quoted thereafter C: the diffraction pattern for the corresponding composition $x = 0.5$ (x is the 6FBz mole fraction) is different from those of both pure components and obviously corresponds to a single phase. Moreover, the comparison of D500 diffraction patterns at 193 K and 223 K (Fig. 2) points out a polymorphic phenomenon for the complex: $C_{II} \rightarrow C_{I}$ at $\simeq 210$ K). Figure 3 shows the most important DSC curves between 203 K and 283 K. This set clearly reveals the presence of four invariants:

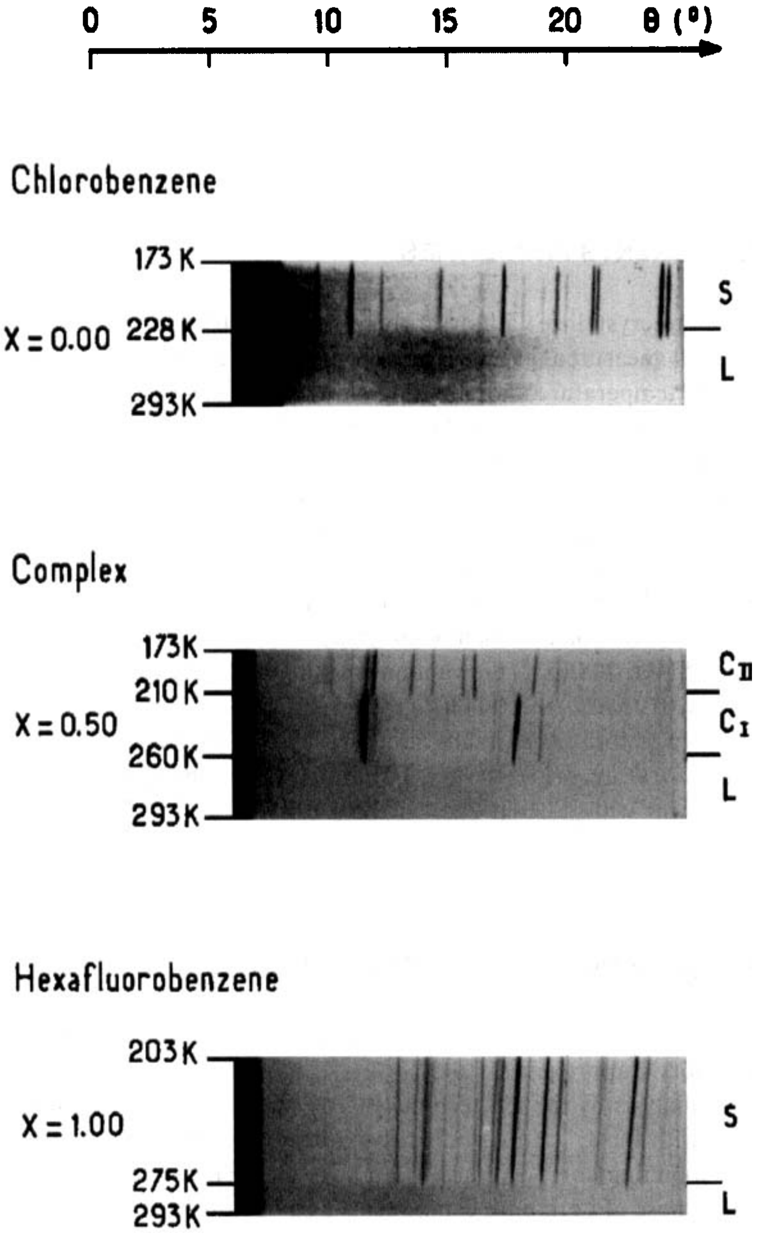

FIGURE 1 Guinier-Simon photographs of chlorobenzene, C-complex and hexafluorobenzene. The film in the middle part shows clearly the C solid-solid transition occuring at $\simeq$ 210 K. For the pure components only melting transition (S → L) appears (at $T_{fus} \simeq 228$ K for chlorobenzene and at $T_{fus} \simeq 275$ K for hexafluorobenzene).

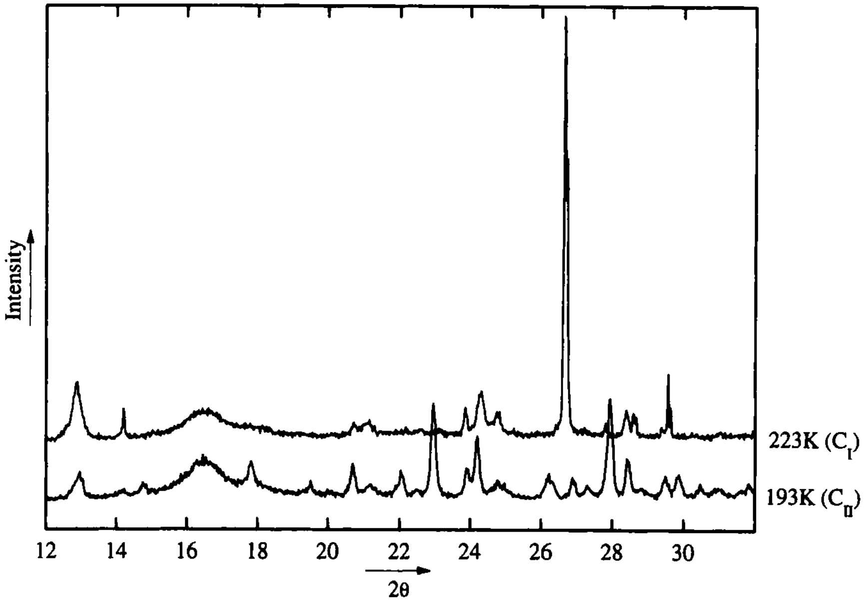

FIGURE 2 Comparison between D500 diffraction patterns at 193 K and at 223 K showing the existence of two forms (C_{II} and C_I respectively) for the C-complex.

- a eutectic E_1 $]K_1L_1M_1[$ at $T_{E_1} = (224.9 \pm 0.7)$ K,
- a eutectic E_2 $]K_2L_2M_2[$ at $T_{E_2} = (254.4 \pm 0.6)$ K,
- a eutectoïd E_3 $]QR[$ at $T_{E_3} = (211.0 \pm 0.5)$ K,
- a eutectoïd E_4 $]RS[$ at the same temperature.

The two former ones are related to the melting phenomena; the latter ones arise from the $C_{II} \rightarrow C_I$ transition. The transition temperatures on both sides of the phase diagram being nearly equal to $T_{trs}(C_{II} \rightarrow C_I)$ imply that the complex phases and the pure components are very little or not at all miscible. This important point is in complete agreement with our crystallographic results which show that the limiting phases in each biphasic domain are always the complex C and one of the pure components (within the experimental limit detection).

In order to determine the compositions of each eutectic invariant point, the Tammann procedure has been used. In the present study, this method is not trivial due to the strong 6Fbz preferential evaporation. Despite numerous precautions for minimizing the 6Fbz preferential loss, corrections are necessary to get the true final x-composition. The corrections have been estimated through the evaluation of the kinetic evaporation of pure substances with

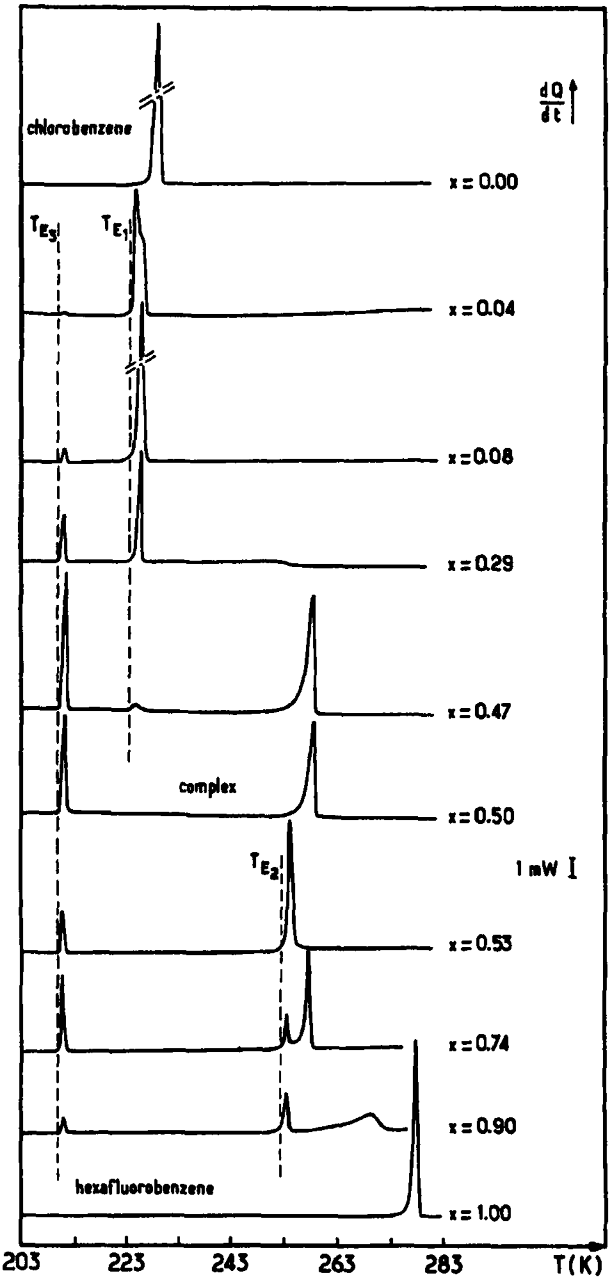

FIGURE 3 Evolution of the DSC curves showing the existence of four invariants E_1, E_2, E_3 and E_4. These invariants (two eutectics and two eutectoïds) correspond respectively to the temperature T_{E_1}, T_{E_2} and T_{E_3} ($T_{E_4} = T_{E_3}$).

known masses. We have verified that these corrections lead to a correct Tammann diagram for the solid-solid transition ($\Delta H_3(x)$ and $\Delta H_4(x)$, Fig. 4). Thereby, these corrections have been adopted for the other Tammann diagram ($\Delta H_1(x)$ and $\Delta H_2(x)$, Fig. 4): the resulting lines confirm that even at high temperature miscibility is nearly equal to zero. Their intersections give the locus of the L_1 and L_2 points with:

$$x_{L_1} = 0.07 \pm 0.01 \qquad \Delta_{fus}H_1 = (9.7 \pm 0.4)\,\mathrm{kJ/mol}$$

$$x_{L_2} = 0.66 \pm 0.01 \qquad \Delta_{fus}H_2 = (8.6 \pm 0.3)\,\mathrm{kJ/mol}.$$

With the same corrections, the experimental phase diagram is built up (Fig. 5). One has to note that the congruent melting-point of the complex lies between those of the pure compounds:

$$T_{fus_C} = (258.5 \pm 0.06)\,\mathrm{K}.$$

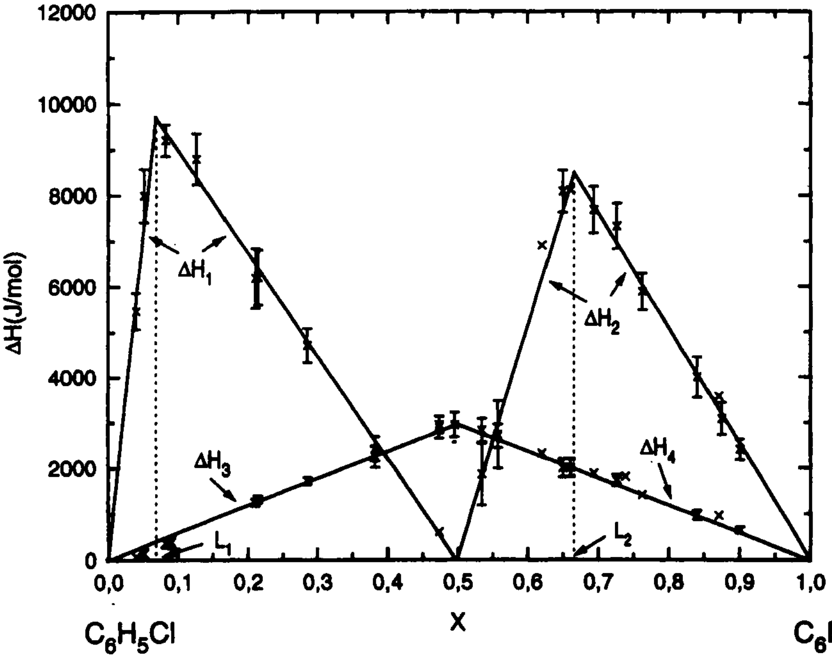

FIGURE 4 Tammann diagrams for the four invariants. ΔH_1 and ΔH_2 for the eutectics and ΔH_3 and ΔH_4 for the eutectoïds versus the corrected x mole fraction in hexafluorobenzene (ɪ are experimental points after the loss-correction); L_1 and L_2 represent the eutectic mole fractions.

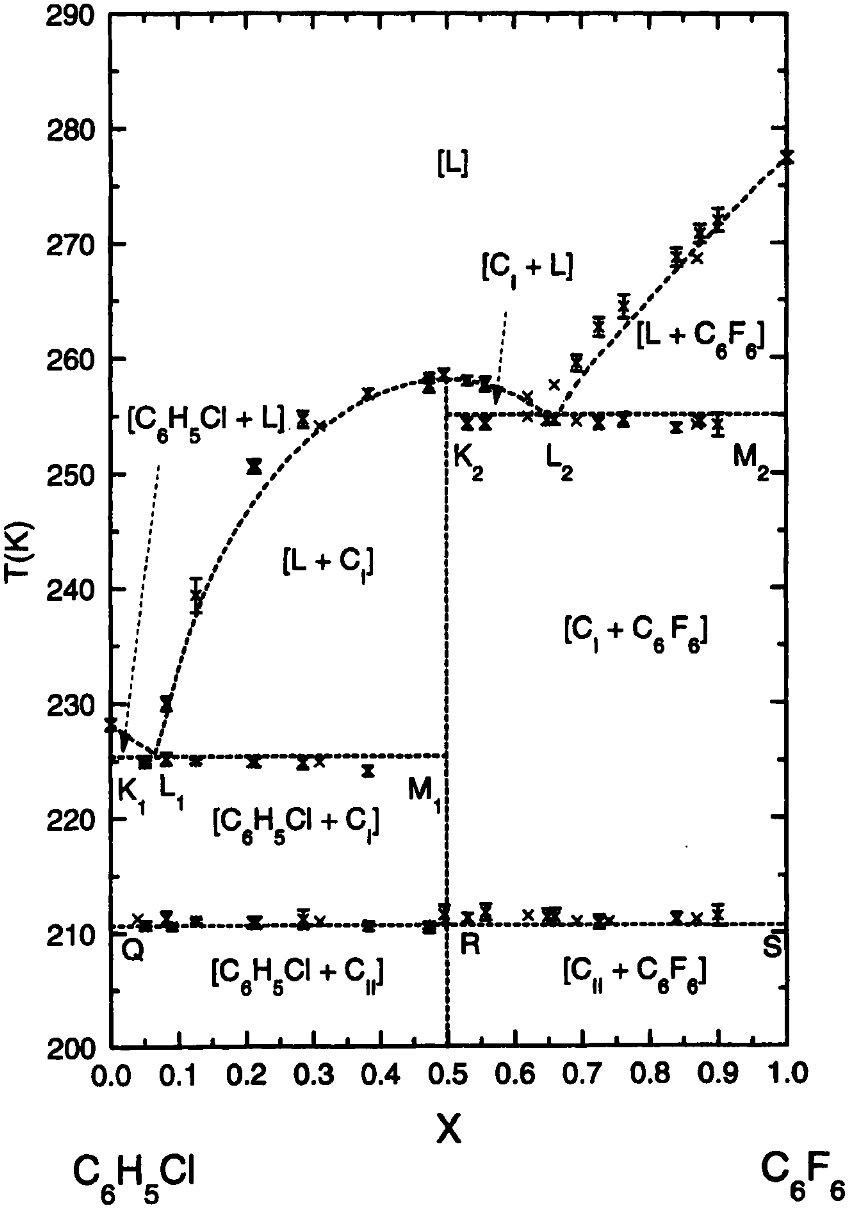

FIGURE 5 Chlorobenzene-hexafluorobenzene binary system. The experimental (I) and calculated (dotted lines) phase diagram are compared (the optimized parameter values are collected in Tab. I): the liquidus line and the four invariants lead to eight biphasic domains (four solid-liquid domains and four solid-solid domains) and one monophasic liquid domain.

THERMODYNAMIC ANALYSIS

The characteristic thermodynamic functions of the different phases (the mixing Gibbs energy of the melt $\Delta_{mix}G_L$, the Gibbs energy of the complex in its high temperature form $\Delta_f G_C^o$) are not known. Therefore, an optimization of the thermodynamic functions of all condensed phases, of the liquidus lines $T = f(x)$, of the L_1 and L_2 positions and the related melting-enthalpies has been made.

The liquid Gibbs free energy is described by a three-parameter Redlich-Kister function [16]:

$$\Delta_{mix}G_L = x(1-x)[H_1 + (1-2x)H_2 - TS_1]$$

$$+ RT[(1-x)\ln(1-x) + x\ln x]. \tag{1}$$

In this model of the substitutional type, three parameters (H_1, H_2 and S_1) are required indeed in order to take into account both the liquidus dissymmetry and the T-evolution of the interactions in the liquid; a greater number of liquid parameters in the relation (1) should not be realistic without excess liquid data (mixing enthalpy, activities, etc...).

Insofar as calorific capacity effects are neglected, the Gibbs free energy of formation of C_I referred to the pure liquid components $\Delta_f G_C^o$ is a linear T-function:

$$\Delta_f G_C^o = \Delta_f H_C^o - T\Delta_f S_C^o. \tag{2}$$

Then, in equation (2) $\Delta_f H_C^o$ and $\Delta_f S_C^o$ which represent respectively the enthalpy and the entropy of formation of C_I referred to the pure liquid components are T non-dependent. $\Delta_f G_C^o$ and T_{fus_C} values can be used as a measure of the C-stability and compared to the equivalent data of other complexes.

All the so-defined functions have been optimized by using the "*BIMING*" program [17]. This evolutionary computing procedure of the "simplex" type [18] allows to calculate the entire phase diagram through a minimization of the total Gibbs free energy of the system. Experimental and optimized data are given in Table I; Figure 5 compares the experimental phase diagram and the calculated one. The L_1 and L_2 eutectic point are correctly located. If we take into account the uncertainty on the experimental liquidus points (never greater than $\Delta T = \pm 1.2\,\text{K}$) and noting that the difference between the experimental

TABLE I Thermodynamic functions of the Clbz-6Fbz system: Comparison between experiments and optimization

Experimental values		*Optimized values*
Complex		
C_I	$\Delta_{fus}H = 14.8 \pm 0.8$	$\Delta_{fus}H = 14.2(4)$
	$T_{fus} = 258.5 \pm 0.6$	$T_{fus} = 258.1(2)$
		$\Delta_f G^o = -12.44(2) + 38.31(8)\ 10^{-3}\ T$
Transition	$\Delta_{trs}H = 6.0 \pm 0.6$	
$C_{II} \rightarrow C_I$	$T_{trs} = 211.0 \pm 0.5$	
		$H_1 = 3.5(3)$
Liquid		$H_2 = 0.49(9)$
		$S_1 = 10(2)\ 10^{-3}$
	$x = 0.07 \pm 0.01$	$x = 0.065(2)$
Eutectic L_1	$T = 224.9 \pm 0.7$	$T = 225.6(3)$
	$\Delta_{fus}H = 9.7 \pm 0.4$	$\Delta_{fus}H = 10.3(1)$
	$x = 0.66 \pm 0.01$	$x = 0.666(5)$
Eutectic L_2	$T = 254.4 \pm 0.6$	$T = 255.0(5)$
	$\Delta_{fus}H = 8.6 \pm 0.3$	$\Delta_{fus}H = 8.5(1)$

Temperatures are in K, thermodynamic function in kJ/mol or in kJ/mol/K.

point position and the calculated curves does not exceed 1.5 K, the agreement is very satisfactory.

The positive value of the H_1 parameter implies repulsive interactions in the melt ($\Delta_{mix}H(0.5)_L = 0.88$ kJ/mol). The weak dissymmetry when $\Delta_{mix}H_L$ varies is the consequence of the presence of the positive H_2 parameter and agrees with the hierarchy of the molar volumes of the pure components: the maximum of this curve will be shifted towards the smaller ClBz ($V_{\text{Clbz}} = 102$ cm^3/mol, $V_{\text{6Fbz}} = 116$ cm^3/mol).

At the invariant point crossings L_1 and L_2, these liquid repulsive interactions yield melting enthalpy values ($\Delta_{fus}H_{L_1} = (10.3 \pm 0.1)$ kJ/mol and $\Delta_{fus}H_{L_2} = (8.5 \pm 0.1)$ kJ/mol) slightly greater than those in the ideal liquid case (10.2 kJ/mol *et* 8.4 kJ/mol respectively). On the other hand, the eutectic temperatures are very sensitive to the H_1, H_2 and S_1 parameter values; as an example, the optimization without excess entropy ($S_1 = 0$) gives:

$$x_{L_1} = 0.06 \qquad T_{E_1} = 226.6\ \text{K}$$

$$x_{L_2} = 0.67 \qquad T_{E_2} = 257.8\ K\ (\simeq T_{fus_C}),$$

whereas experimental T-values are lower:

$$x_{L_1} = 0.07 \pm 0.01 \qquad T_{E_1} = (224.9 \pm 0.7)\ \mathrm{K}$$

$$x_{L_2} = 0.66 \pm 0.01 \qquad T_{E_2} = (254.4 \pm 0.6)\ \mathrm{K}$$

DISCUSSION

The melting-point of the complex Clbz:6Fbz ($T_{fus} = 258.1$ K) lies between the Clbz one ($T_{fus} = 228.2$ K) and the 6Fbz one ($T_{fus} = 277.5$ K). The lattice stability of this complex may be evaluated through the Gibbs free energy: at the melting-point, $\Delta_f G_C^o = -2.56$ kJ/mol. This value must be brought to the repulsive character of the interactions between Clbz and 6Fbz molecules in the melt.

On the other hand, in the Bz-6Fbz binary system, the 1:1 complex (quoted thereafter D) melts at a temperature value ($T_{fus_D} = 297.6$ K [13]) beyond that of the Bz one ($T_{fus} = 278.6$ K [13]) and the 6Fbz one. At the same time, the mixing enthalpy of the Bz-6Fbz liquid is negative and T-dependent ($\Delta_{mix}H$ (0.5, 313.2 K)$_L = -0.433$ kJ/mol [19]).

It is well known that the nature of the liquid interactions and the stability of the complex in binary systems between benzene-derived components are closely connected [6, 13, 20]). When the mixing enthalpy at the $x = 0.5$ composition ($\Delta_{mix}H(0.5)_L$) is negative, the 1:1 complex has a melting-point higher than those of the pure components, which indicates a significant stabilization. The intermolecular interactions in the lattice are of the quadrupole-quadrupole type and act between face-to-face molecules. If the enthalpy $\Delta_{mix}H_L$ has a dissymmetric x-shape and is T-dependent, one may suspect the existence of partial complexation in the melt (associated liquid): the Bz-6Fbz system and the D-complex seem to answer to these criterions.

In order to achieve this comparison between these two systems, we have to study the thermodynamic behaviour of the Bz-6Fbz system. Its thermodynamic data set has been extracted from the litterature (x is again the 6Fbz mole fraction):

- mixing enthalpy in the melt $\Delta_{mix}H_L$ at various temperatures (298.2, 313.2, 328.2 and 343.2 K, [19]),
- melting enthalpy ($\Delta_{fus}H_D = (20.50 \pm 0.28)$ kJ/mol), melting temperature ($T_{fus_D} = 297.2$ K and transition temperature ($T_{trs_D} = 249.2$ K), for the D-complex [13, 14],

- invariant eutectics (L_1: $x = 0.12$, $T = 270.9\,\mathrm{K}$, $\Delta_{fus}H = (9.70 \pm 0.11)$ kJ/mol; L_2: $x = 0.85$, $T = 268.8\,\mathrm{K}$, $\Delta_{fus}H = (10.63 \pm 0.11)$ kJ/mol, [13, 14]) and eutectoïd at 249.2 K [14],
- liquidus [13].

Only a associated liquid model [21, 22] allows to achieve the complete data optimization. This model takes into account in a classical manner an associated "species" (Bz:6Fbz) in chemical equilibrium with the pure species Bz and 6Fbz. In this pseudoternary melt, the molecular species interact:

- in an attractive manner when concerning Bz and 6FBz species,
- in a repulsive way when one of the involved partners is the associated species (Bz:6Fbz).

Then, the Gibbs free energy of the liquid $\Delta_{mix}G_L$ is expressed in terms of the mole fractions of the three types of species Bz (x_1), 6Fbz (x_2) and (Bz:6Fbz) (x_3) and of the standard Gibbs energy of dissociation to the pure liquid components for (Bz:6Fbz) ($\Delta_{diss}G^o$):

$$\begin{aligned}\Delta_{mix}G_L = \{ & x_1x_2[H_1^{12} - TS_1^{12} + (H_2^{12} - TS_2^{12})(x_1 - x_2)] \\ & + x_1x_3[H_1^{13} - TS_1^{13}] + x_2x_3[H_1^{23} - TS_1^{23}] \\ & - x_3\Delta_{diss}G^o\}/(1 + x_3) \\ & + RT[(1 - x)\ln(1 - x) + x\ln x]. \end{aligned} \quad (3)$$

The optimization (Tab. II) through the "BIMING" program allows the calculation of phase diagram (Fig. 6) and gives an association percentage in the liquid (i.e. the (Bz:6Fbz) mole fraction x_3), corresponding to the melting of the D-complex, equal to 18%.

The Gibbs free energy of the complex at its melting point $\Delta_f G_D^o$ is found to be equal to -4.12 kJ/mol, a lower value than for the C-complex, and then, a higher stability. Quadrupole-quadrupole interaction energy calculations performed by [6] on the D-complex show that face-to-face orientations of the Bz and 6Fbz molecules are responsible for its high melting temperature with respect to those corresponding to the pure components. We assume the same geometry could exist in the C-lattice.

We can see also the $\mathrm{D_{II}} \rightarrow \mathrm{D_I}$ transition is weakly energetic ($\Delta_{trs}H_D = (0.66 \pm 0.27)$ kJ/mol [14]), in contrast with the $\mathrm{C_{II}} \rightarrow \mathrm{C_I}$ one ($\Delta_{trs}H_C = (6.0 \pm 0.6)$ kJ/mol); in other words, the corresponding entropy variation has the 2.65

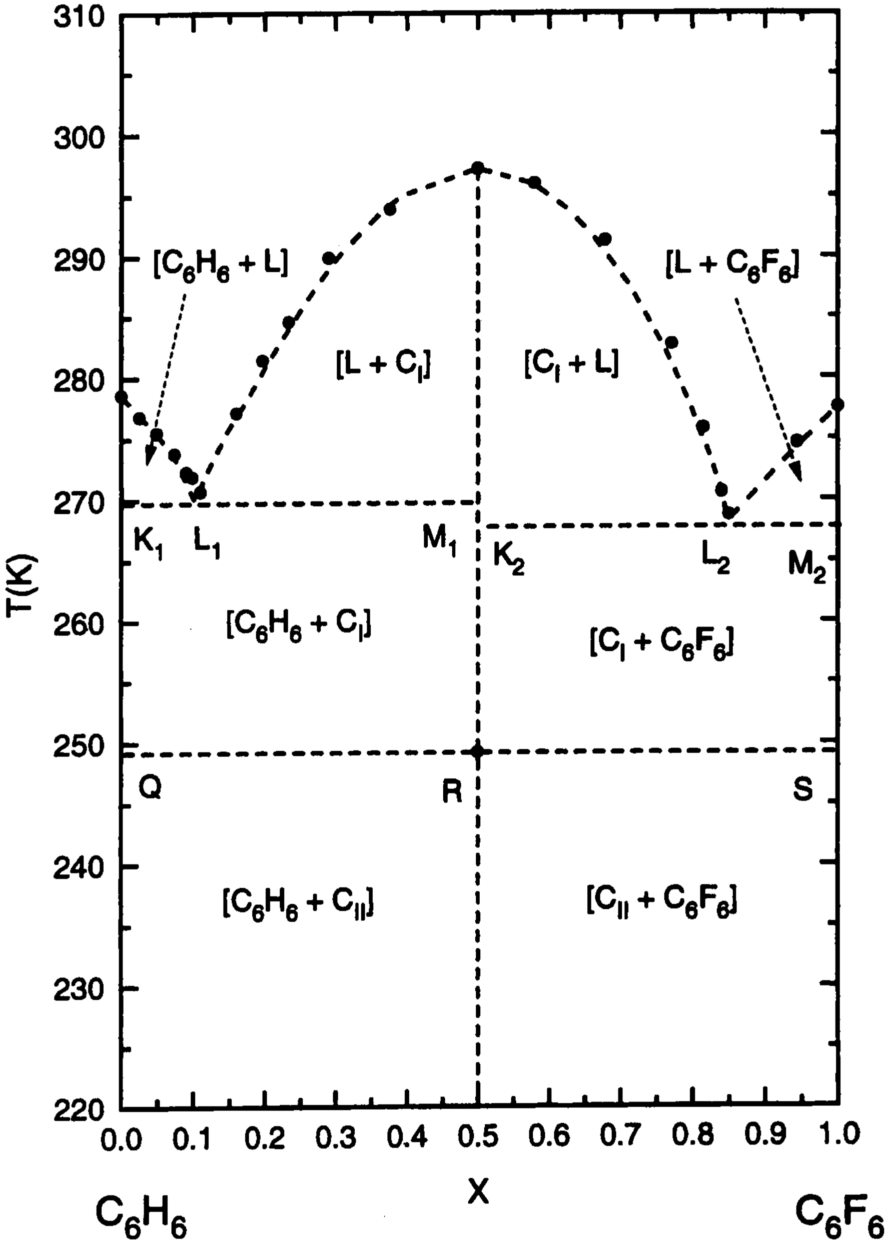

FIGURE 6 Benzene-hexafluorobenzene binary system: comparison between experimental (●[13]) and calculated (dotted lines) phase diagrams (the optimized parameter values are collected in Tab. II). As in the previous phase diagram, the eight biphasic domains are the consequence of the liquidus line and of the four invariants.

TABLE II Thermodynamic functions of the Bz–6Fbz system: Comparison between experiments [13–14] and optimization

Experimental values		*Optimized values*
Complex		
D_I	$\Delta_{fus}H = 20.50 \pm 0.28$ $T_{fus} = 297.6$	$\Delta_{fus}H = 20.5(5)$ $T_{fus} = 297.2(2)$ $\Delta_f G^o = -21.12(2) + 57.20(8)\,10^{-3}\,T$
Transition $D_{II} \rightarrow D_I$	$\Delta_{trs}H = 0.66 \pm 0.27$ $T_{trs} = 249.2$	
Liquid	$x = 0.12$	$H_1^{12} = 0\ H_2^{12} = 0.08(5)$ $S_1^{12} = 0.3(1)\,10^{-3}\ S_2^{12} = -0.05(9)\,10^{-3}$ $H_1^{13} = 2.0(1)$ $S_1^{13} = 3.4(5)\,10^{-3}$ $H_1^{23} = 5.8(2)$ $S_1^{23} = -0.07(9)\,10^{-3}$ $\Delta_{diss}G^o = 6.39(5) - 14(1)\,10^{-3}\,T$ $x = 0.102(5)$
Eutectic L_1	$T = 270.9$ $\Delta_{fus}H = 9.70 \pm 0.11$ $x = 0.85$	$T = 270.4(7)$ $\Delta_{fus}H = 10.1(1)$ $x = 0.849(5)$
Eutectic L_2	$T = 268.8$ $\Delta_{fus}H = 10.63 \pm 0.11$	$T = 268.2(7)$ $\Delta_{fus}H = 10.7(1)$

Temperatures are in K, thermodynamic function in kJ/mol or kJ/mol/K.

J/mol/K value for D and the 28.44 J/mol/K one for C. We suppose therefore that, in contrast with D_I [14], the degree of disordering should be high in the C_I-phase.

Therefore, C appears to be less stable than D: that means that Cl—F intermolecular interactions are probably repulsive or smaller than the H—F ones. In its high temperature modification C_I seems to be more disordered than D_I.

CONCLUSION

Experimental investigations on the chlorobenzene-hexafluorobenzene phase diagram prove the existence of a congruent melting 1:1 molecular complex with polymorphism. The thermodynamic analysis of all the data allows to conclude that *i*) the strength of the molecular interactions is high enough to yield a complex, but *ii)* not sufficient to preserve the complexation phenomenon in the melt where the mixing enthalpy is positive. The homologous benzene-hexafluorobenzene binary phase diagram has been optimized in the same manner and show 1:1 complexation both in solid state and in the liquid where the mixing enthalpy is negative. The comparison between the two binary systems shows that the substitution of hydrogen by chlorine on the benzenic ring *i)* decreases the complex stability and *ii)* increases the disorder in the high temperature form of the complex lattice. Then in this benzenic family, it would be interesting to test the influence of heteroatoms on the existence and the stability of complex phases by varying their number and/or their nature.

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