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Destabilizing Effects of Chlorine on Complexes Belonging to the Benzene Family: *p*-$C_6H_4Cl_2$−C_6F_6 and *p*-$C_6H_4CH_3Cl$−C_6F_6 Systems

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Equilibrium phase diagrams of the *p*-dichlorobenzene−hexafluorobenzene and the *p*-chlorotoluene−hexafluorobenzene binary systems are experimentally determined by differential scanning calorimetry and X-ray diffraction analysis and optimized by computational thermodynamic analyses. Resulting data are thermodynamically assessed through a substituted model for liquid phase and lead to the Gibbs free energy of complexation in the case of the *p*-chlorotoluene−hexafluorobenzene system. The first diagram is of the eutectic type, and the second one presents an equimolar complex. The comparison of these two systems with the benzene−hexafluorobenzene and the chlorobenzene−hexafluorobenzene binaries shows that the stability of the complex decreases with number of H atoms substituted by Cl atoms in the benzenic ring.

Introduction

The organic binary systems are known to give different types of structural alliances: either random molecular alloys or ordered molecular complexes. The formation of alloys between pure components depends on the degree of homeomorphism, which is related to the molecular shape and size, and on the crystalline isomorphism, which is related to the similarity of symmetry and cell parameters.[1−4] The formation of molecular complexes results from specific attractive interactions such as charge transfer between molecules of different type[5] and quadrupole−quadrupole interactions.[6]

To study and to characterize the different interactions, we have investigated systems involving hexafluorobenzene (C_6F_6) and mono- or polysubstituted benzenes. Indeed, the presence of molecules with fluorine atoms increases the probability of having a hydrogen-bonding character or charge transfer. In a previous paper, we reported on the stabilizing effect of CH_3 groups when substituting H for the complex formation in the benzene family.[7] A question arises from the influence of other substitutes, such as halogens (which are known to be electrophiles), in the complexation strength. The purpose of the present work has been to study the influence of chlorine on the complexation phenomenon. The two systems presented here are {(1−*x*) mole of *p*-dichlorobenzene + *x* mole of hexafluorobenzene} and {(1 − *x*) mole of *p*-chlorotoluene + *x* mole of hexafluorobenzene}.

Table 1. Crystallographic Characteristics of the Pure Components

compound	C_6F_6	*p*-$C_6H_4Cl_2$ [ref 4]			*p*-$C_6H_4CH_3Cl$ [refs 12, 13]
phase	I	β	α	γ	I
Z	6	1	2	2	2
group	$P2_1/n$	$P\bar{1}$	$P2_1/a$	$P2_1/c$	$P2_1/a$
symmetry	monoclinic	triclinic	monoclinic	monoclinic	monoclinic
cell parameters					
T (K)	123	300	293	100	273
a (Å)	16.766(7)	7.361(2)	14.792(6)	8.624(2)	6.028(1)
b (Å)	9.029(3)	5.963(1)	5.839(2)	6.021(2)	7.294(2)
c (Å)	5.899(1)	3.959(1)	4.036(2)	7.414(2)	7.740(1)
α (deg)	90	92.13(2)	90	90	90
β (deg)	93.94(3)	113.24(2)	112.52(4)	127.51(2)	94.61(2)
γ (deg)	90	91.42(2)	90	90	90

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(1) Haget, Y.; Oonk, H. A. J.; Cuevas-Diarte, M. A. In *Les Equilibres entre Phases, JEEP XVI*; Kaloustian, J., Pastor, J., Eds.; Marseille, 1990; pp 35−36.

(2) Haget, Y.; Bonpunt, L.; Michaud, F.; Négrier, P.; Cuevas-Diarte, M. A.; Oonk, H. A. J. *J. Appl. Crystallogr.* **1990**, *23*, 492.

(3) Oonk, H. A. J.; van der Linde, P. R.; Haget, Y.; Bonpunt, L.; Chanh, N. B.; Cuevas-Diarte, M. A. *J. Chim. Phys.* **1991**, *88*, 329.

(4) Haget, Y. *J. Chim. Phys.* **1993**, *90*, 313.

(5) Forster, R. *Organic Charge-Transfer Complexes;* Blomquist, A. T., Ed.; Academic Press: London, 1969; Chapter 10, pp 276−299.

(6) Hernandez-Trujillo, J.; Costas, M.; Vela, A. *J. Chem. Soc., Faraday Trans.* **1993**, *89*, 2441.

(7) Mikaïlitchenko, D.; Marbeuf, A.; Haget, Y.; Oonk, H. A. J. *Mol. Cryst. Liq. Cryst.* **1998**, *319*, 291.

(8) Marbeuf, A.; Mondieig, D.; Métivaud, V.; Négrier, P.; Cuevas-Diarte, M. A.; Haget, Y. *Mol. Cryst. Liq. Cryst.* **1997**, *293*, 309.

(9) Boden, N.; Davis, P. P.; Stam, C. H.; Wesselink, G. A. *Mol. Phys.* **1973**, *25*, 81.

(10) Counsell, J. F.; Green, H. S.; Hales, J. L.; Martin, J. F. *Trans. Faraday Soc.* **1965**, *61*, 212.

(11) van der Linde, P. Tesis, University Utrecht, The Netherlands, 1992.

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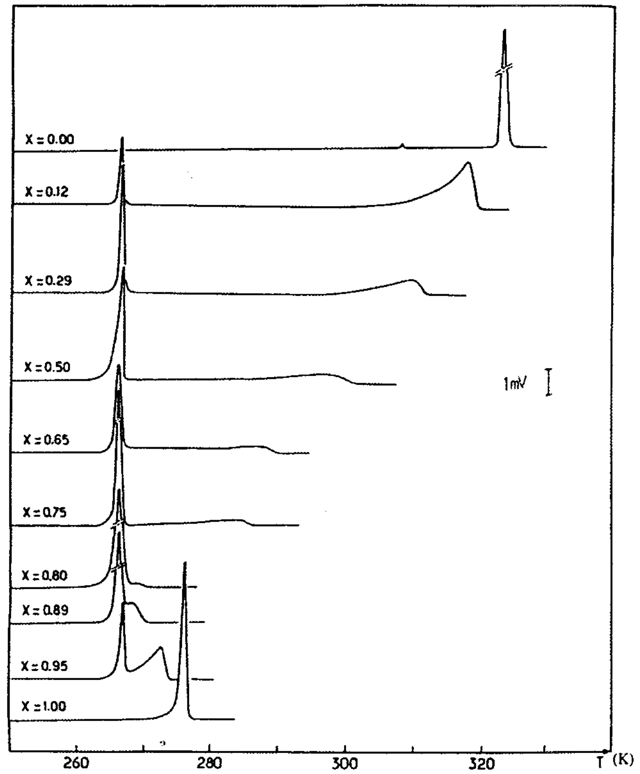

Figure 1. Evolution of DSC curves (with increasing molar fraction of hexafluorobenzene) of the p-dichlorobenzene−hexafluorobenzene system showing only one eutectic invariant.

They are finally compared to {(1 − x) mole of benzene + x mole of hexafluorobenzene} and to {(1 − x) mole of chlorobenzene + x mole of hexafluorobenzene} systems.[8]

Experimental Section

Experimental Procedure. Calorimetric measurements are made with a Perkin-Elmer DSC7 differential scanning calorimeter. The temperature range is between 160 and 320 K, and all our experiments are carried out with the same procedure as in ref 7: heating or cooling rate 2 K/min, sample mass 4 mg.

Table 2. Thermodynamic Data of the Pure Components

phase	T_{fus} (K)	$\Delta_{fus}H$ (kJ/mol)	T_{trs} (K)	$\Delta_{trs}H$ (kJ/mol)
C_6F_6	277.5 ± 0.5^a	11.20 ± 0.17^a		
p-$C_6H_4Cl_2$(β)	326.3 ± 0.5	17.74 ± 0.18		
p-$C_6H_4Cl_2$(α)	326.1 (m)^c	17.92 (m)	306 ± 1 $\alpha \rightarrow \beta^b$	0.18 ± 0.01 $\alpha \rightarrow \beta^b$
p-$C_6H_4Cl_2$(γ)	322.2 (m)	19.16 (m)	275.0 ± 0.2 $\gamma \rightarrow \alpha^b$	1.24 ± 0.01 $\gamma \rightarrow \alpha^b$
p-$C_6H_4CH_3Cl$	280.6 ± 0.5	13.6 ± 0.1		

^{a} Reference 8. ^{b} Reference 11. ^{c} m = metastable value.

In order to characterize the different phase transitions, X-ray diffraction patterns are obtained with a Guinier-Simon camera (GS) and with an Inel CPS 120 (Cu Kα_1 radiation, λ = 1.5406 Å).

By combining all these methods, the T−x phase diagram can be determined.

Pure Components. *a. Hexafluorobenzene (C_6F_6).* The product was purchased from Aldrich (purity higher than 99.5%) and was used without further purification.

The lattice parameters deduced from the X-ray diffraction pattern are given in Table 1 and are in good agreement with the results published by Boden et al.[9] at 120 K: a = 16.82 Å, b = 9.17 Å, c = 5.76 Å, β = 95.80°. Thermodynamic properties determined previously[8] are given in Table 2. Hexafluorobenzene, which is a liquid at room temperature, is very volatile[10] and therefore necessitates a precise evaluation of the mole fraction at the end of the preparation of mixed samples.

b. p-Dichlorobenzene (p-$C_6H_4Cl_2$). The product was purchased from Merck (purity over 99%). It presents polymorphism with three phases which are labeled β, α, and γ in order of decreasing temperature. Corresponding crystallographic data are given in Table 1.

The melting temperature T_{fus} and melting enthalpy $\Delta_{fus}H$ of form β are given in Table 2. The transition temperature T_{trs} and enthalpy $\Delta_{trs}H$ between solid phases ($\gamma \rightarrow \alpha$, $\alpha \rightarrow \beta$) from ref 11 are also reported. The melting of form γ and form α is metastable. The corresponding melting values (melting temperature, $T_{fus\gamma}$, $T_{fus\alpha}$, and melting enthalpy, $\Delta_{fus}H_{\gamma}$, $\Delta_{fus}H_{\alpha}$) are deduced by using the ones of the form β and the transition

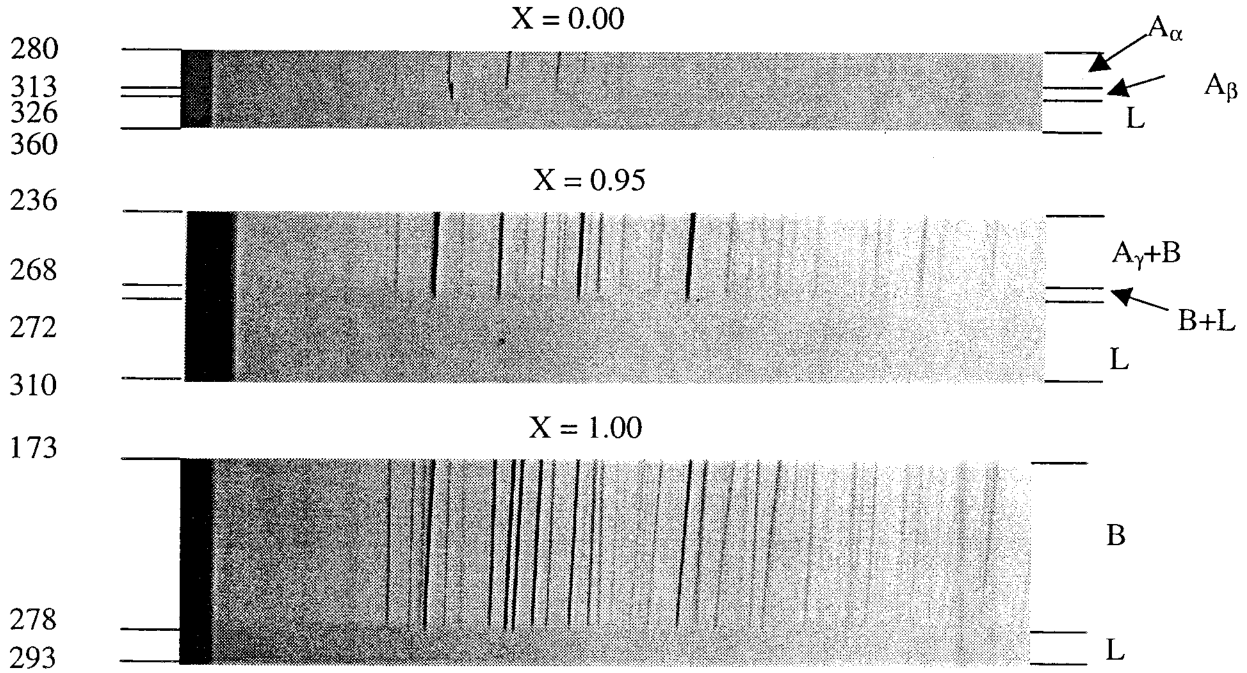

Figure 2. Guinier−Simon photographs of p-dichlorobenzene, labeled A (corresponding to x = 0), and hexafluorobenzene, labeled B (corresponding to x = 1), and the composition x = 0.95.

Table 3. Thermodynamic Data (in SI Units) of the *p*-Dichlorobenzene−Hexafluorobenzene System: Experimental and Optimized Properties

	exptl values	optimized values
liquid		$H_{1,2}^{(1)} = 6900(10)$ $S_{1,2}^{(1)} = 19.4(2)$ $H_{1,2}^{(2)} = 800(10)$
metatectic M$_2$		
T_{M2}	306.0 ± 0.5	306.0(1)
x_{M2}	0.440 ± 0.010	0.441(2)
metatectic M$_1$		
T_{M1}	275.0 ± 0.5	275.0(1)
x_{M1}	0.790 ± 0.010	0.800(1)
eutectic E		
T_E	268.2 ± 0.4	268.2(1)
x_E	0.845 ± 0.010	0.845(1)
$\Delta_{fus}H_E$	13200 ± 1800	13238(10)

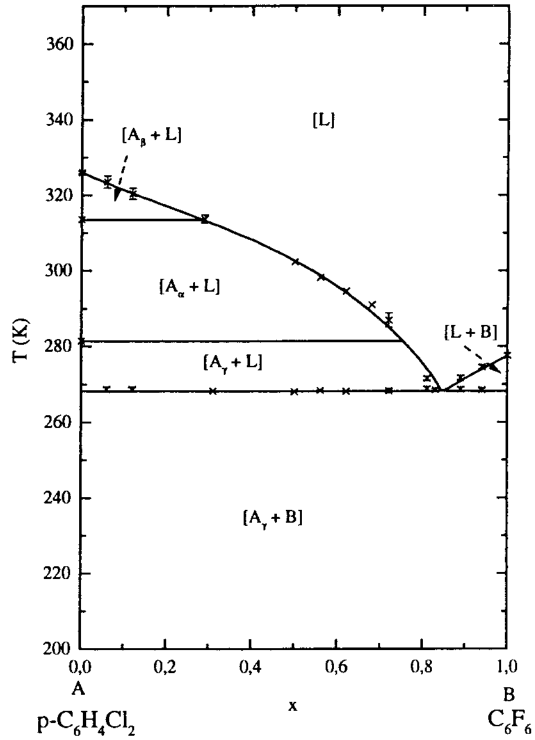

Figure 3. The *p*-dichlorobenzene−hexafluorobenzene system. Comparison between experimental (×) and calculated phase diagram (solid line). The values of the optimized parameters are collected in Table 3.

values (temperatures of transition, $T_{trs,\gamma\to\alpha}$, $T_{trs,\alpha\to\beta}$, and enthalpies of transition, $\Delta_{trs,\gamma\to\alpha}H$, $\Delta_{trs,\alpha\to\beta}H$). The corresponding values are given in Table 2.

c. p-Chlorotoluene (p-$C_6H_4CH_3Cl$). The product was purchased from Aldrich (purity 98%) and was used without further purification. Its crystallographic[12,13] and thermodynamic characteristics are given in Tables 1 and 2, respectively. In our experimental temperature range (160−280 K), no phase transition is detected.

The Phase Diagrams. *a. The p-Dichlorobenzene−Hexafluorobenzene System.* We studied 12 compositions by means of DSC and three with the Guinier-Simon camera. DSC curves (Figure 1) and GS films (Figure 2) clearly reveal only one eutectic invariant.

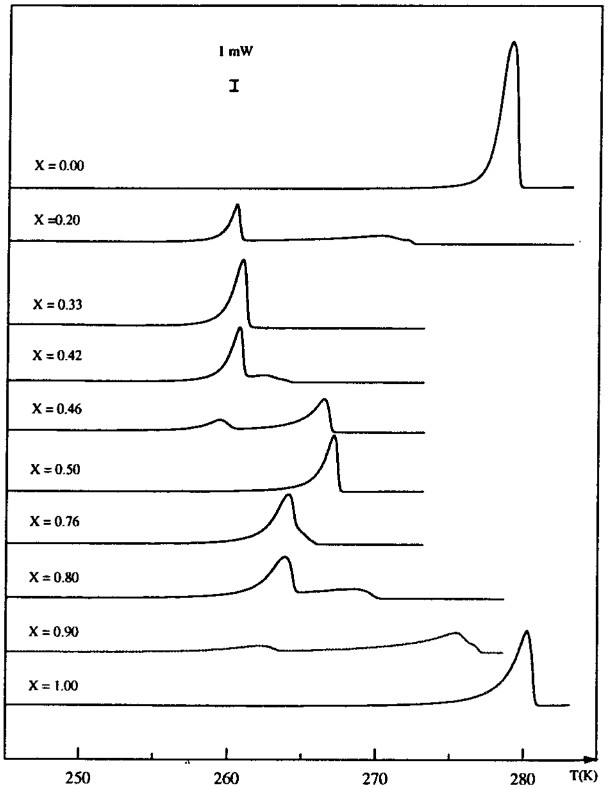

Figure 4. DSC curve evolution (with increasing molar fraction of hexafluorobenzene) of the *p*-chlorotoluene−hexafluorobenzene system showing two eutectic invariants.

Table 4. Thermodynamic Data (in SI Units) of the *p*-Chlorotoluene−Hexafluorobenzene System: Comparison between Experimental and Optimized Properties

	exptl values	optimized values
liquid		$H_{1,2}^{(1)} = 7350(10)$ $H_{1,2}^{(2)} = 1040(10)$ $H_{1,2}^{(3)} = 1030(10)$ $S_{1,2}^{(1)} = 31.6(5)$
complex		
T_{fusC}	266.5 ± 0.5	266.6(1)
$\Delta_{fus}H_C$	20600 ± 500	20600(10)
$\Delta_f G_C^\circ$		$-16930(10) + 49.9(5)T$
eutectic E$_1$		
T_{E1}	261.5 ± 1.0	262.3(5)
x_{E1}	0.33 ± 0.01	0.33(1)
$\Delta_{fus}H_{E1}$	11000 ± 500	11390(50)
eutectic E$_2$		
T_{E2}	257.8 ± 1.2	257.8(5)
x_{E2}	0.73 ± 0.01	0.73(1)
$\Delta_{fus}H_{E2}$	11000 ± 1000	11120(50)

The solid−solid transition α → β of *p*-dichlorobenzene on the DSC curve ($x = 0$) emerges from the baseline at $T = 306 \pm 1$ K. Thermodynamic data characterizing this system are given in Table 3. The consistency of the entire experimental data set allows us to establish the equilibrium phase diagram (Figure 3).

b. The p-Chlorotoluene−Hexafluorobenzene System. Our study of this system [15 samples by DSC (Figure 4) and five by GS experiments (Figure 5)] revealed a 1:1 complex, labeled C, and two three-phase equilibria. In contrast to the previous systems,[7,9] no polymorphism of C has been detected in the temperature range studied. The congruent melting temperature $T_{fus,C}$ and the melting enthalpy $\Delta_{fus}H_C$ of C are given in Table 4 with data corresponding to the two three-phase equilibria. The consistency of the entire experimental data set allows us to establish the equilibrium phase diagram (Figure 6).

Thermodynamic Analysis. For the Gibbs energy of the liquid mixtures referred to the liquid pure components, we use

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(12) Palacios Perez, L. Tesina, Universitat de Barcelona, 1997.

(13) Palacios Perez, L.; Labrador, M.; Tauler, E.; Cuevas-Diarte, M.-A. *Les Equilibres entre Phases, JEEP XX;* Haget, Y., Marbeuf, A., Eds.; Bordeaux; 1994; pp 171−172.

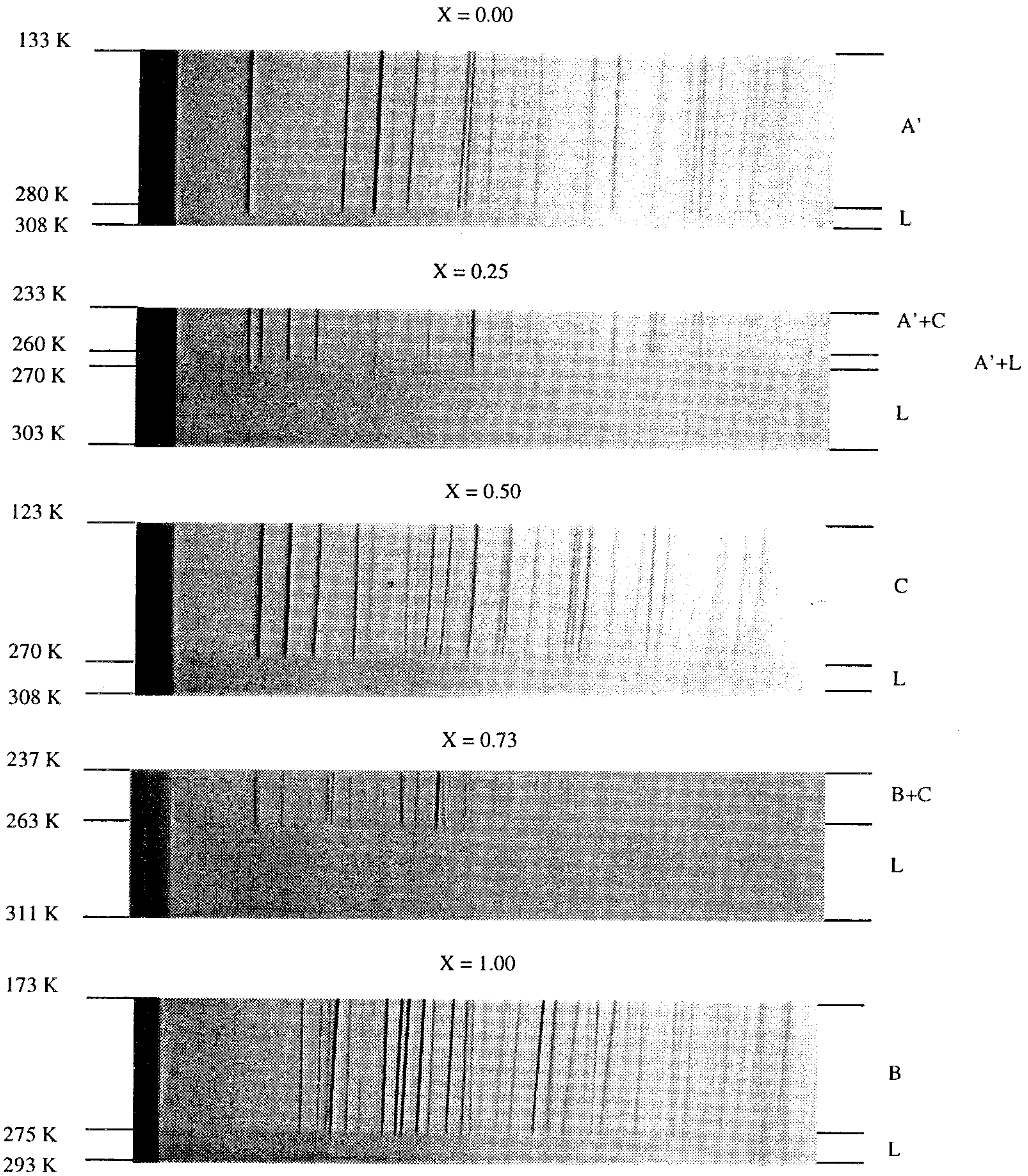

Figure 5. Guinier−Simon photographs of p-chlorotoluene (labeled A′; corresponding to $x = 0$), the C complex (labeled C), hexafluorobenzene (labeled B), and two compositions ($x = 0.25$ and $x = 0.73$), the latter corresponding to the second eutectic composition.

the expression (see also ref 8)

$$\Delta_{\text{mix}}G_{\text{L}} = x(1 - x)\sum_{k=1}^{n}(H_{1,2}^{(k)} - TS_{1,2}^{(k)})(1 - 2x)^{k-1} + RT[(1 - x)\ln(1 - x) + x \ln x] \quad \text{(a)}$$

where R is the gas constant and $H_{1,2}^{(k)}$ and $S_{1,2}^{(k)}$ are enthalpies and entropies parameters which are adjusted to the properties of the system (k is the order of the parameters $H_{1,2}^{(k)}$ and $S_{1,2}^{(k)}$).

For the Gibbs free energy of formation of the complex i from the pure liquid components, we use the expression

$$\Delta_{\text{f}}G_i^\circ = \Delta_{\text{f}}H_i^\circ - T\Delta_{\text{f}}S_i^\circ \quad \text{(b)}$$

which is linear in temperature (because of the small temperature range, heat capacity effects are neglected) and in which $\Delta_{\text{f}} H_i^\circ$ and $\Delta_{\text{f}} S_i^\circ$ are the enthalpy and entropy of complex formation, respectively.

The thermodynamic functions $\Delta_{\text{mix}}G_{\text{L}}$ and $\Delta_{\text{f}} G_i^\circ$ in both systems are optimized by the computer program BIMING[14] which searches equilibrium states by minimizing the total Gibbs energy of the biphasic system at given T and global mole fraction $x°$.

a. The p-Dichlorobenzene−Hexafluorobenzene System. In this system without complex, data optimization requires only three parameters for $\Delta_{\text{mix}}G_{\text{L}}$ ($H_{1,2}^{(1)}$, $H_{1,2}^{(2)}$, and $S_{1,2}^{(1)}$). Optimized values of the invariant points are reported in Table 3 and compared with the experimental ones. The calculated phase diagram is represented in Figure 3 with one solid−solid domain [p-$C_6H_4Cl_2(\gamma)$ + C_6F_6] and four solid−liquid domains. Experimental and calculated phase diagrams are in excellent agreement: the difference between experimental and calculated liquid mole fractions does not exceed 0.030.

b. The p-Chlorotoluene−Hexafluorobenzene System. In this system, four parameters are required in the expression for $\Delta_{\text{mix}}G_{\text{L}}$ as given by eq a ($H_{1,2}^{(1)}$, $H_{1,2}^{(2)}$, $H_{1,2}^{(3)}$, and $S_{1,2}^{(1)}$) and two for $\Delta_{\text{f}}G_{\text{C}}^\circ$($\Delta_{\text{f}}H_{\text{C}}^\circ$ and $\Delta_{\text{f}}S_{\text{C}}^\circ$ in (b)). The last two parameters are not independent because of the congruent melting character of C:

$$\Delta_{\text{f}}H_{\text{C}}^\circ = -\Delta_{\text{fus}}H_{\text{C}} + 2H_{1,2}^{(1)}$$

$$\Delta_{\text{f}}S_{\text{C}}^\circ = -\Delta_{\text{fus}}H_{\text{C}}/T_{\text{fusC}} + 2S_{1,2}^{(1)} + 2R \ln 2$$

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(14) Marbeuf, A. Code “BIMING”, 1991.

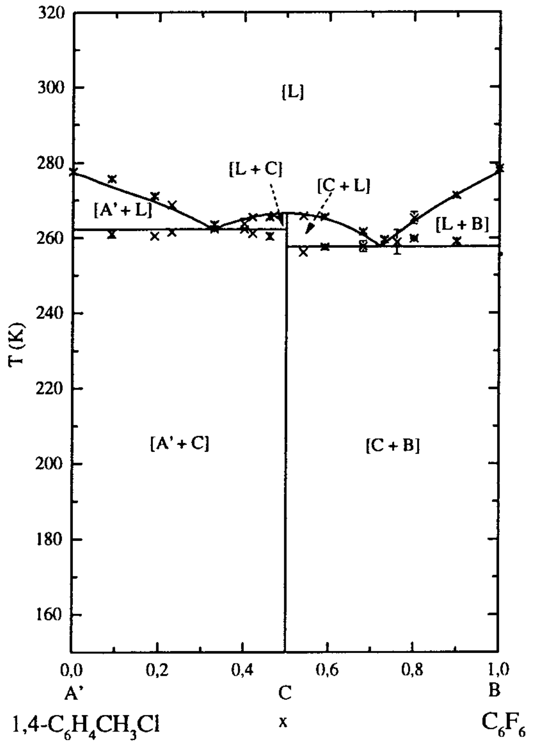

Figure 6. The *p*-chlorotoluene−hexafluorobenzene system. Comparison of experimental (×) and calculated (solid lines) phase diagram. The values of the optimized parameters are collected in Table 4.

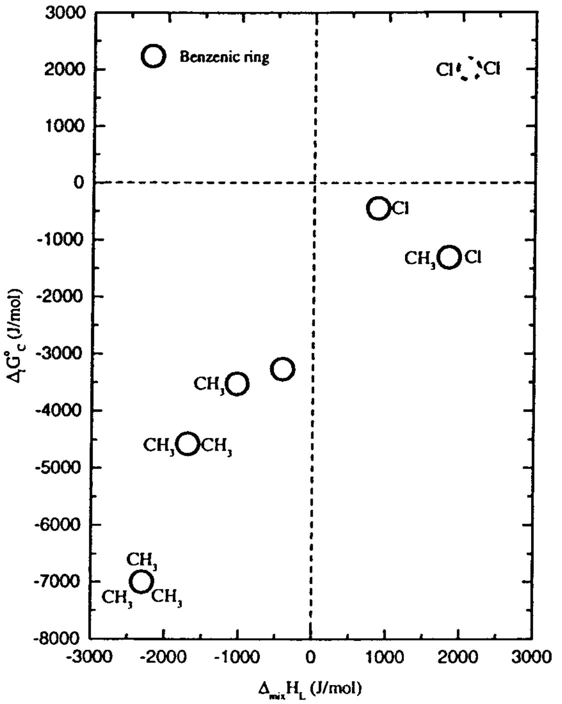

Figure 7. Correlation between enthalpy of mixing in the liquid state and Gibbs energy of formation of the complex (at 313.2 K).

The optimization of the experimental data is achieved through the four parameters for the liquid state. The results are given in Table 4. The calculated eutectic points and the experimental ones are in good agreement. The calculated phase diagram is represented in Figure 6 with the experimental points: the difference between experimental and calculated mole fraction does not exceed 0.034.

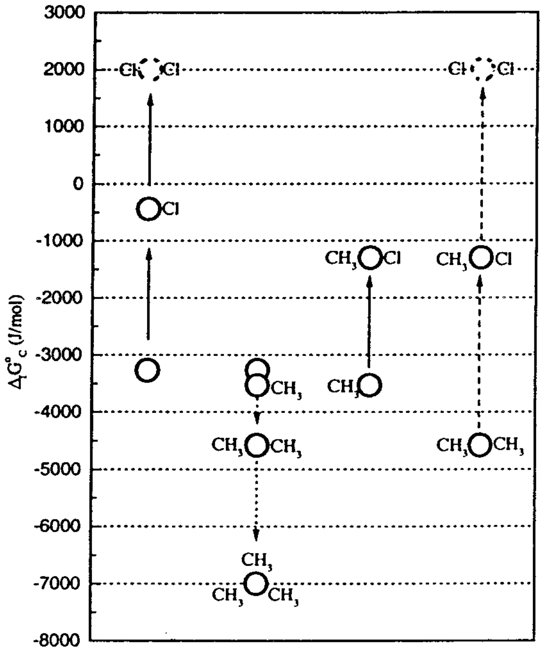

Figure 8. Comparison of the Gibbs energies of formation of the complexes in the benzene family.

c. The Benzene−Hexafluorobenzene and Chlorobenzene−Hexafluorobenzene Systems. The study of two other systems (the benzene−hexafluorobenzene system and the chlorobenzene−hexafluorobenzene system) has been published before:[7,8] both systems present an equimolar complex phase acting as a line compound; the liquid phase in the benzene−hexafluorobenzene is associated.

Results and Discussion

The stability of the C complex in the *p*-chlorotoluene−hexafluorobenzene system appears to be weak: the Gibbs free energy of C ($\Delta_f G^\circ_C$) at its melting point (266.6 K) is equal to −3.63 kJ/mol.

At the same time, the mixing enthalpy of the corresponding melt appears to be positive ($\Delta_{mix}H_L = 1.84$ kJ/mol).

With the new information, we are able to study the effect of chlorine in complexes belonging to the benzene family. Four systems can be compared: $C_6H_6-C_6F_6$[7], $C_6H_5Cl-C_6F_6$[8], *p*-$C_6H_4Cl_2-C_6F_6$, *p*-$C_6H_4CH_3Cl-C_6F_6$. As observed before,[7] the influence of a substitute can be seen on a system by inspecting the value of the Gibbs free energy of formation of the complex C ($\Delta_f G^\circ_C$) and the value of the equimolar liquid enthalpy of mixing ($\Delta_{mix}H_L$) at a given temperature (here 313.2 K).

Figure 7 shows the correlation between $\Delta_f G^\circ_C$ and $\Delta_{mix}H_L$ for a number of cases studied. (The values of these thermodynamic functions for the 1,3,5-trimethylbenzene−hexafluorobenzene[15] system come from our optimization which will be published later.) We can see a linear relationship between $\Delta_f G^\circ_C$ and $\Delta_{mix}H_L$. Using this relationship and knowing the value of $\Delta_{mix}H_L$ for the system *p*-dichlorobenzene−hexafluorobenzene, we can evaluate the $\Delta_f G^\circ_C$ of the hypothetical complex: $\Delta_f G^\circ_C(313.2\ \text{K}) \approx 2$ kJ/mol, showing the instability of this phase.

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(15) Duncan, W. A.; Sheridan, J. P.; Swinton, F. L. *Trans Faraday Soc.* **1966**, *62*, 1090.

Figure 8 compares the values of $\Delta_f G^\circ_C$ for all the benzene systems studied. When a hydrogen atom is substituted by a chlorine atom, $\Delta_f G^\circ_C$ increases by 2.5 kJ/mol (solid arrow): the Cl atom appears to have a destabilizing effect in the formation of molecular complexes. This effect is also shown when CH_3 group is substituted by a Cl atom: $\Delta_f G^\circ_C$ increases by 3.2 kJ/mol from the *p*-xylene−hexafluorobenzene complex to the *p*-chlorotoluene−hexafluorobenzene complex and from the *p*-chlorotoluene−hexafluorobenzene complex to the hypothetical *p*-dichlorobenzene−hexafluorobenzene complex (dashed arrows). We can see here the coherency of our model because in the two types of substitution (H atom substituted by a Cl atom and a CH_3 group substituted by a Cl atom), we obtain the same $\Delta_f G^\circ_C$ for the hypothetical *p*-dichlorobenzene:hexafluorobenzene complex when two Cl atoms are present.

Our results strengthen the model used to describe the liquid mixture (eq a when a H atom is substituted by a Cl atom, associated liquid model for benzene, and when a H atom is substituted by *a* CH_3 group[7,8]) and show the coherency of thermodynamic properties for the family studied. As follow-up of the research reported in this paper, it will be interesting to study the effect of chlorine and methyl substitutions in the case of the naphthalene family.

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