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MOLECULAR ALLOYS IN THE SERIES OF *para*-DISUBSTITUTED BENZENE DERIVATIVES.
Part 6. The *para*-dichlorobenzene–*para*-chloroiodobenzene system

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ABSTRACT

The binary system between *para*-dichlorobenzene and *para*-chloroiodobenzene is presented. The phase diagram shows a peritectic phenomenon at high temperature for concentrations very close to pure *para*-dichlorobenzene due to the $\alpha-\beta$ polymorphism of this compound. The main characteristic of this diagram is a syncrystallisation domain in all proportions for the α-phases with a Gibbs' minimum. Crystalline parameters of all the molecular alloys are given.

INTRODUCTION

The work reported here is part of the REALM research program (Réseau Européen sur les Alliages Moléculaires). REALM embraces research groups from Bordeaux, Barcelona and Utrecht. The research deals with the miscibility of organic substances and the properties of their mixed crystals (molecular alloys). Several systems composed of di, tri- and tetra-R-substituted benzenes, with R = Cl, Br, I, and CH_3, have already been studied (ref. 1 and references therein). This series will be used to test the prediction rules concerning syncrystallisation proposed by our group [2].

The system studied here, *para*-dichlorobenzene–*para*-chloroiodobenzene belongs to the family of *para*-dihalobenzene derivatives and is the fifth of a series between $C_6H_4Cl_2$, $C_6H_4Br_2$, C_6H_4ClBr, $C_6H_4ClI_2$, C_6H_4BrI [3–6].

The *para*-dichlorobenzene–*para*-chloroiodobenzene system is mainly characterised by a syncrystallisation domain in all proportions with a

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minimum; nevertheless, a peritectic invariant derived from the polymorphism of the *para*-dichlorobenzene component is observed at high temperature at concentrations near the pure compound.

EXPERIMENTAL

Para-dichlorobenzene (*p*DCB) was from Merck–Schuchardt and *para*-chloroiodobenzene (*p*ClB) was from Fluka AG. The purity of both starting compounds, monitored by vapour phase chromatography and thermal analysis, was over 99%.

The solid solutions were prepared by the dissolution-crystallisation method. The mixtures of the components in suitable molar proportions were first dissolved and then evaporated at controlled temperature. The solvent used was diethyl ether and the evaporation was carried out at 293 K under a weak stream of nitrogen with constant shaking. The behaviour of this system does not require [7] complementary methods, such as fusion-quenching or sublimation-crystallisation.

The thermal characterisation was carried out using a Perkin–Elmer model DSC-4 differential scanning calorimeter. The sample weights ranged between 1 and 3 mg. A heating rate of $2°C\ min^{-1}$ and a total scale sensitivity of 0.4 mwatts were used. The fusion and transition temperatures and energies were obtained with reference to indium fusion under the same experimental conditions. The uncertainty was evaluated by performing several independent experiments and using the Student's formula with a confidence index of 95%.

The crystallographic characterisation was performed by X-ray diffraction by the crystalline powder method at 293 K, using a Philips vertical diffractometer with 17 cm between focus and sample, a curved graphite monochromator in the diffracted beam and a proportional counter. Goniometer speed was $1/8°\ (2\theta)\ min^{-1}$. The working radiation was $K\alpha_1$, wavelength 1.54056 Å. The experimental bichromatism of the $K\alpha$ radiation was corrected by a purpose-built abacus. A minimum of three diagrams were obtained for each compound and alloy, two with internal standard. The crystalline parameters were refined from the reflections observed in the diffraction diagrams, according to the least-squares method [8]. The reflections which gave imprecise readings of Bragg's angle, due to overlapping, were not taken into account.

PHASE DIAGRAM

The two components of the system, *p*DCB and *p*ClB, have already been studied and their characteristics and bibliographic references can be found in our early papers [3,6].

TABLE 1

Cell parameters of βpDCB (at 300 K), αpDCB (at 293 K) and αpClB (at 293 K)

	a (Å)	b (Å)	c (Å)	α (°)	β (°)	T (°)
βpDCB	7.361(2)	5.963(1)	3.959(1)	92.13(2)	113.24(2)	91.42(2)
αpDCB	14.792(6)	5.839(2)	4.036(2)	90.00	112.52(4)	90.00
pClB	15.818(5)	5.912(3)	4.212(2)	90.00	113.61(1)	90.00

pDCB exhibits a strong polymorphism which we have reviewed and studied [3]. It should be noted that it presents three phases but only the α- and β-phases are stable above 293 K. The α-phase is monoclinic, $P2_1/a$ with $Z = 2$. The β-phase is triclinic, $P\bar{1}$ with $Z = 1$.

pClB exhibits a unique monoclinic phase of $P2_1/a$ symmetry with $Z = 2$ from liquid nitrogen temperatures to the temperature of fusion. The existence of four general positions and only two molecules per unit cell implies

TABLE 2

Temperatures and enthalpies of transition and fusion of αpDCB, βpDCB and pClB

	T_{trans} (K)	T_{fus} (K)	ΔH_{trans} (J mol^{-1})	ΔH_{fus} (J mol^{-1})
αpDCB	313.5	–	164 ± 17	–
βpDCB	–	326.0 ± 0.3	–	17740 ± 180
pClB	–	326.2 ± 0.2	–	16100 ± 180

TABLE 3

Solidus and liquidus temperature evolution according to the pClB content in the alloys

Alloys (mol.% pClB)	T_{solidus} (K)	T_{liquidus} (K)
pDCB	326.0 ± 0.3	
5	320.7 ± 0.3	323.5 ± 0.4
10	316.8 ± 0.3	321.7 ± 0.4
20	313.3 ± 0.4	318.2 ± 0.4
30	311.6 ± 0.3	313.6 ± 0.3
40	311.6 ± 0.4	311.8 ± 0.4
45	311.4 ± 0.3	311.6 ± 0.3
50	312.0 ± 0.3	312.5 ± 0.6
55	312.1 ± 0.3	313.0 ± 0.4
60	312.6 ± 0.4	315.1 ± 0.5
70	314.3 ± 0.5	317.9 ± 0.6
80	315.9 ± 0.4	320.4 ± 0.5
90	320.0 ± 0.5	322.9 ± 0.4
pClB	326.2 ± 0.3	

that the symmetry centre is located inside the entity, i.e. that this entity is necessarily a statistical one resulting from a disorder that may be interpreted as either that of orientation or of occupation (refs. 4 and 9, and references therein).

The crystalline parameters, as well as the fusion temperatures and enthalpies of both pure compounds are summarised in Tables 1 and 2, respectively.

A total of 17 compositions were studied: nine compositions of varying molar proportions at intervals of 10% and additional ones in the proximity of the minimum point and in the zone rich in *p*DCB.

The analysis of the diffraction spectra shows that the Bragg angles of all the reflections vary continuously with the composition, i.e. the miscibility is total at 293 K.

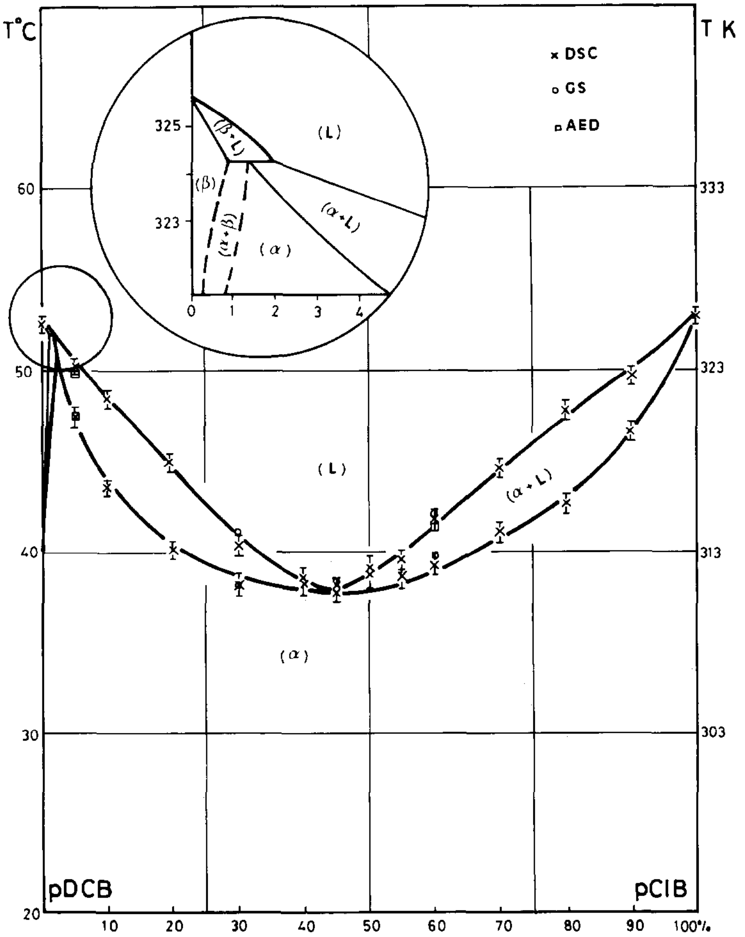

Fig. 1. Phase diagram.

The thermal signals of the alloys prepared at 293 K were analysed using the method of "shape factors" developed by our groups in former studies [10,11]. It enabled, in particular, the determination of the characteristic temperatures of the solid–liquid domain (Table 3).

The phase diagram (Fig. 1) is characterised by the presence of a Gibbs' minimum at a temperature of 311.4 K for the alloy $p\mathrm{DCB}_{0.55}p\mathrm{ClB}_{0.45}$. The biphasic solidus–liquidus equilibrium zone is similar for both sides of the minimum point. The width of this zone is 5 K in the largest zone (Table 3). These data are in good agreement with the partial studies already reported

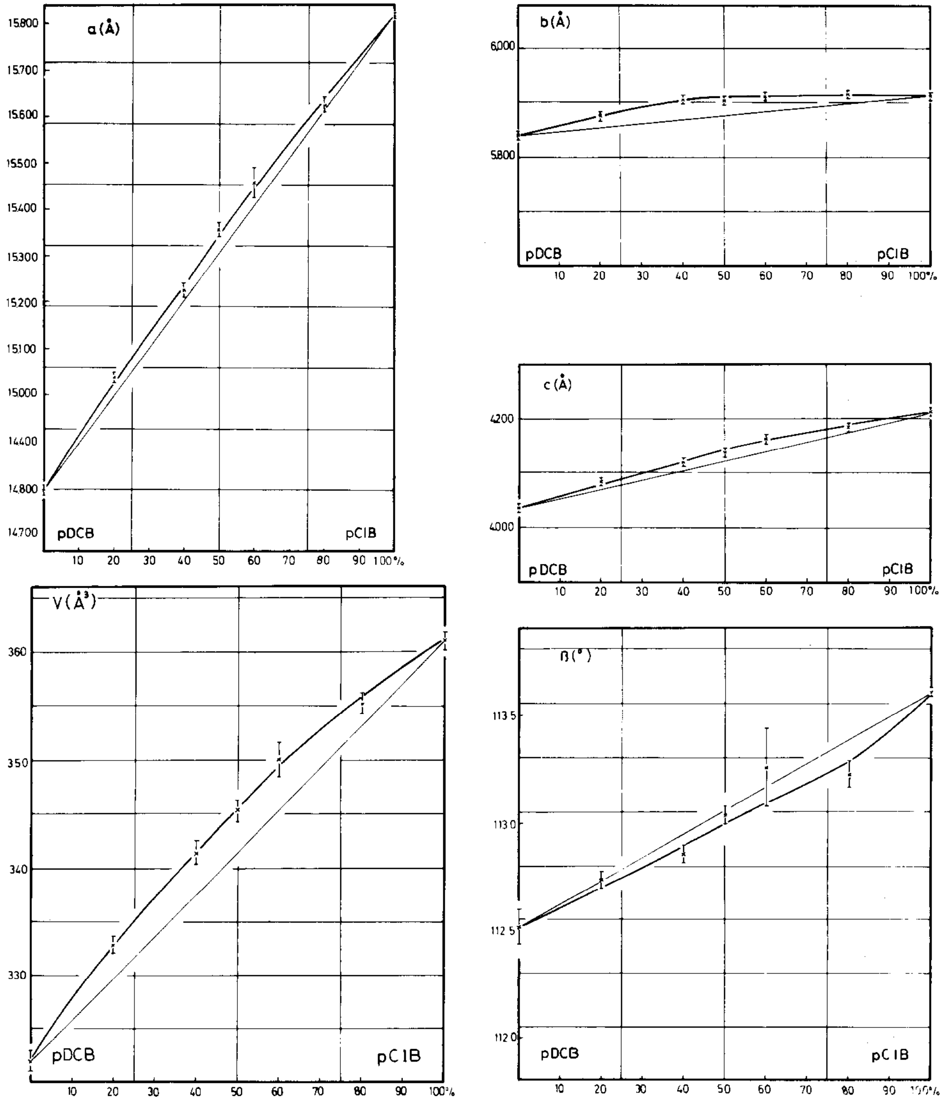

Fig. 2. Variation of the unit cell parameters with composition.

by other authors [12,13]. Another characteristic of this diagram is the presence of a very narrow peritectic invariant in the *p*DCB-rich zone. The latter is the consequence of the existence of the α–β transition of *p*DCB. An accurate study of this zone shows a very narrow equilibrium region of β-type alloys and a biphasic domain (α-alloy + β-alloy) which intersects with the solid–liquid domain, resulting in a very narrow peritectic invariant ($T_p = 324.4$ K; peritectic composition near to 2 mol.% *p*ClB).

The crystalline parameters of the alloys are shown in Fig. 2, from which the expansion of the crystalline lattice from *p*DCB to *p*ClB can be observed, with a rise in its three parameters: *a* has a total increase of 6.9% throughout the system; *b* increases by 1.3%; and *c* by 4.4%. The angle β increases by 1%. This leads to an increase in volume of about 12%.

However, these variations are not wholly linear (they do not follow Vegard's line). Thus, there are positive deviations from the linear variation in *a*, *b*, and *c*. The volume shows a positive deviation which indicates that the molecular alloys are less compacted than would be observed if their crystalline structures were built according to merely geometric packing criteria.

However, the relative deviations from the linear variation ("excess crystalline parameter") are not very pronounced. The maximum deviations are 0.26% for parameter *a*, 0.56% for *b* and 0.32% for *c*. This leads to a maximum in excess volume of 1.10%, which lies around the equimolar composition.

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