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MOLECULAR ALLOYS IN THE SERIES OF *PARA* DISUBSTITUTED BENZENE DERIVATIVES. PART III. THE *PARA*-BROMOCHLOROBENZENE–*PARA*-DIBROMOBENZENE SYSTEM

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ABSTRACT

This paper discusses the binary system between *para*-bromochlorobenzene and *para*-dibromobenzene. The phase diagram and crystalline parameters of the molecular alloys of this system have been determined by DSC and X-ray diffraction. The miscibility versus temperature study has shown a miscibility in all proportions in the solid state between room temperature and the melting points. The evolution of the alloy crystalline parameters with the composition shows that the deformation of the *para*-bromochlorobenzene (*p*BCB) by introducing *para*-dibromobenzene (*p*DBB) takes place mainly in the *a* direction.

INTRODUCTION

The present work is to be considered within the wider context of syncrystallization between organic materials and their alloys.

Until recently, only the binary systems among aliphatic diacids [1] and among naphthalene β-substituted derivatives [2] have been studied.

The system studied here, *para*-bromochlorobenzene–*para*-dibromobenzene, belongs to the family of benzene disubstituted derivatives and is the third of a series which starts with the *para*-dichlorobenzene–*para*-dibromobenzene system [3] and the *para*-dichlorobenzene–*para*-bromochlorobenzene system [4]. This series will be used to test the prediction rules concerning syncrystallization which have been proposed by our group [5].

The *para*-bromochlorobenzene–*para*-dibromobenzene system is characterized by a syncrystallization domain in all proportions with a virtually ideal crystallographic behaviour.

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EXPERIMENTAL

Preparation of samples

The compounds, *para*-bromochlorobenzene (*p*BCB) from Aldrich and *para*-dibromobenzene (*p*DBB) from Merck Schuchardt, were purified by successive crystallizations, the *p*BCB in diethyl ether, and the *p*DBB in methanol. Analyses by gas chromatography have demonstrated a purity of over 99%.

The solid solutions were obtained by the dissolution–crystallization method. For each one, a mechanical mixture of the constituents in the correct molar proportions was diluted in ethyl ether. Then the solvent was evaporated at a controlled temperature T (normally 293 K), supplied by a gentle nitrogen flow and with continual shaking of the solution to avoid differential crystallizations in the solution itself.

In this way, the stable phases are obtained directly at temperature T: with a monophasic equilibrium domain, a unique solid solution of composition equal to the starting mixture would be obtained; with a biphasic equilibrium, where there is a miscibility gap, a binary solid mixture would be obtained, in which the compositions are those of the boundary phases at temperature T. As discussed below, there is no miscibility gap in the system under study and the effective efficiency of the method described renders other methods, such as the fusion–quenching method or the sublimation–crystallization method unnecessary [6].

Thermal characterizaton

The thermal and energetic study was carried out using a Perkin–Elmer model DSC-4 differential scanning calorimeter. The sample weights ranged, between a 1 and 3 mg. A heating rate of 2° C min^{-1} and a total scale sensitivity of 0.4 mwatts were used.

In thermal analysis, the fusion of a pure compound is reflected by a unique peak and the characteristic temperature is given by the extrapolated temperature "onset temperature" (T_o) (Fig. 1a).

The notion of "shape factor" developed by our group in former works [3,7] enables, in particular, the determination of the characteristic temperatures of a solid–liquid domain when this is developed over a narrow range of temperatures.

The first temperature phenomenon is given by the extrapolated value of the fusion peak temperature ($I_{\text{solidus}} = I_o$), while the second is the maximum described by the "shape factor", defined by ΔT, or by the final temperature ΔT_{fin}, with reference to the experimental peak (see Fig. 1). The "shape factor" determination and a detailed explanation of its use can be found in refs. 8 and 9.

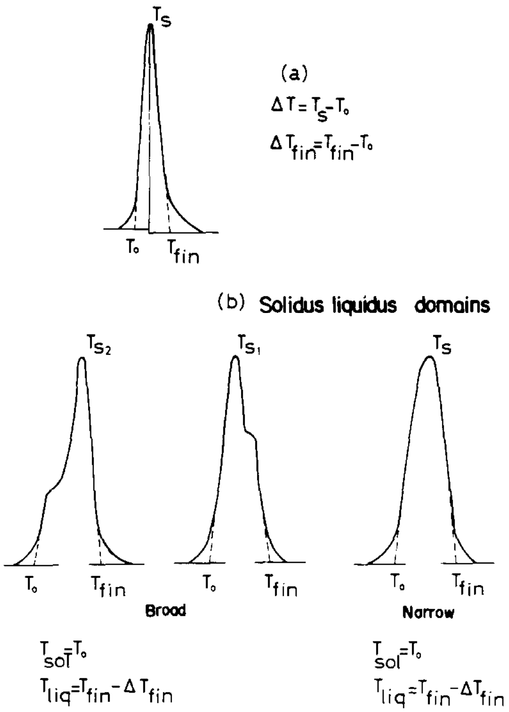

Fig. 1. Thermal signal exploration: (a) shape factor definition; (b) application to a solidus–liquidus equilibrium characteristic temperatures determination where $T_{\rm sol}$ = solidus temperature and $T_{\rm liq}$ = liquidus temperature.

Because of the uncertainty in the determination of ΔT, the final fusion characteristic temperature has been determined as $T_{\rm liquidus} = I_{\rm fin} - \Delta T_{\rm fin}$ (Fig. 1b).

The fusion energies were obtained by integrating the DSC peaks with reference to indium fusion under the same experimental conditions.

The uncertainty has been evaluated by performing several independent experiments and the use of the Student's formula with a confidence index of 95%.

Crystallographic characterization

The X-ray diffraction analysis was made using the crystalline powder method at 293 K, with a Philips diffractometer using a goniometer speed of 1/8 of 20 $\rm min^{-1}$ and 1/0 mm $\rm min^{-1}$ recording speed.

The wavelength used was Cu $K\alpha$ with quartz α phase as internal standard. The influence of the $K\alpha_2$ of Cu was corrected by use of an abacus built for the purpose.

For each composition a minimum of three diagrams were drawn, one of them with the internal standard.

CHARACTERISTICS OF THE COMPONENTS

Both of the system components, *p*BCB and *p*DBB, have already been studied. The crystallographic and energetic characteristics and bibliographic references can be found in published papers [3,4,10].

Work by our group has shown that both components exhibit a unique monoclinic and isomorphous phase of $P2_1/a$ symmetry with $Z = 2$, from liquid nitrogen temperature to the temperature of fusion. The existence of four general positions and two molecules per unit cell implies that the symmetry centre is located inside the molecule, which apparently contradicts the evidence available for *p*BCB. This fact has been studied by several authors [11–13] all of them confirming that this compound is characterized by a disorder of orientation or of occupation in its crystalline cell; therefore, the statistical entity is centro-symmetric.

The crystalline parameters determined at 293 K, as well as the fusion temperatures and enthalpies of both products are: for parabromochlorobenzene, $a = 15.134(4)$ Å, $b = 5.843(2)$ Å, $c = 4.073(1)$ Å, $\beta = 112.53(1)°$, $T = 337.1 \pm 0.3$ K and $H = 18570 \pm 140$ J mol^{-1}; for paradibromobenzene, $a = 15.487(2)$ Å, $b = 5.836(2)$ Å, $c = 4.108(1)$ Å, $\beta = 112.74(1)$ °, $T = 359.6 \pm 0.3$ K and $H = 20220 \pm 510$ J mol^{-1}.

PHASE DIAGRAM

Samples having 10% compositional differences prepared at 293 K were studied. Diffraction spectra show that the Bragg angles of the reflections vary continuously with the composition over the range of values for the

TABLE 1

Solidus (T_{solidus}) and liquidus (T_{liquidus}) temperature evolution according to the *p*DBB content in the alloys

Alloy	T_{solidus} (K)	T_{liquidus} (K)
*p*BCB	337.1 ± 0.3	
10%	337.2 ± 0.6	337.2 ± 0.6
20%	338.5 ± 0.3	339.2 ± 0.3
30%	340.1 ± 0.6	341.9 ± 0.4
40%	342.2 ± 0.6	344.5 ± 0.4
50%	344.5 ± 0.3	347.4 ± 0.4
60%	347.3 ± 0.5	349.3 ± 0.3
70%	350.5 ± 0.6	352.0 ± 0.5
80%	352.9 ± 0.3	353.7 ± 0.4
90%	355.3 ± 0.3	355.7 ± 0.4
*p*DBB	359.6 ± 0.3	

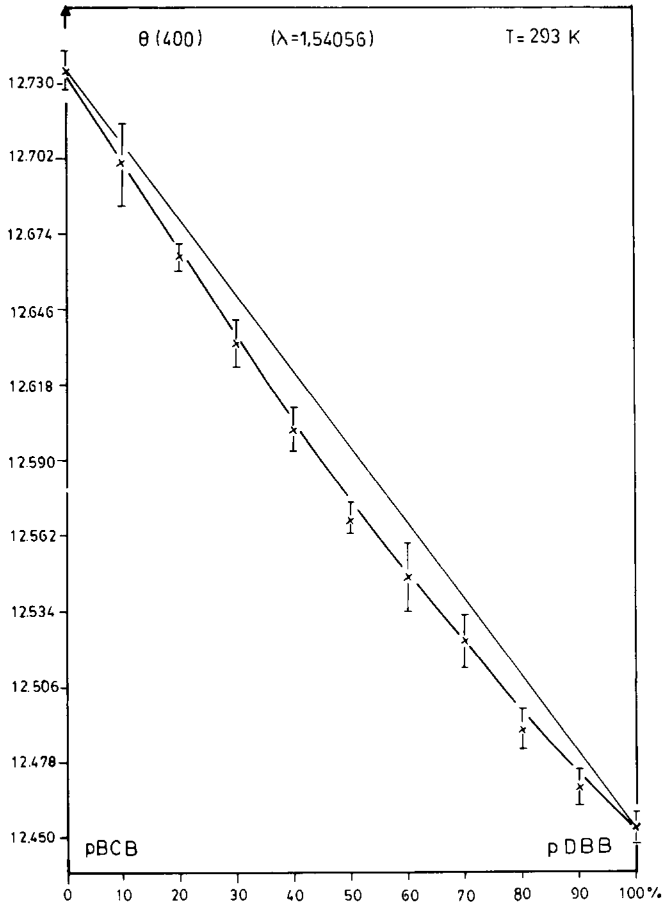

Fig. 2. Bragg angle (400) reflection as a function of composition at 293 K.

starting compounds. This continuous variation is clearly detected on those reflections having a very different diffraction angle in the pure compounds. As an example, Fig. 2 shows the (400) reflection variation as a function of molar composition in *p*DBB.

The thermal analysis of alloys prepared at 293 K has enabled the whole phase diagram to be determined, as shown in Fig. 3.

As can be seen, this corresponds to a system in which both constituents are miscible in all proportions over the temperature range studied (from 293 K). The biphasic solidus–liquidus equilibrium zone is narrow for all compositions. The width of this domain ($|T_{\text{liquidus}} - T_{\text{solidus}}|$) reaches a maximum at equimolar composition, where it is less than 3 K (Table 1).

These results match those obtained by calorimetry [14] and in a study of the electronic absorption bands of the molecular alloys of this system [15].

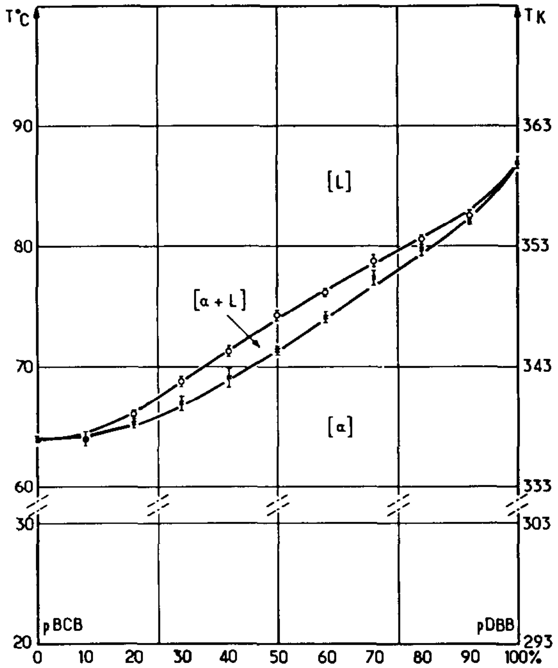

Fig. 3. Phase diagram.

CRYSTALLOGRAPHIC CHARACTERISTICS OF THE MOLECULAR ALLOYS

The crystalline parameters were determined by the least-squares method applied to the data obtained from the crystalline powder diffraction diagrams at 293 K, about 15 reflections for each composition [16]. The results are shown in Table 2. As the proportion of *p*DBB increases, the absolute values of the parameters increase.

TABLE 2

Solid-solution crystalline-parameter variation at 293 K according to composition

Alloy	a (Å)	b (Å)	c (Å)	β (deg)	V (Å^3)
*p*BCB	15.134(4)	5.843(2)	4.073(1)	112.53(1)	332.7(3)
10%	15.176(6)	5.847(3)	4.078(2)	112.57(3)	334.2(4)
20%	15.222(7)	5.847(3)	4.083(2)	112.60(3)	335.5(4)
30%	15.260(5)	5.839(2)	4.084(2)	112.57(1)	336.1(3)
40%	15.298(4)	5.845(3)	4.091(2)	112.60(2)	337.7(3)
50%	15.340(4)	5.844(2)	4.092(2)	112.60(2)	338.7(3)
60%	15.370(5)	5.843(2)	4.097(2)	112.62(2)	339.6(3)
70%	15.404(6)	5.840(2)	4.100(2)	112.67(2)	340.3(3)
80%	15.437(5)	5.842(2)	4.103(2)	112.66(2)	341.4(3)
90%	15.468(4)	5.838(2)	4.104(2)	112.70(2)	341.9(3)
*p*DBB	15.487(2)	5.836(2)	4.108(1)	112.74(1)	342.5(3)

DISCUSSION AND CONCLUSION

The energetic results together with the crystalline powder diffraction results have confirmed the absence of any polymorphic changes in both components and have shown that the compounds *p*BCB and *p*DBB form a binary system which is completely miscible in the solid state, with all proportions of the molecular alloy being obtainable and stable within the temperature range studied. The fusion is characterized by a very narrow solidus–liquidus biphasic equilibrium zone.

Syncrystallization between the compounds is not surprising; the high degrees of molecular homeomorphism (0.95) and crystalline isomorphism (0.97) which have previously been determined [6] had predicted its existence.

From the crystallographic point of view, when the *p*DBB content of the molecular alloys is increased, there is a regular increase in the volume of the

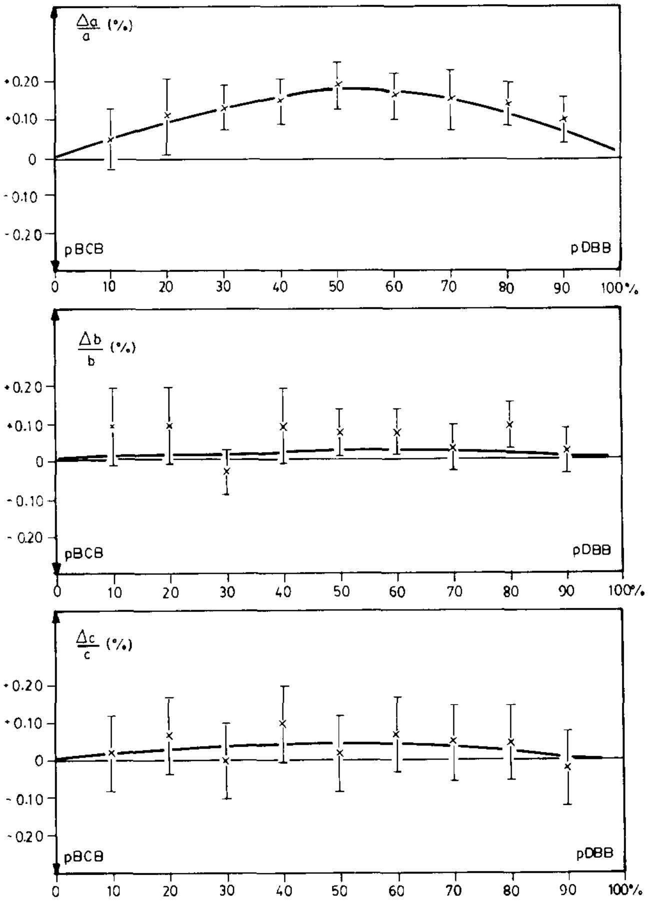

Fig. 4. Relative variation of the *a*, *b* and *c* parameters.

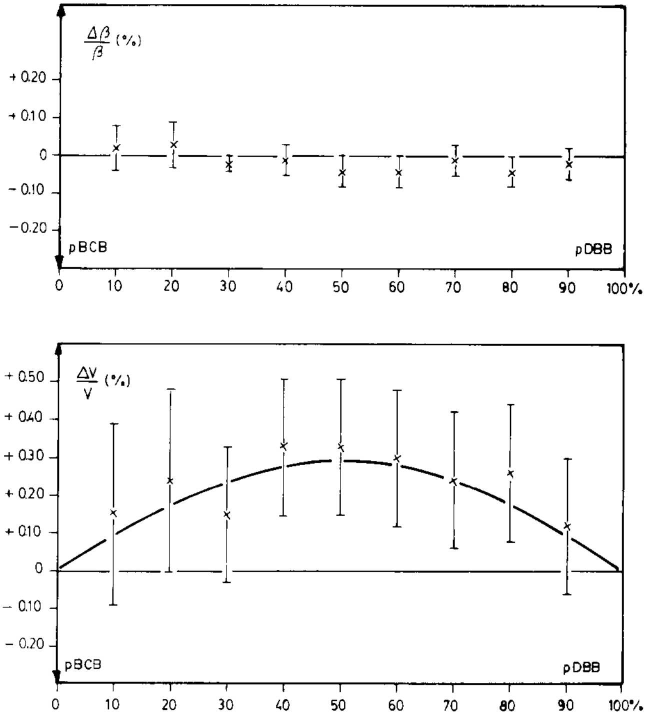

Fig. 5. Variation of β angle and relative volume with composition.

unit cell. However, this expansion is not very isotropic, the *b* and *c* parameters vary slightly with *p*DBB content, while the *a* parameter is very sensitive to substitution of *p*BCB by *p*DBB, so that the cell volume variation essentially reflects the change in *a*.

It can be shown that the deviations from linear behaviour behave in the same way. They have been quantified in relative terms, $(\Delta p/p_v) \times 100$, where p_v is the parameter value calculated by linear extrapolation, and Δp is the difference between the experimental value p and p_v for a set composition.

Figures 4 and 5 clearly show that these variations are almost zero for the *b*, *c* and β parameters, while $\Delta a/a$, and consequently $\Delta V/V$, show a limited, mainly positive deviation being always inferior or equal to 0.2% for $\Delta a/a$ and to 0.3% for $\Delta V/V$.

Consideration of the structure of both compounds will help to explain the behaviour of the crystalline parameters in the molecular alloys: they are flat molecules with almost parallel (001) planes piled on (*h*00)-type layers, it being among these layers that the shorter halogen–halogen contacts are located. Thus the cell variation when *p*BCB is substituted by *p*DBB should be in the *a* direction and the deviations from linear behaviour reflect the mutual Cl–Br interactions. It seems reasonable to believe in the present case that the intermolecular Cl–Br interactions are weaker than the pure Cl–Cl or Br–Br intermolecular interactions.

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