

## Molecular alloys in the series of *para*-disubstituted benzene derivatives.

### Part 8. The *para*-dichlorobenzene + *para*-bromiodobenzene system

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#### Abstract

Experimental data are given for the solid–liquid equilibrium in the system  $(1 - X)p$ -dichlorobenzene +  $X$  *p*-bromiodobenzene. The significance of the data is supported by a thermodynamic phase-diagram analysis.

*Keywords:* Alloy; DSC; SLE; Thermodynamics

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#### 1. Introduction

This paper deals with the solid–liquid phase diagram of the system  $(1 - X)$  *p*-dichlorobenzene +  $X$  *p*-bromiodobenzene, designated  $[(1 - X)\text{ClCl} + X\text{BrI}]$  with  $X$  denoting denoting mole fraction. The two substances belong to the *p*-dihalobenzene (sub) family with halo being Cl, Br, I. With the exception of *p*-

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diiodobenzene, the members of this family at room temperature all have the same crystal structure, space group  $P2_1/a$ , with two molecules per unit cell. Of the isomorphous members of the family ClCl and BrI show the greatest difference in size: their coefficient of crystalline isomorphism [1] is the lowest value of the family, i.e.  $\epsilon_m = 0.857$ . In conformity, the solid state miscibility of the ClCl + BrI system is less pronounced than those of the other *p*-dihalo binary systems.

This paper reports the experimental solid–liquid phase diagram. The experimental information, which will be presented first, is followed by a thermodynamic analysis of the data.

## 2. Experimental

For more experimental details, see Ref. [2].

### 2.1. Materials

*p*-Dichlorobenzene was purchased from Merck–Schuchardt, purity 99%. It was purified by zone refining and the material used in the investigation had a purity higher than 99%, by gas chromatography.

*p*-Bromiodobenzene, from Aldrich > 98%, was purified by recrystallization from acetone and showed a purity higher than 99%, by gas chromatography.

Prior to X-ray and thermal analysis, mixed samples of the two components were prepared by quenching from the melt as well as by rapid crystallization from a solvent. The experimental results described below were virtually independent of sample preparation.

### 2.2. X-ray analysis

X-ray powder diffraction was carried out at 20°C to establish the degree of mutual miscibility. In particular, the reflexion at (210) was studied as a function of overall sample composition. Apart from the pure components, eight mixed samples were studied. For six of these, which had  $0.10 \leq X \leq 0.80$ , the (210) peak was split into two. The two samples which showed a single peak had  $X = 0.05$  and  $X = 0.90$ .

### 2.3. Thermal analysis

From the X-ray results, a solid–liquid phase diagram with a three-phase equilibrium was expected. Indeed, differential scanning calorimetry (DSC) revealed the existence of a eutectic three-phase equilibrium. The area of the eutectic peak as a function of overall sample composition was used, according to the Tammann procedure, to find the compositions of the two solid phases at the three-phase equilibrium point. This resulted in the mole fraction values of  $0.11 \pm 0.02$  and  $0.81 \pm 0.02$ . The results of the thermal analyses are summarized in Table 1 and plotted in Fig. 1 along with their random errors. The liquidus temperatures were derived from the DSC scans employing the form factor method [3].

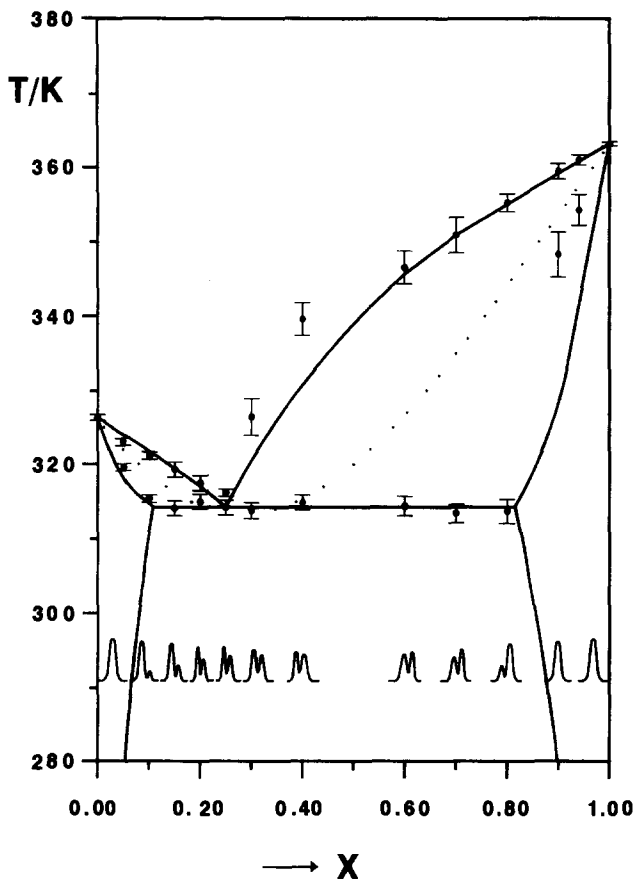


Fig. 1. The calculated phase diagram, corresponding to the numerical values in Tables 2 and 3, along with the experimental data and the experimental uncertainties therein. The symbols at the bottom of the figure refer to the isothermal (293 K) X-ray investigation on samples of given overall composition for which the (210) reflexion was split or not.

### 3. Thermodynamic analysis

From the thermodynamic description of the mixed states of the system we adopt the  $(A, B, \theta)$  model which is characterized by the following formula for the molar excess Gibbs energy

$$G^E(T, X) = A(1 - T/\theta)X(1 - X)[1 + B(1 - 2X)] \quad (1)$$

and the corresponding expressions for excess enthalpy and excess entropy

$$H^E(T, X) = H^E(X) = AX(1 - X)[1 + B(1 - 2X)] \quad (2)$$

$$S^E(T, X) = S^E(X) = (A/\theta)X(1 - X)[1 + B(1 - 2X)] \quad (3)$$

Table 1

Temperatures of the eutectic three-phase equilibrium and of the solidus and liquidus, as a function of overall sample mole fraction, read from the DSC recordings

$X$	$T_{\text{eut}}/\text{K}$	$T_{\text{sol}}/\text{K}$	$T_{\text{liq}}/\text{K}$
0.00			$325.7 \pm 0.4$
0.05		$319.6 \pm 0.5$	$323.0 \pm 0.5$
0.10		$315.4 \pm 0.5$	$321.1 \pm 0.5$
0.15	$314.1 \pm 1.0$		$319.3 \pm 1.0$
0.20	$315.0 \pm 1.0$		$317.5 \pm 1.0$
0.25	$314.2 \pm 1.0$		$316.2 \pm 1.0$
0.30	$313.8 \pm 1.1$		$326.4 \pm 2.5$
0.40	$314.9 \pm 1.0$		$339.6 \pm 2.2$
0.60	$314.4 \pm 1.3$		$346.6 \pm 2.2$
0.70	$313.4 \pm 1.2$		$350.9 \pm 2.4$
0.80	$313.7 \pm 1.6$		$355.3 \pm 1.2$
0.90		$348.3 \pm 3.0$	$359.5 \pm 1.0$
0.94		$354.3 \pm 2.1$	$361.0 \pm 0.7$
1.00			$363.2 \pm 0.3$

$A$ ,  $B$  and  $\theta$  are system-dependent parameters:  $A$  is a measure of the magnitude of the excess Gibbs energy,  $B$  of its asymmetry and  $\theta$  of its change with temperature.

In the case of the system studied, two Gibbs energy functions and, accordingly, two excess Gibbs energy functions are involved: one for the liquid state and, the component substances being isomorphous, one for the solid state.

As a consequence, the thermodynamic analysis amounts to the determination of two sets of ( $A$ ,  $B$ ,  $\theta$ ) values using the phase diagram data and the thermodynamic melting properties of the pure components, summarized in Table 2.

The ( $A$ ,  $B$ ,  $\theta$ ) values of the solid state,  $A^{\text{sol}}$ ,  $B^{\text{sol}}$ ,  $\theta^{\text{sol}}$ , were obtained as follows. First,  $\theta^{\text{sol}}$  was set at 575 K, in conformity with the rule, formulated recently [4], for the relation between  $\theta$  and  $T_{\text{EGC}}(X = 1/2)$

$$\log \theta = (1.10 \pm 0.5) \log T_{\text{EGC}}(X = 1/2) \quad (4)$$

$T_{\text{EGC}}(X = 1/2)$  represents the equal- $G$  curve (EGC) temperature [5] for the solid to liquid transition for  $X = 1/2$ . Next,  $A^{\text{sol}}$  and  $B^{\text{sol}}$  were derived from the experimental limits of the region of demixing, giving priority to the three-phase equilibrium data. This yielded  $A^{\text{sol}} = 14\,225 \text{ J mol}^{-1}$  and  $B^{\text{sol}} = 0.10$ .

Table 2

Pure component melting properties, i.e. melting point and entropy of melting, used for the calculations. Note that the "stable melting point" of  $\text{ClCl}$  is 0.2 K higher than the value given in this table

	$T/\text{K}$	$\Delta S^*/(\text{J K}^{-1} \text{ mol}^{-1})$
$\text{ClCl}$	326.03	55.48
$\text{BrI}$	363.15	51.88

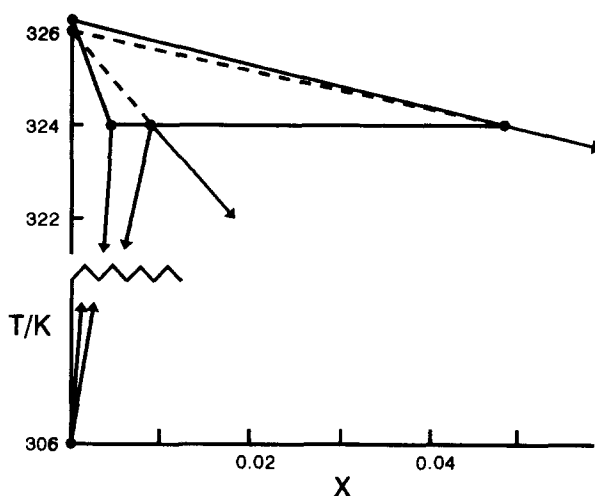


Fig. 2. The estimated position of the three-phase equilibrium corresponding to the polymorphic transition of *p*-dichlorobenzene.

For the liquid state, first  $\theta^{\text{liq}}$  was given the solid state value of 575 K (which, in a sense, is arbitrary). Thereafter, the remaining two parameters  $A^{\text{liq}}$  and  $B^{\text{liq}}$  were found by analyzing the EGC. The position of the EGC could be found easily using the phase diagram calculated earlier (figure IV.72 in [2]). The resulting values are  $A^{\text{liq}} = 2625 \text{ J mol}^{-1}$  and  $B^{\text{liq}} = -1.0$ .

The phase diagram calculated with the two ( $A$ ,  $B$ ,  $\theta$ ) triplets (Table 3) and the pure component data (Table 2) is shown in Fig. 1, along with the experimental data. The calculated diagram does not take into account the effect of the phase transition in  $\text{ClCl}$  at 306 K; the kind of correction to be applied is shown in Fig. 2. The calculated coordinates of the three-phase equilibrium are: temperature, 314.5 K; mole fractions of solid phases, 0.111 and 0.809 mole fraction of liquid phase, 0.255.

Table 3

Values of the ( $A$ ,  $B$ ,  $\theta$ ) parameters obtained in the present study

	$A/(\text{J mol}^{-1})$	$B$	$\theta/\text{K}$
Solid	14225	0.10	575
Liquid	2625	-1.0	575

#### 4. Discussion

It can be seen from Fig. 1 that the experimental liquidus points for  $X = 0.30$  and  $X = 0.40$  and the solidus points for  $X = 0.90$  and  $X = 0.94$  are in disagreement with

the calculated diagram, even more than can be justified by the (considerable) experimental uncertainties. Inspection of the original DSC recordings (figure IV : 66 in Ref. [2]) shows that the samples with  $X = 0.30$  and  $X = 0.40$  both have very pronounced eutectic peaks. It is virtually impossible to make a distinction between the tail of the melting effect and the reappearance of the base line. The same can be observed, mutatis mutandis, for the onset of melting in the case of the samples with  $X = 0.90$  and  $X = 0.94$ . In view of these observations it can safely be remarked that the calculated phase diagram is in full agreement with the hard (and major) part of the experimental data.

The system studied is the one with the lowest  $\epsilon_m$  value of the *para*-dihalobenzene subfamily, as was mentioned above. This fact puts the system into a key position and it implies that any new result on the system will have a direct influence on a global description of the complete family or, more concretely, on the global thermodynamic description which was presented by Calvet et al. [6], the first in which the idea of a characteristic temperature, a common  $\theta$  value, was elaborated for a family of molecular mixed crystals. Without going into detail it can be remarked that the result of this paper corresponds to a (metastable) critical mixing temperature of 347 K, whereas the global description (taking the liquid state as an ideal mixture) gave rise to the value of 267 K.

To conclude, it may be remarked that the physical significance of the liquid state ( $A$ ,  $B$ ,  $\theta$ ) parameters, i.e. the parameters derived in the present thermodynamic analysis, is rather uncertain. A systematic investigation on the thermodynamic properties of liquid mixtures of the *p*-dihalobenzene family is still lacking.

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