

THE SYSTEM *p*-DIBROMOBENZENE + *p*-CHLOROIODOBENZENE + *p*-BROMOIODOBENZENE—A METHODOLOGICAL STUDY ON THERMAL ANALYSIS AND THERMODYNAMIC PHASE-DIAGRAM ANALYSIS

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ABSTRACT

Liquidus temperatures were measured of the ternary system *p*-dibromobenzene + *p*-chloriodobenzene + *p*-bromiodobenzene. The liquidus data of the three binary subsystems were subjected to a thermodynamic analysis, the outcome of which was used to calculate the ternary liquidus surface. The results of the measurements and the calculations are used to discuss the possibilities and the limitations of rapid thermal analytical methods in solid–liquid phase-diagram research in the field of molecular mixed crystals.

INTRODUCTION

In the field of molecular mixed crystals the experimental work of Campbell and Prodan on the system *p*-dichlorobenzene + *p*-bromochlorobenzene + *p*-dibromobenzene, which was published in 1948 [1], has become classical. With the help of “an apparatus for refined thermal analysis”, Campbell and Prodan studied the liquid–solid transition, using carefully purified materials. Liquid samples having a mass of about 40 g (our estimate) were cooled at a rate of 0.3 K min⁻¹. During the experiment, the sample was agitated by means of a fluctuating air pressure. As a result, cooling curves were obtained on which the onset of crystallization was clearly marked; the inconvenient side-effect of undercooling was apparently absent. In view of all this, the liquidus points reported by Campbell and Prodan must be regarded as the thermodynamically true liquidus points. That is to say, the temperature at which a really homogeneous liquid phase, of which the composition is equal to the overall sample composition, is in equilibrium with an infinitesimal amount of solid phase.

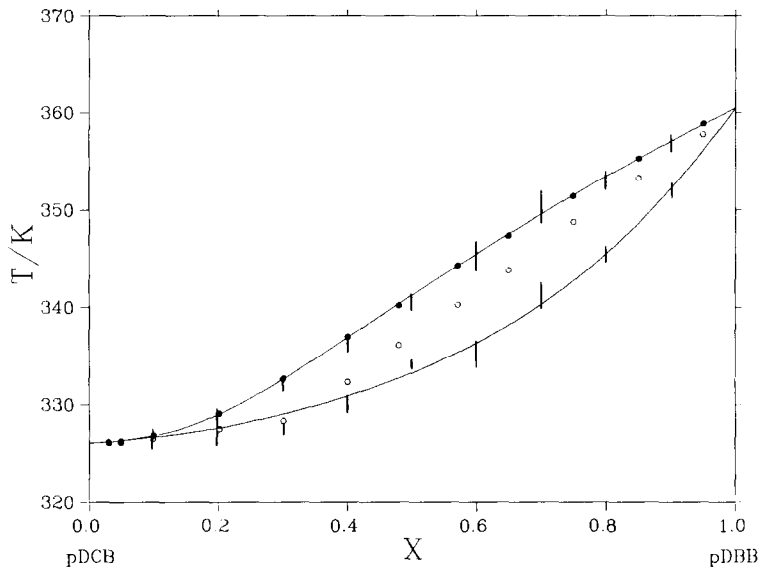


Fig. 1. The system *p*-dichlorobenzene + *p*-dibromobenzene; solid-liquid equilibrium diagram. Curves: calculated solidus and liquidus (the curves originate from the metastable melting point of *p*-dichlorobenzene). Filled and open circles: experimental liquidus and solidus points by Campbell and Prodan [1]. Bars: DTA data by Haget et al. [3].

A thermodynamic analysis of Campbell and Prodan's data was made by Moerkens et al. [2]. The data on the three binary subsystems were analyzed by means of the LIQFIT method. LIQFIT is an iterative procedure in which, by means of intermediate phase-diagram calculations, the calculated liquidus is made to pass through the experimental liquidus points. In the case of the three subsystems, the mean difference between the experimental and calculated temperatures was about 0.1 K. The results obtained for the three subsystems were used by Moerkens to calculate the ternary liquidus surface. The calculated surface showed close agreement with the experimental data: the mean difference between experimental and calculated temperatures for 57 points inside the composition triangle was about 0.1 K. The result of Moerkens' calculations can be regarded as a proof of the high internal accuracy of Campbell and Prodan's data.

Moerkens' calculations also revealed that the experimental solidus data are not thermodynamically consistent with the liquidus data, see Fig. 1. This is not surprising, because the employed experimental method does not guarantee thermodynamic equilibrium, from the beginning to the end of the experiment, between the liquid phase and the complete amount of solid material. This observation is of general validity: solid-liquid phase diagrams (of organic as well as inorganic systems) determined by cooling curve methods as a rule show incorrect solidus curves.

With the development of automated DSC and DTA instruments, the kind of investigation carried out by Campbell and Prodan has become obsolete.

The main advantage of these instruments lies in the enormous reduction of the amount of material needed and, therefore, indirectly, in the reduction of time. The disadvantages of these instruments, from a thermodynamic equilibrium point of view, are no less significant than those met with the cooling curve technique. An additional inconvenience is the phenomenon of undercooling (small samples, absence of agitation). As a consequence, experiments have to be made in the increasing temperature mode. And that means that the signals will also depend on the manner of sample preparation; the onset of melting does not necessarily correspond to the solidus (the onset temperature shown by a mixed crystalline material obtained in a cooling curve experiment generally differs from the onset temperature of a material of the same composition prepared by quenching from the liquid). On the other hand, one may expect that the last amount of solid disappears at the liquidus temperature. Unfortunately, the exact temperature at which the melting is completed, before the curve returns to the baseline, cannot be read that easily from the thermogram. In spite of these inconveniences, the results obtained by Haget et al. [3], by applying the form-factor method [4] to their DTA data, are in virtual agreement with the calculated phase diagram based on Campbell and Prodan's data, see Fig. 1.

The present paper is written around the system *p*-dibromobenzene + *p*-chloriodobenzene + *p*-bromiodobenzene. It is the report of an investigation which is, in fact, a repetition of Campbell and Prodan's and Moerkens' work, with the distinction that the thermal analysis part is made by differential scanning calorimetry. In a period of about one month, about 100 samples, including 17 ternary samples, were scanned using a Perkin-Elmer DSC-2 instrument. The data on the binary subsystems were subjected to a thermodynamic analysis. The result of that analysis was subsequently used to calculate the ternary liquidus surface.

The main aim of this paper is to use the results as a basis for a discussion on methodological matters and on the possibilities and limitations of using rapid thermal analytical methods for the determination of solid-liquid phase diagrams in the field of molecular mixed crystals. The experimental data presented below have a preliminary character, the individual numerical values are given without an indication of their precision. The results of a parallel and more thorough investigation of the binary subsystems will be published in a forthcoming paper [5].

EXPERIMENTAL

Stock samples of the component substances were made by repeated vacuum sublimation of amounts of commercially available materials and had purities of 99.5% or better.

DSC experiments on the component substances were made to determine their melting points, their enthalpies of melting and the peak width as a

TABLE 1

Melting points and heats of melting for indium, anthracene, *p*-dibromobenzene (*p*DBB), *p*-chloriodobenzene (*p*CIB) and *p*-bromiodobenzene (*p*BIB)

Substance	T_0 (K)	T_0 (ref. 5) (K)	ΔH (kJ mol ⁻¹)
In	429.8		3.267
Anthracene	489		28.86
<i>p</i> DBB	360.6	359.6 ± 0.3	19.6
<i>p</i> CIB	326.2	326.2 ± 0.3	16.0
<i>p</i> BIB	363.7	363.2 ± 0.3	18.8

function of sample mass (1–10 mg). Indium and anthracene were used for calibration. The heats of melting and the melting points are given in Table 1. All experiments on the pure substances as well as on the mixed samples were made with a heating rate of 2.5 K min⁻¹ and a sensitivity of 0.1 mcal s⁻¹. Mixed samples were prepared by weighing amounts of the component substances directly into the sample cups, such that the total mass was about 2 mg. The mechanically mixed samples were melted in the DSC instrument and then rapidly cooled, as a result of which the samples instantaneously solidified (at an undercooling of up to 30 K). Thereafter each sample was measured twice. The liquidus temperatures were derived from the thermograms, following the method of Courchinoux et al. [4] and using the relation

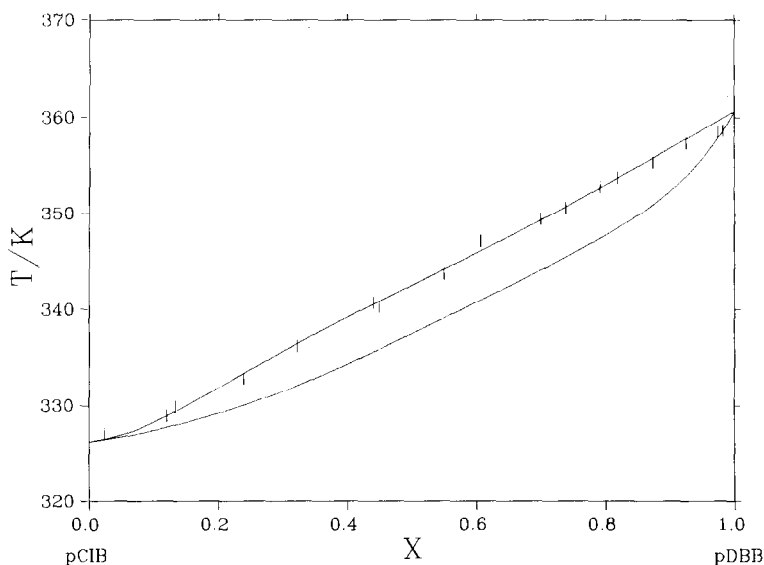


Fig. 2. The system *p*-chloriodibenzene + *p*-dibromobenzene; solid-liquid equilibrium diagram. Curves: calculated solidus and liquidus. Bars: experimental liquidus data obtained by DSC.

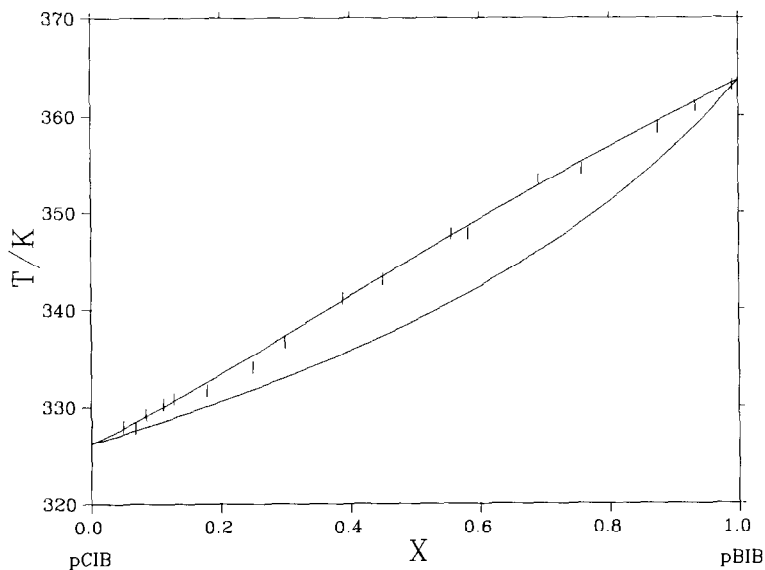


Fig. 3. The system *p*-chloriodobenzene + *p*-bromiodobenzene; solid-liquid equilibrium diagram. Curves: calculated solidus and liquidus. Bars: experimental liquidus data obtained by DSC.

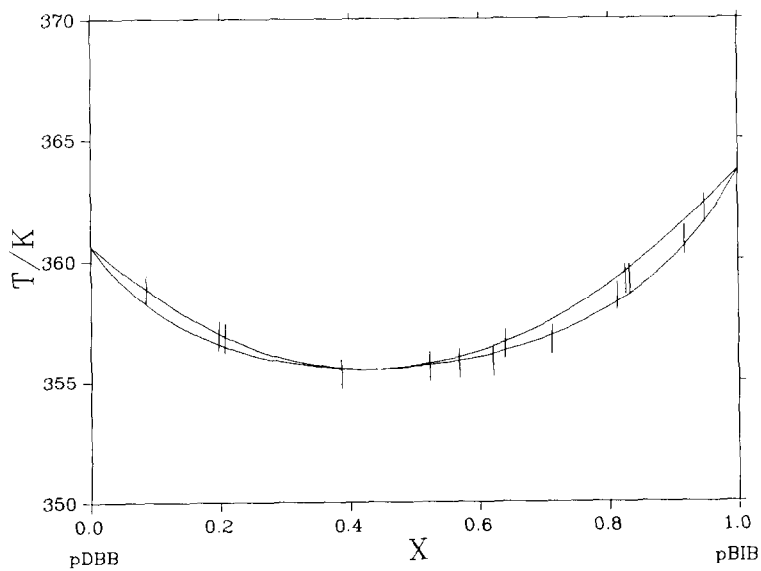


Fig. 4. The system *p*-dibromobenzene + *p*-bromiodobenzene; solid-liquid equilibrium diagram. Curves: calculated solidus and liquidus. Bars: experimental liquidus data obtained by DSC.

TABLE 2

Ternary mixtures: mole fractions, experimental liquidus temperature, calculated liquidus temperature and the difference between experimental and calculated temperature

X_{bi}	X_{ci}	X_{db}	T_{exp} (K)	T_{calc} (K)	$T_{exp} - T_{calc}$ (K)
0.480	0.300	0.220	348.3	348.50	-0.2
0.403	0.076	0.521	352.0	353.15	-1.2
0.735	0.141	0.123	355.4	355.80	-0.4
0.071	0.401	0.528	344.3	344.72	-0.4
0.174	0.716	0.110	335.4	334.70	0.7
0.064	0.163	0.774	352.7	353.08	-0.4
0.957	0.036	0.007	360.2	362.32	-2.1
0.386	0.173	0.441	351.1	350.50	0.6
0.256	0.413	0.331	343.7	343.80	-0.1
0.098	0.777	0.124	332.4	332.40	0.0
0.066	0.066	0.868	356.4	356.70	-0.3
0.240	0.403	0.357	342.6	344.00	-1.4
0.325	0.460	0.208	341.6	343.10	-1.5
0.160	0.352	0.488	346.7	345.50	1.2
0.146	0.322	0.522	347.6	346.40	1.2
0.619	0.333	0.048	349.0	350.56	-1.6
0.067	0.555	0.377	338.3	339.90	-1.6

between peak width and sample mass found for the component substances. The results obtained for the binary subsystems are shown in Figs. 2, 3 and 4; they are indicated by bars, the centre of a bar corresponding to the mean liquidus temperature of the two measurements. The results obtained for 17 ternary samples are collected in Table 2.

COMPUTATIONS

LIQFIT analysis of binary data

LIQFIT, of which a detailed description can be found elsewhere [6,7], is a method of thermodynamic phase-diagram analysis. Its input consists of the thermodynamic properties of the pure components, the measured liquidus points and, if available, part of the thermodynamic mixing properties. Its output is a calculated phase diagram (of which, at any rate, the liquidus passes through the experimental liquidus points) and, in addition, the coefficients of the difference excess Gibbs energy function expressed in the Redlich-Kister form and valid for the mean temperature of the data

$$\Delta G^E(X) = X(1-X) \left[\Delta G_1 + \Delta G_2(1-2X) + \Delta G_3(1-2X)^2 + \dots \right]$$

TABLE 3

Results of LIQFIT computations: values of the mean mole fraction difference, the mean temperature difference and values of the solid state excess Gibbs energy coefficients

System		ΔX	ΔT (K)	G_1 (solid) (J mol ⁻¹)	G_2 (solid) (J mol ⁻¹)	G_3 (solid) (J mol ⁻¹)
Component 1	Component 2					
<i>p</i> CIB	<i>p</i> DBB	0.013	0.43	885	-167	762
<i>p</i> CIB	<i>p</i> BIB	0.011	0.43	697		
<i>p</i> DBB	<i>p</i> BIB	0.014	0.16	1384	25	307

where X is the mole fraction of the second component of the binary system and ΔG_i stands for $G_i(\text{liquid}) - G_i(\text{solid})$.

For each of the binary systems the input liquidus data were those of Figs. 2, 3 and 4. The pure component input data were the observed melting points and entropies of melting. The melting points are those of Table 1; the entropies of melting, which can be derived from the data in Table 1, are the following, expressed in J K⁻¹ mol⁻¹: 54.4 (*p*DBB); 48.9 (*p*CIB) and 51.8 (*p*BIB). The calculations were made assuming ideal mixing behaviour of the liquid phase (in that case the output difference excess Gibbs energy function represents the excess Gibbs energy function of the solid, with opposite sign).

The results of the computations are the calculated phase diagrams, i.e. the solidus and liquidus curves in Figs. 2, 3 and 4, and the solid state excess function coefficients given in Table 3. As a rule, LIQFIT calculations are made with a number of G coefficients which varies from one to four. Two of the three systems gave the best results with three adjustable G parameters. The system *p*CIB + *p*BIB needed just one G coefficient. The criterion which is used to end the computations and to distinguish between the four different solutions is the ΔX value. The latter is the mean mole fraction difference, which is defined as the arithmetic mean of the absolute difference between experimental mole fraction and the mole fraction calculated for the liquidus at the temperature of the experimental point. The mean absolute (in the mathematical sense) temperature differences, which can be derived from Figs. 2, 3 and 4, are included in Table 3.

The ternary liquidus surface

The entropies of melting of the pure components and the excess Gibbs energy functions found by LIQFIT for the three binary subsystems were used to calculate the ternary liquidus surface. In other words, it is assumed that the ternary excess Gibbs energy can be composed of the three binary functions; see Moerkens [2] for the exact procedure. Just as for the analyses of the subsystems, the liquid state was taken as an ideal mixture.

Instead of a detailed description of the liquidus surface, just the temperatures corresponding to the compositions of the measured samples are given in Table 2. The mean difference between the experimental and calculated temperatures is -0.4 K.

DISCUSSION

Random errors

Because LIQFIT is, in fact, a smoothing method, the mean mole fraction and temperature differences, ΔX and ΔT , are indications of the random errors of the experimental data rather than a measure of the success of the computations, see Figs. 1–4. Comparison of the ΔX and ΔT values obtained by Moerkens [2] for Campbell and Prodan's data [1] and the values obtained in the present investigation, see Table 3, shows that the latter are about six times the former. In rounded values for ΔT , 0.1 K against 0.5 K.

As a result of the smoothing procedure, the uncertainty in the calculated liquidus temperature due to random errors will be less than the ΔT value. For the present investigation the uncertainty due to random errors may be estimated at 0.2 K. The conclusion that the results that can be obtained for molecular mixed crystals by applying LIQFIT to DTA and DSC data come into the vicinity of 0.1 K precision seems to be justified.

Systematic errors

The fact that the combination of experimentation on a DSC instrument and thermodynamic analysis can be used to determine liquidus temperatures with a precision of 0.2 K or less, makes it worthwhile to consider systematic errors. This statement implies that one should try to reduce the systematic errors of the experimental technique to less than 0.2 K.

In fact, there are two sources of systematic errors. These are related to the calibration of the instrument and to the reading of the liquidus temperatures from the thermograms. As for calibration, the use of reference materials and the use of thermocouples for temperature measurement imply a systematic uncertainty which may be less than 0.2 K but, at any rate, is higher than 0.1 K. With regard to the reading of the liquidus temperatures from the thermograms, the disappearance of the last amount of solid is not an event which is clearly marked on the thermogram. In the method followed to derive the liquidus temperatures from the thermograms, corrections of about 2 K are applied to account for the finite response time of the experimental set-up. These corrections are derived from the thermograms of the pure components, which invariably show sharp peaks in contrast to the thermograms of most of the mixtures. Therefore, it may be possible that the method

of making corrections can be refined, for instance by using computer simulations in which sample preparation, phase diagram and thermal properties of sample and apparatus are taken into account.

In terms of the calculated excess function coefficients, a systematic error in temperature due to calibration does not affect the calculated excess function provided it is constant over the whole temperature range. On the other hand, a systematic error which is a function of mole fraction does give rise to an error in the calculated excess function. For example, a systematic error in the liquidus temperature in the middle region of the system *p*CIB + *p*DBB, Fig. 2, of +0.25 K would imply that the calculated coefficient G_1 (885 J mol^{-1}) is about 50 J mol^{-1} lower than it should be.

The ternary liquidus surface

The calculation of a ternary equilibrium from binary data has become common practice in phase diagram research. The significance of the calculated result can be verified by a small number of carefully defined experiments. The latter give rise to corrections which as a rule are relatively small. In the case of the two ternary systems considered in this paper, *p*-dichlorobenzene + *p*-bromochlorobenzene + *p*-dibromobenzene and *p*-dibromobenzene + *p*-chloriodobenzene + *p*-bromiodobenzene, the mean differences between the experimental liquidus data and the calculated liquidus temperatures have the same order of magnitude as the binary LIQFIT ΔT values, about 0.1 K for the former and about 0.5 K for the latter system. In other words, in the case of these two examples of molecular mixed crystals, the calculated liquidus surface can be considered to be in full agreement with the experimental data. Therefore, for molecular mixed crystals it seems to be more advantageous to improve the determination of the binary data than to study ternary and higher systems by means of a rapid non-equilibrium experiment.

A kink in the liquidus curve

In the discussion above on the influence of random errors, it was implicitly assumed that the liquidus is part of a phase diagram corresponding to a continuous series of mixed crystals (complete subsolidus miscibility). An inconvenient aspect of the larger random errors is that they can hide a moderate jump in the slope of a liquidus curve. Such a jump accompanies a peritectic three-phase equilibrium, either due to the fact that the pure components are not isomorphous or to demixing in the solid state. In the demixing case, the three-phase equilibrium will possibly be found by LIQFIT. In the case of isodimorphism [8], the three-phase equilibrium will not be found by LIQFIT, i.e. when the fact of isodimorphism is ignored.

Another phase-diagram item that may be submerged in the error bars is a minimum or a eutectic point close to the axis of the lower melting component. As an example, we may again consider *p*-dichlorobenzene + *p*-dibromobenzene, which has such a point at 1.22 mol.% and 0.18 K lower than the melting point of pure *p*-dichlorobenzene. It was observed by Campbell and Prodan, who identified it as a minimum, not knowing that in the vicinity of the melting point the two substances have different crystal structures, see also reference 3. (In Fig. 1, the liquidus and solidus start from the metastable melting point of *p*-dichlorobenzene, which is 0.12 K below the real melting point.)

The subliquidus characteristics

So far, the discussion has focussed on the liquidus. In order to structure the discussion on the subliquidus characteristics of the phase diagram, the following division has been made: (1) systems in which the components are isomorphous and show complete solid miscibility; (2) systems in which the components are isomorphous but not completely miscible in the solid state; and (3) systems in which the two components are not isomorphous.

(1) In the case of complete solid miscibility the only subliquidus characteristic to be discussed is the solidus. In the approach followed in this investigation, the solidus curve is the result of a thermodynamic–equilibrium computation, based on the assumption that the liquidus is correct. It implies that the accuracy with which the solidus can be located comes in the vicinity of the liquidus' accuracy. The precision of the method is, to a certain extent, dependent on the excess Gibbs energies of the liquid mixtures [7], which should be introduced in the LIQFIT computations. The latter are usually unknown. On the other hand, molecular substances that form mixed crystals as a rule form liquid mixtures with small deviations from ideal-mixing behaviour. Consequently, there are no a priori reasons to question the precision of the LIQFIT method. As a result, the calculated solidus can be used as a reference for a discussion on the determination of that curve by means of experimental methods.

In cooling experiments of the kind used by Campbell and Prodan, inhomogeneous solid material is formed. This is due to the fact that low mobility in the solid state is an obstacle for global equilibrium. It implies that the last amount of liquid disappears at a temperature which is close to the lowest temperature of the liquid field in the phase diagram (the melting point of the lower melting component in the case of a phase diagram without a minimum). This explains the fact that reported solidus curves derived from cooling curves are often too low, in terms of temperature. (In contrast, however, Campbell and Prodan's solidus points are too high, see Fig. 1, a result of their method of analyzing the form of the cooling curve). When used in a DTA experiment, the solid material obtained in a cooling

experiment of the kind of Campbell and Prodan will probably produce a thermogram that has characteristics corresponding to eutectic behaviour.

One of the most reliable experimental procedures used to determine the solidus is to prepare homogeneous solid material and to observe the onset of melting in an experiment during which the temperature is raised at an infinitesimal rate. An example is the work of Bouwstra [9] on the system *trans*-azobenzene + *trans*-stilbene, another time- and material-consuming investigation. Samples prepared by zone leveling were studied by adiabatic calorimetry. It yielded heat capacity versus temperature curves on which the onset and the completion of melting are sharply marked. In addition, Bouwstra's liquidus points, used as a basis for LIQFIT computations, produced a calculated solidus curve which was in full agreement with her solidus points.

In another investigation, van Genderen et al. [10] used the zone leveling technique to prepare homogeneous material of *p*-dichlorobenzene + *p*-dibromobenzene. When heated in a DSC, the material produced melting peaks of which the onset temperatures correspond to the calculated Equal-G Curve (Equal Gibbs energy Curve). The latter is a curve in the phase diagram lying between solidus and liquidus [11].

With rapid measurements of small samples of mixed molecular material, as a result of the above observations, it may be concluded that, depending on sample preparation and scanning speed, there are tendencies that raise the onset of melting with respect to the solidus (with the *p*-dichlorobenzene + *p*-dibromobenzene samples prepared by zone levelling) and there are other tendencies that lower the onset of melting (with samples obtained in a cooling curve experiment). The extent to which these effects balance out, as well as the extent to which Bouwstra's ideal conditions are approached, is hard to quantify a priori. For the time being, the form-factor method of Courchinoux et al. [4] is the most reliable means of determining the experimental solidus.

(2) In terms of thermodynamic properties, mixed crystals of isomorphous substances usually have positive excess Gibbs energies. The latter correspond to regions of demixing as well as to the tendency to produce phase diagrams with a minimum. In the case of large positive deviations, the solid-liquid equilibrium and the region of demixing will interfere, giving rise to a phase diagram with either a eutectic or a peritectic three-phase equilibrium. The most delicate aspect of these phase diagrams is in the compositions of the two solid phases at the three-phase equilibrium. Here, both thermal-analytical methods and phase-diagram analysis based on liquidus data reach their limits. This means that the extent of solid miscibility, at both sides of the system, should be determined by an independent method, preferably an equilibrium method by which the system is brought to equilibrium at constant temperature and the solid phases analyzed, e.g. by means of X-ray diffraction. After the determination of the liquidus and the

limits of miscibility, thermodynamic phase-diagram analysis should be applied to examine the mutual consistency of the data and to calculate the complete phase diagram.

(3) Systems in which the components show solid state miscibility, in spite of the fact that the components are not isomorphous, display phase diagrams with either eutectic or peritectic three-phase equilibria. In the case of these systems, a thermodynamic analysis in terms of LIQFIT requires the metastable melting points of the pure components. That is to say that, when the first component crystallizes in, say, the α structure and the second in the β structure, it must be known at what temperature the first/second component would melt if it had the β/α structure. Once the metastable melting points are known, the treatment of the liquidus data by means of LIQFIT may result in a reasonable estimation of the boundaries of the solid state two-phase region. Such a calculation must be verified by determining those boundaries by means of equilibrium experiments. An example of a system which was studied this way is naphthalene + 2-fluoronaphthalene, whose phase diagram was measured by Meresse [12]; a thermodynamic analysis based on Meresse's data was made by van Duijneveldt et al. [13].

As a final remark, and in view of the observations made above, the subliquidus characteristics of the phase diagrams displayed in Figs. 2–4 should be considered as tentative.

CONCLUSION

In the field of molecular mixed crystals, reliable solid–liquid phase diagrams can be obtained by the combined approach of thermal analysis, X-ray crystallography and thermodynamics. It is advisable to give priority to the publication of phase diagrams for which the combined approach has led to consistent results. The latter should be related to the original thermal analytical data in order to improve the precision of thermal analysis in determining solidus and liquidus points. The limits of solid state miscibility should be determined by means of equilibrium (X-ray) methods.

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