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ALEACIONES MOLECULARES BINARIAS EN FASE PLÁSTICA. ESTUDIO TERMODINÁMICO GLOBAL EN ALGUNOS DERIVADOS DEL NEOPENTANO.

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Two-component systems of isomorphous orientationally disordered crystals . Part I: Packing of the mixed crystals.

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Abstract

Five experimental two-component phase diagrams between Orientationally Disordered Crystals (ODICs) have been established from the low-temperature phase to the liquid state using thermal analysis and x-ray powder diffraction techniques. The high-temperature orientationally disordered phases for the pure components, which belong to the series $(CH_3)_{4-n1} C(CH_2OH)_{n1}$ ($n_1=1,2,3$) and $(NO_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ ($n_2=0,1$) are all of them face centered cubic. Continuous disordered mixed crystals in the whole range of concentration have been found, which means that an isomorphism relationship exist. The intermolecular interactions in ODIC state of these systems and other related two-component systems are discussed using the evolution of the packing coefficient as a function of the composition.

1.- INTRODUCTION

Organic compounds characterised by globular or pseudoglobular molecules with weakly

angle-dependent interactions are capable of forming orientationally disordered (ODIC) [1-4]

phases (also called plastic phases) before the liquid state.

An extensive study has been undertaken for many years on the ODIC state from the

investigation of single compounds in order to relate both macroscopic (heat capacity, phase

transition, ...) or microscopic (molecular dynamics, crystallographic structure, ...) physical

properties to the intermolecular interactions. These studies have been performed in most cases

by analysing the dependence of some physical measurable properties as a function of one

intensive variable, either temperature or pressure, in order to change the intermolecular

interactions by modifying the local order in this kind of materials. A different way to modify

these microscopic parameters consists in the change of the molecular surroundings by adding a

guest molecule in the host crystal. Assuming that the geometry permits the substitution of a

molecule of the host crystal and that the guest molecule does not possess the symmetry elements

of the lattice, a symmetry simulation has been proved to be present [5]. Such a simulation is

carried out by the guest molecule by achieving as many orientations as required by the symmetry

of the crystallographic site of the host molecule. This well known rule [5] is of fundamental

importance in the analysis of mixed crystals in the ODIC state, where a large number of possible

energetically feasible orientations exist. Such an experimental evidence has been found even in

compounds whose molecules present some groups able to form strong interactions, either by

means of hydrogen bonds or by the existence of large dipole-dipole interactions [7-10]. Many

studies have concluded that the characteristic relaxation time of the overall tumbling in the

ODIC state is considerably high when compared to similar molecules lacking of these kind of

molecular interactions [7]. Moreover, the geometrical factor for orientationally disordered mixed

crystals should play a decisive role. Nevertheless, it has been also well established for pure compounds that for an asymmetric molecule the reorientational motion has to couple with the lattice vibrations in order to make compatible its orientation in the ODIC state with the short-range repulsive forces of the neighbouring molecules in the generally close-packed lattice. This coupling between reorientational and vibrational modes produces a diminution of both temperature range of the orientationally disordered phase and entropy change at the melting, because the vibrational modes must be activated during the reorientation itself [11]. This coupling is one of the most studied effects in organic materials displaying the conventional glasses [12]. A particular category of them is the so-called glassy crystal [13] which is obtained by freezing of the orientationally disordered phase of molecular crystals. Although the substitution of a guest molecule in the host crystal is not at all necessary to get the orientational freezing, several works can be found where the disordered mixed crystals display the glassy state [13,14] in such a way that the experimental conditions are more easily reached.

In the present study, which is enclosed in the general framework of the mixed crystals [15-17], we have spanned a wider number of two-component systems [6,18,19] where the orientationally disordered phases of pure compounds are isostructural and, then, candidates to be isomorphous. In this first article we deal with the experimental systems as well as the establishment of common relations from a crystallographic point of view. In a foregoing article the thermodynamic mixing properties will be examined and a link between both point of view will be presented. To do so, several pure substances which are branched or tetrahedral molecules belonging to the series $(CH_3)_{4-n1} C(CH_2OH)_{n1}$ $(n_1=1,2,3)$ and $(NO_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ $(n_2=0,1)$ have been considered. Whatever the substance, strong molecular interactions by means of hydrogen bonds or by means dipole-dipole intermolecular interactions $(n_2=0)$ are displayed.

2. EXPERIMENTAL

2.1. Materials

The pure materials were purchased from Aldrich Chemical Company with a purity of 99 % for all of them. They were submitted to an additional purification process consisting in a repeated vacuum sublimation at 313 K for $n_1=1$ ($(CH_3)_3C(CH_2OH)$, 2,2-dimethyl, 1-propanol, NPA), 343 K for $n_1=2$ $((CH_3)_2C(CH_2OH)_2$, 2,2-dimethyl, 1-3-propanediol, NPG), 393 K for $n_1=3$ $((CH_3)C(CH_2OH)_3$, 1,1,1-tris(hydroxymethyl) propane, PG) and 353 K for $n_2=1$ ($(NO_2)(CH_3)_2C(CH_2OH)$, 2-methyl,2-nitro, 1-propanol, MNP). For $n_2=0$ ($(NO_2)C(CH_3)_3$, 2-methyl,2-nitro, propane, TBN) the sublimation was performed on a low-pressure Ar atmosphere at 303 K. Molecular sieves was initially mixed with all the materials. Two-component mixtures were prepared from the melt of the pure materials in the selected composition by slow cooling ($\cong 2$ K·min^{-1}) to room temperature. The samples invariably were treated under a controlled Ar atmosphere.

2.2. Thermal Analysis

All the transition temperatures of the two-component systems as well as enthalpy changes were determined by means of a Perkin-Elmer DSC-7 calorimeter equipped with a home-made cooling attachment which enables us to reach temperatures of about 140 K in a control mode. The powder samples sealed into aluminium calorimetric cells weighed between 5 and 10 mg. Heating and cooling rates of 2 K·min^{-1} were typically used. The solid-solid transition of CCl_4 and the melting of In were used for temperature and energy calibration.

The characteristic temperatures of the equilibria were determined from the thermograms using the shape factor method [20].

The C_p measurements for the glassy transitions were performed with a commercial modulated DSC TA2910 system from TA Instruments Inc. equipped with the cooling accessory which enables to cool up to about 130 K. Heating rate of 2 K·min^{-1}, modulation amplitudes of

the sample temperature of ±0.2 or ±0.5 K and a period of 60 s were chosen in all the temperature range. Sample masses were about 5-10 mg and, as usual, sapphire was used for calibration.

2.3. X-ray Powder Diffraction

The X-ray powder diffraction measurements were performed with a horizontally mounted INEL cylindrical position-sensitive detector (CPS-120) [21] equipped with a liquid nitrogen INEL CRYO950 (80-330 K). The detector, placed in Debye-Scherrer geometry, permits a simultaneous recording of the powder pattern over the range of 0-120° (2θ). Monochromatic Cu $K\alpha_1$ radiation was selected with an asymmetric focusing incident beam curved quartz monochromator (λ=1.54059 Å). The beam section was 6.3 mm high by 0.3 mm wide. The powdered samples were sealed into 0.5 mm Lindemann capillaries which rotate during the measurement in order to improve the averaging of the crystallites. External calibration using the cubic phase of $Na_2Ca_3Al_2F_4$ (NAC) [22,23] was applied in the 0-55° (2θ) range due to the lack of reflections for higher angles. In the case of diffraction at constant temperature acquisition times of 30 min for the patterns and 10 min of stabilisation time were used, being the slewing speed 1 K·min^{-1}. After the indexing of the patterns lattice parameters were refined by means of the AFMAIL program.

3. RESULTS

3.1 Polymorphism of the Pure Components

3.1.1. TBN ($(NO_2)C(CH_3)_3$)

Solid TBN is known to occur in three different crystalline forms. Phase III (the structure of which is unknown, hereafter denoted as [D]) transforms to an orthorhombic structure [24] ([O]) where the molecules perform uniaxial rotations (C'_3) around the C-NO$_2$ axis (librational phase) [25-27]. The high-temperature solid phase I is an orientationally disordered phase where the molecules display overall rotation. In spite of the large molecular dipole, previous studies

[28] revealed no specific correlations, giving rise to a high symmetry fcc lattice [24]. The thermodynamic properties characterising the phase transitions as well as the lattice parameters for the different solid phases are gathered in Table 1.

3.1.2. MNP ((NO₂)(CH₃)₂C (CH₂OH))

3.1.2. MNP $((NO_2)(CH_3)_2C$ $(CH_2OH))$

The low-temperature ordered form of MNP ([M]) transforms to an orientationally disordered face centered cubic phase, which remains up to the melting point. Several NMR and IR spectroscopic studies have revealed the existence of intramolecular hydrogen bonds between the nitro and hydroxylic groups, producing the existence of an equilibrium between several conformers [30,31].The thermodynamic and crystallographic parameters are enclosed in Table 1.

3.1.3. NPA ((CH₃)₃C(CH₂OH))

3.1.3. NPA $((CH_3)_3C(CH_2OH))$

The low-temperature ordered phase of NPA ([T]) has been recently determined to be triclinic [32]. This phase II transforms to an orientationally disordered phase I. The latter phase is stable up to the melting at 329.8 K. The thermodynamic parameters of the phase transitions determined in this work (see Table 1) match up quite well with previously reported values [34,35].

It must be pointed out that the phase behaviour of NPA will have strong influences on the two-component systems (section 3.2) and, therefore it deserves an special attention. The thermal hysteresis in the I to II transition depends on the cooling conditions. When NPA in its orientationally disordered phase I is cooled fast enough to prevent the transition towards the ordered phase II, the disordered system is supercooled and a glassy state (I_g) is formed [36]. Such an state is characterised by the existence of the (average) translational order of the plastic phase being the orientational order partially frozen. It has been largely proved for this new condensed state that the averaged space groups of the plastic phase I, supercooled plastic phase I' and the glassy state (I_g) are all identical [37,38]. This property enables to follow easily the lattice parameter evolution with temperature. In Figure 1 we depict the cubic lattice parameter for the I, I' and I_g phases as a function of temperature together with the volume expansivity. At

123 K a change in the expansivity, which is known to be a general thermodynamic signature of the glass transition [39], is found. When increasing temperature from the glassy state, the relaxation phenomenon corresponding to the I_g to I' phases (at T_g) takes place. It must be pointed out that such a process is sample history dependent. At higher temperatures the supercooled phase I' can crystallise irreversibly to the stable phase II (this is the most common effect) or to a new intermediate metastable ordered phase (as for example in cyclohexanol [13]). As NPA behaves as the second case, single crystal studies would be needed in order to characterise the structural properties of this new metastable solid phase.

Due to the low temperature value of the glass transition determined by X-ray powder diffraction, it was not possible to measure the heat capacity change associated to the relaxation effect by means of our calorimetric devices. In a previous reported work the dielectric relaxation time was studied in the plastic phase as a function of temperature and pressure [34]. It is well-known that the glass transition occurs when the characteristic time of the isotropic reorientational motion reaches 10^3 s [40], whereas other possible anisotropic larger amplitude motions continue to exist within the glass state. The extrapolation of the relaxation time *vs.* temperature (at normal pressure) by considering an Arrhenius law corresponding to the mentioned work provides a temperature of about 125 K, which is certainly very close to the experimental temperature determined in this work. Nevertheless, in the neighbourhood of the glass transition non-Arrhenius behaviour might occur giving rise to relevant differences between the extrapolated and the experimental values.

3.1.3. NPG $((CH_3)_2C(CH_2OH)_2)$

The crystallographic properties of the low-temperature ordered ([M]) and ODIC phases [41,42,43] as well as the thermodynamic properties of the phase transitions [35] are gathered in Table 1. A recently published dielectric study on the disordered phase has revealed significant deviations from the single Debye relaxation, showing that strong intermolecular interactions via

hydrogen bonds are present [10]. Such results confirm previous findings on the role played for those interactions which control the molecular packing in the mixed crystals of two-component systems [18,19,44]. On the other hand, a theoretical temperature (also calculated from the extrapolation of the relaxation time assuming an Arrehnius behaviour) corresponding to the freezing of the large-amplitude motions (glass transition) was determined to be about 120 K.

3.1.3. PG ($(CH_3)C(CH_2OH)_3$)

Basic crystallographic and thermodynamic data corresponding to the ordered and disordered phases and the phase transitions are reported in Table 1. Structural details can be found in references [6,45,46].

3.2 Two-Component Systems

3.2.1.- TBN / NPA system

The main characteristics of the TBN/NPA two-component (Figure 2) system are the existence of a low-temperature peritectoid invariant (between ≈0.03 and ≈0.94) concerning the [D+T+O] three-phase equilibrium at 217.9 K, a eutectoid invariant relating the three-phase equilibrium [O+T+C$_F$] at 227.8 K and a very narrow orientationally disordered-liquid loop. The eutectoid limiting points were determined to be at 0.02 and 0.94 by means of the Tammann diagrams [47]. In Figure 3 we show the enthalpy change for the orientationally disordered – liquid equilibrium as a function of the mole fraction.

Crystallographic study at 293.2 K

The continuous evolution of the lattice parameter vs. concentration for the fcc phase ([C$_F$]) at 293.2 K, shown in Figure 4, together with the continuous evolution of the temperatures characterising the plastic-liquid equilibrium, prove the formation of orientationally disordered substitutional mixed crystals in the whole concentration range. In addition, this crystallographic

characterisation shows that the orientationally disordered phase of TBN is isomorphous to the corresponding one of the NPA, confirming the fcc lattice symmetry found recently by the authors for TBN [6] in contrast to previous works [49].

3.2.2.- TBN / MNP system

The experimental two-component phase diagram TBN/MNP from 223 K to the liquid state is displayed in Figure 2. The low temperature side of the phase diagram shows a eutectic invariant at 250.0 K in the range of 0 to 0.95 molar fraction of MNP (the eutectic point at about 0.13). Such values were obtained from the Tammann diagram associated to the eutectic transformation [47]. The influence of the III to II phase transition of TBN on this two-component system was not studied. The enthalpy change for the melting process as a function of the mole fraction is depicted in Figure 3.

Crystallographic study at 293.2 K

In order to verify the possible isomorphism relationship between the disordered phases of the two components, an isothermal x-ray powder diffraction study in the molecular alloys was undertaken at 293.2 K. Moreover, this study enables to analyse the evolution of the volume of the unit cell as a function of the mole fraction at constant temperature. For samples with mole fraction $X \geq 0.7$ of MNP the two phases [M] and [C_F] coexist at 293.2 K. Therefore, the measurements for these samples were carried out on the experimentally metastable orientationally disordered phase. For the pure component MNP (X=1) it was not possible to retain its ODIC phase at 298.2 K, the lattice parameter at such temperature being obtained by means of its evolution with the temperature between 323 to 303 K. Figure 4 depicts the results corresponding to the continuous evolution of the lattice parameter with the mole fraction.

3.2.3.- NPG / PG system

The NPG/PG two-component system was early published [51]. It has been submitted now to a revision due to the considerable difference in the melting temperatures of the pure components as a consequence of the purification process. The low-temperature side (Figure 2) displays no qualitative changes with the previously published. A small shift in the eutectoid temperature (at 306.5 K) as well as in the eutectoid composition has to be mentioned. On the contrary the orientationally disordered – liquid equilibrium is determined to be a narrow loop, in contrast to the Gibbs minimum reported in [52]. The evolution of the enthalpy change for the melting of molecular alloys is depicted in Figure 3. Some measurements by x-ray powder diffraction have been performed in order to determine the cubic lattice parameters for the molecular alloys at 356 K and no noticeable differences were found in relation to the previously published data.

3.2.4.- NPA / NPG system

As in the previous two-component systems, NPA and NPG are found to be isomorphous in the ODIC state. As displayed in Figure 2, disordered mixed crystals melt in such a way that the two-phase orientationally disordered-liquid equilibrium is a loop. The enthalpy change of the molecular alloys in such a process is shown in Figure 3.

Crystallographic study at 313.2 K

The variation of the cubic parameter as a function of mole fraction at 313.2 K is displayed in Figure 4. The continuous evolution of such a parameter *vs.* mole fraction together with the loop for the melting process enables to state the existence of continuous mixed crystals, i.e., the establishment of an isomorphic relationship between the high-temperature disordered phases of both pure components NPA and NPG.

Glassy mixed crystals

Concerning the low-temperature phase equilibria between the orientationally disordered phase and the ordered triclinic (NPA) and monoclinic (NPG) phases, the DSC curves did not show the typical thermograms corresponding to the standard solid-solid transformations. In order to distinguish between the two possibilities, that is to say, metastable supercooled ODIC molecular alloys or the existence of a glassy state, C_p measurements at low temperature (from 130 K) as well as x-ray powder diffraction measurements (from 80 K) were performed. The formers are shown in Figure 5 for several molecular alloys ($X \leq 0.5$) as a function of the temperature. The typical relaxation process from the glassy state to the supercooled plastic phase characterised by a C_p change was found. The later, performed on the $NPA_{0.7}NPG_{0.3}$ mixed crystal is displayed in Figure 6. The evolution of the cubic lattice parameter *vs* temperature as well as the discontinuity on the lattice expansivity are the irrefutable signatures of the existence of a glassy state. Although the T_g temperature is not an equilibrium temperature, these values as a function of the mole fraction have been also included in the equilibrium phase diagram. Due to the different time-scaling of the experimental techniques used, the T_g temperatures are relatively different. This fact explains the breakdown of the T_g evolution *vs* mole fraction shown in Figure 2 between the pure component NPA and the mixed crystals. Unlike the preceding published cases concerning the formation of a glassy state in mixed crystals, as those formed by chloroadamantane and cyanoadamantane [14,38,52,53], a strong variation of T_g with the mole fraction is found. This fact shows that the freezing mechanisms are hardly influenced for the presence of the guest molecule. It is also worth noting that this binary system displays a very interesting phase stability sequence which gives rise to a unique opportunity to study the dynamics of the glassy state as well as the supercooled plastic phase. On the one hand, the quench, which is necessary to by-pass the first-order phase transition toward the lower symmetry crystalline (ordered) phase to reach the glassy state, is easily achievable in these molecular

alloys (cooling rates about 2 K·min⁻¹ are required). On the other hand, after the glassy to supercooled ODIC phase transition has been carried out, the orientationally disordered phase is placed in a metastable situation in regard to the low-temperature ordered crystalline phase that remains until the temperature where it becomes stable. Therefore, the temperature domain where the dynamical behaviour of such phases can be studied is considerably large and would enable to analyze the evolution of physical properties *vs.* temperature.

For molecular alloys with mole fraction higher than 0.5 the kinetic behaviour is different and the glassy state for all the samples is not reached. Particularly, for the mixed crystals with $X \geq 0.9$ the ordered solid phase [M] is partially achievable giving rise to the possibility to obtain in some cases the upper solvus corresponding to the crystalline ordered (monoclinic) – orientationally disordered equilibrium. There was no mole fraction for which the necessary three-phase invariant [T+M+C$_F$] was detected.

3.2.5.- NPA / MNP system

The loop corresponding to the orientationally disordered – liquid equilibrium is depicted in Figure 2. The associated enthalpy change for this melting process is shown in Figure 3. With regard to the low temperature equilibria, the phase behaviour is strongly dependent on the mole fraction. For mole fractions $X \geq 0.6$ the DSC scans display the signals corresponding to a three-phase eutectic equilibrium at 227.4 K, in addition to the upper solvus corresponding to the [M+C$_F$] to [C$_F$] transition. For mole fractions with $X \leq 0.5$ the thermodynamic equilibrium is not reached due to the fact that the triclinic structure of the necessary limiting solid solution does not appear on cooling. Therefore, on the heating runs only the upper solvus corresponding to the [M+C$_F$] to [C$_F$] transition is present. Such an experimental fact can be probably associated to the easiness of the orientationally disordered phases of NPA to be undercooled and subsequently to be frozen in a glassy state. Unlike the previous two-component NPA/NPG system, no glass

transition was detected for the low mole fraction samples in the experimentally available temperature domain.

Crystallographic study at 303.2 K

The continuous variation of the cubic lattice parameters of the disordered mixed crystals *vs.* mole fraction at 303.2 K (see Figure 4) states the isomorphism between the orientationally disordered phases of NPA and MNP.

3.3 Packing of the Orientationally Disordered Molecular Alloys

The most of the ordered low-temperature structures of the compounds belonging to the series studied in this work $(CH_3)_{4-n1}C(CH_2OH)_{n1}$ and $(NO_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ as well as similar series as $(NH_2)(CH_3)_{3-n3}C(CH_2OH)_{n3}$ have been solved. The common feature is the existence of strong intermolecular interactions by means of the bonds generated by the -OH groups and, when present, -NH$_2$ groups. Nevertheless, due to the disordered character of the high-temperature phase, no structures describing this form have been published for the mentioned compounds. In order to obtain information on the degree of interactions in molecular alloys, the approach proposed by Kitaigorodsky [55], which lies in the analysis of the packing coefficient, has been used. Previous works have shown that this parameter is a powerful tool to account for the intermolecular interactions in molecular alloys [19,44].

Packing coefficient is defined as the ratio between the volume of the molecule V_m (or the average molecule for the molecular alloys) and the available volume in the lattice (V_Z=V/Z, where V is the unit-cell volume and Z is the number of molecules in the unit cell). The average molecular volume $V_m(X)$ for a given molecular alloy of mole fraction X can be assumed to be :

$$V_m(X)=(1-X)\cdot V_{mA} + X \cdot V_{mB}$$

being V_{mA} and V_{mB} the molecular volume for the A and B components of the mixed crystal, respectively. Thus, the temperature-dependent and composition-dependent packing coefficient $\xi(X,T)$ is defined as:

$$\xi(X,T) = \frac{(1-X)\cdot V_{mA} + X\cdot V_{mB}}{V_Z(X,T)}$$

being $V_Z(X,T)$ the available unit-cell volume per molecule of the molecular alloy.

In order to account for the influence of the substitution process in the molecular alloys by analysing the packing evolution *vs.* composition the temperature effect must be avoided by measuring the lattice volume at constant T (as it has been shown in previous sections). To evaluate V_m the molecules have been built up by means of the standard distances between atoms (irrespective of the type of molecule) and van der Waals radii. The values were taken from references [56-58]. Table 2 summarises the calculated molecular volumes.

In Figure 7 we depict the evolution of the packing coefficient against composition for the preceding two-component systems analysed in the previous sections together with those formerly published. The B component of the $A_{1-X}B_X$ molecular alloy has been chosen as the molecule having the largest number of CH_2OH groups. Whatever the two-component system is analysed, the experimental results confirm that the packing parameter is an increasing function of the number of potential intermolecular interactions by hydrogen bonds. Going into details to reinforce this idea, two additional experimental findings must be pointed out. On the one hand, the highest change in the packing coefficient on going from $X=0$ to $X=1$ is determined to be for the $MNP_{1-X}PG_X$ ($(NO_2)(CH_3)C(CH_2OH)$ / $(CH_3)C(CH_2OH)_3$) molecular alloys, which corresponds to the system where the largest differences in the number of $-CH_2OH$ groups exists, producing the largest differences on the intermolecular interactions for the pure components. On the other hand, the variation of the packing coefficient with the molar fraction for the system

NPA/MNP $((CH_3)_3C(CH_2OH) / (NO_2)(CH_3)_2C(CH_2OH))$ is almost flat, which is completely reasonably taking into account that the number of available groups to generate dynamical hydrogen bonds is equal. In addition, Figure 7 shows that the packing variation for each system does not deviate noticeably from the linear behaviour (Vegard's law) in spite of the large molecular volume differences. This result implies that the lattice deformation due to the steric factor is not important. Also according to Kitaigorodsky [55] the steric factor (shape and size of molecules) can be analysed by a coefficient similarity ε_K, the so-called degree of molecular homeomorphism. Such a coefficient is calculated as $\varepsilon_K = 1 - \Gamma/\Delta$, being Γ the non-overlapping parts and Δ the overlapping parts when the molecules are superimposed so as to maximise the overlapping parts. Kitaigorodsky proposed a limiting value of 0.85 to achieve complete miscibility. As can be seen in Table 2, the ε_K values are ranged between 0.826 and 0.976 and, therefore the limiting value previously mentioned does not account for the miscibility of orientationally disordered phases. This result is completely reasonable if we consider that in the substitution process, which takes place in the formation of disordered mixed crystals, the symmetry simulation is already present due to the overall tumbling motion of the molecules in such a disordered phase. That is to say, the shape of the molecule is missing and the steric conditions will be totally controlled by the molecular size, a parameter which is included in the packing coefficient calculation.

As a conclusion of these results when continuous disordered mixed crystals from X=0 to X=1 are formed (*i.e.* isomorphism exists), the intermolecular interactions control the structure of the orientationally disordered molecular alloys. Such a conclusion was already announced for ODIC's in the case of molecular alloys between non-isomorphous plastic phases [19]. To go further into the research in two-component systems of this type of materials, an approach connecting this structural parameter with the thermodynamic properties has been performed and will be presented in a foregoing article.

Acknowledgements

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Figure Captions

Figure 1.- Cubic lattice parameter (o) and volume expansivity (□) for plastic (I), supercooled (I')

and glassy state (I_g) phases vs. temperature for NPA ($(CH_3)_3C(CH_2OH)$)

Figure 2.- Two-component phase diagrams. (•) Transition temperatures obtained from DSC

measurements. The non-equilibrium glass transition temperatures ((O), from C_p and (Δ) from X-

ray powder diffraction measurements have been included in the equilibrium phase diagram for

brevity. [L] Liquid phase; [M] monoclinic, [T] triclinic and [Q] tetragonal low-temperature

ordered solid forms; [C_F] orientationally disordered fcc phase. (For compound abbreviations see

Table 1).

Figure 3.- Enthalpies of melting as a function of the composition for the orientationally

disordered mixed crystals in the two-component systems. (For compound abbreviations see

Table 1).

Figure 4.- Lattice parameter as a function of the composition for the cubic orientationally

disordered mixed crystals for the two-component systems. (For compound abbreviations see

Table 1).

Figure 5.- C_p variation as a function of temperature for several $NPA_{1-X}NPG_X$

($[(CH_3)_3C(CH_2OH)]_{1-X}$ / $[(CH_3)_2C(CH_2OH)_2]_X$) mixed crystals in the temperature range

corresponding to the glass transition. (● X=0.1, O X=0.2, ■ X=0.3 and □ X=0.5).

Figure 6.- Cubic lattice parameter (o) and volume expansivity (□) for plastic (I), supercooled (I')

and glassy state (I_g) phases vs. temperature for the $NPA_{0.7}NPG_{0.3}$ ($[(CH_3)_3C(CH_2OH)]_{0.7}$/

$[(CH_3)_2C(CH_2OH)_2]_{0.3}$) molecular alloy.

Figure 7.- Packing coefficient (ξ) at T^* as a function of composition of the cubic orientationally

disordered mixed crystals for the two-component systems. (For compound abbreviations see
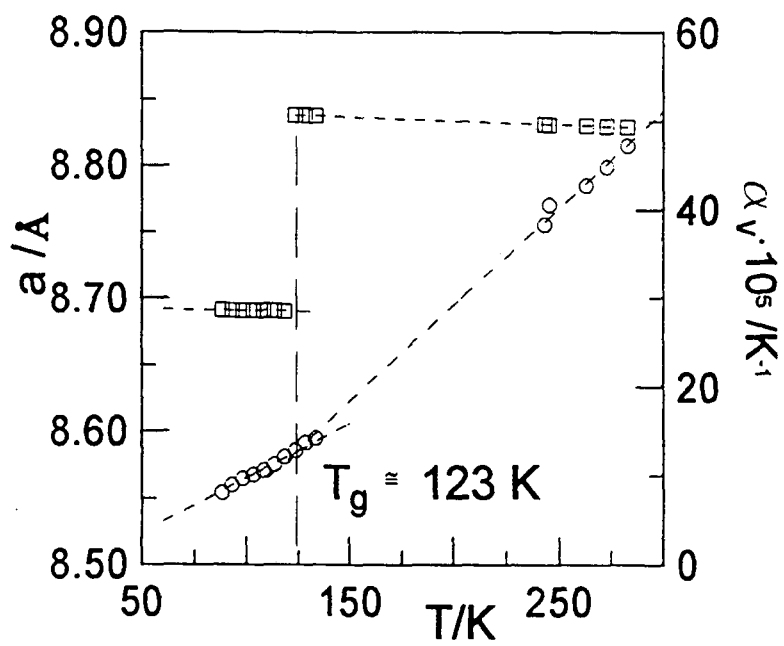
Table 2).

Table 1.- Summary of the crystallographic properties and the thermodynamic characteristics of the phase transitions for the pure components.
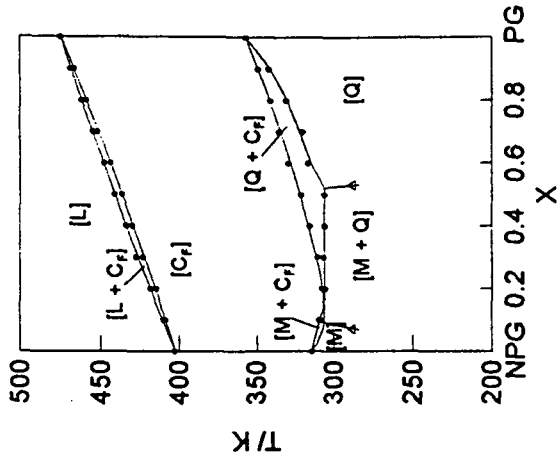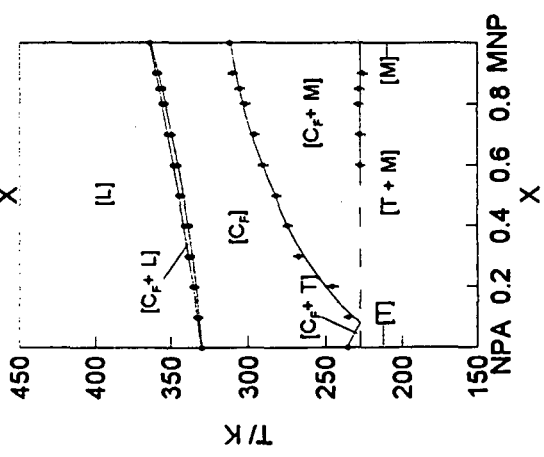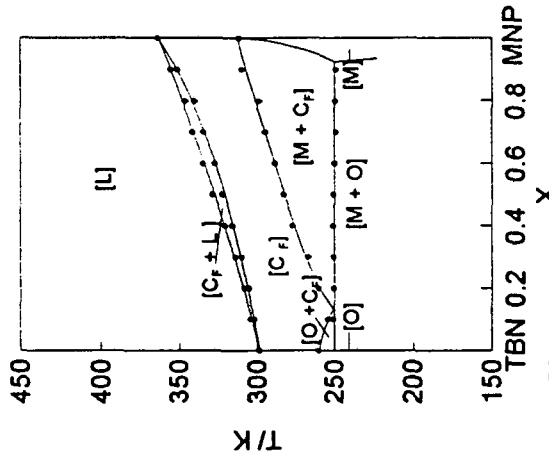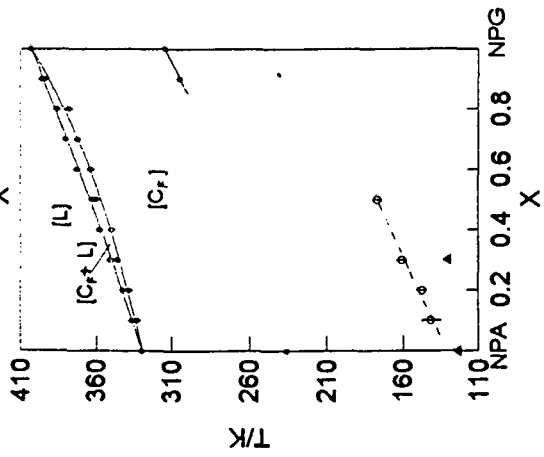
Formula	III - II		Phase II	II - I		Phase I	I - L	
	T/K	ΔH / kJ·mol^{-1}		T/K	ΔH / kJ·mol^{-1}		T/K	ΔH / kJ·mol^{-1}
TBN $(NO_2)C(CH_3)_3$	216.4[a]	4.34[a]	Orthorhombic[b] a=10.280(6)Å b=9.993(5) Å c=6.205(4) Å (Z=4, T=233.2 K)	260.0[a]	4.64[a]	Fcc[b] a=8.765(5) Å (Z=4, T=273.2 K)	298.5[a]	2.56[a]
MNP $(NO_2)(CH_3)_2C$ (CH_2OH)	-	-	Monoclinic P2$_1$/c[c] a=6.195(3) Å b=19.115(8) Å c=16.601(9) Å β=90.12(2) (Z=12, T=293.2 K)	311.5[a]	14.64[a]	Fcc[d] a=8.857(10) Å (Z=4, T=356 K)	363.9[a]	3.17[a]
NPA $(CH_3)_3C$ (CH_2OH)	-	-	Triclinic[e] a=10.304(10) Å b=10.418(9) Å c=11.398(12) Å α=90.146(6)° β=99.51(3)° γ=107.08(1)° (Z=7, T=233.3 K)	235.4[a]	4.14[a]	Fcc[a] a=8.815Å (Z=4, T=293 K)	329.8[a]	3.73[a]
NPG $(CH_3)_2C$ $(CH_2OH)_2$	60.4[f]	0.177[f]	Monoclinic P2$_1$/n[g] a=5.979(1) Å b=10.876(2) Å c=10.099(2) Å β=99.78(1) (Z=4, T=293.2 K)	314.4[a]	12.43[a]	Fcc[h] a=8.854(8) Å (Z=4, T=353 K)	402.8[a]	4.34[a]
PG $(CH_3)C$ $(CH_2OH)_3$	-		Tetragonal I$\bar{4}$ [i,j] a=6.052(2) Å b=8.872(3) Å (Z=2, T=293.2 K)	356.7[a]	20.94[a]	Fcc[k] a=8.876(8) Å (Z=4, T=363 K)	474.4[a]	4.72[a]

[a] This work; [b][24]; [c][29]; [d][51]; [e][32]; [f][35]; [g][41]; [h][50]; [i][45]; [j][46]; [k][48]
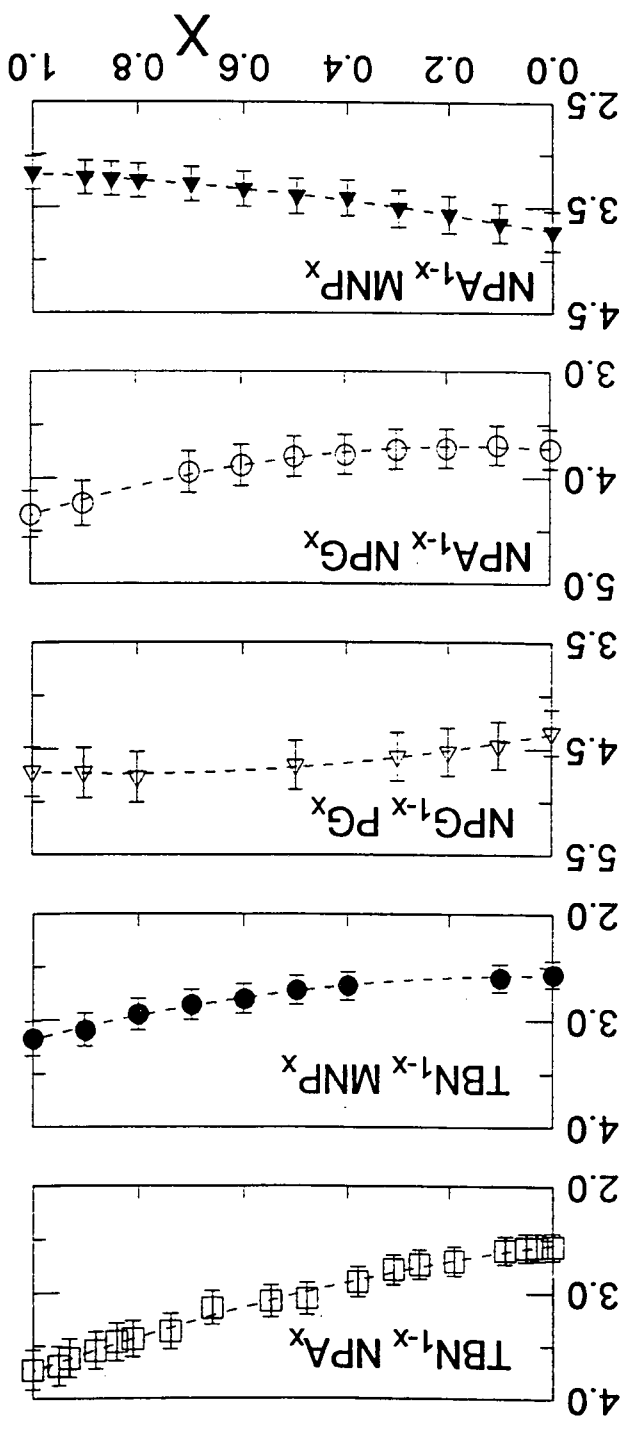
Table 2.- Molecular Volumes (V_m) for the Pure Components and ϵ_K values for the two-component systems.

System A/B	$V_{mA}(\text{Å}^3)$	$V_{mB}(\text{Å}^3)$	ϵ_K
NPA / MNP $[(CH_3)_3C(CH_2OH)] / [NO_2(CH_3)_2C(CH_2OH)]$	102.6	103.7	0.904
NPA / NPG $[(CH_3)_3C(CH_2OH)] / [(CH_3)_2C(CH_2OH)_2]$	102.6	108.9	0.938
NPG / PG $[(CH_3)_2C(CH_2OH)_2] / [(CH_3)C(CH_2OH)_3]$	108.9	115.2	0.941
TBN / NPA $[NO_2C(CH_3)_3] / [(CH_3)_3C(CH_2OH)]$	97.4	102.6	0.882
TBN / MNP $[NO_2C(CH_3)_3] / [NO_2C(CH_3)_2(CH_2OH)]$	97.4	103.7	0.935
PG / PE $[(CH_3)C(CH_2OH)_3] / [C(CH_2OH)_4]$	115.2	121.4	0.946
MNP / NPG $[NO_2C(CH_3)_2(CH_2OH)] / [(CH_3)_2C(CH_2OH)_2]$	103.7	108.9	0.889
MNP / PG $[NO_2C(CH_3)_2(CH_2OH)] / [(CH_3)C(CH_2OH)_3]$	103.7	115.2	0.826
AMP / TRIS $[NH_2C(CH_3)(CH_2OH)_2] / [NH_2C(CH_2OH)_3]$	103.6	109.9	0.939

Top-right plot (NPG - PG):
- T/K axis: 500, 450, 400, 350, 300, 250, 200
- X axis: NPG 0.2 0.4 0.6 0.8 PG
- Labels: [L], [L + C_F], [C_F], [Q + C_F], [M + C_F], [M + Q], [M], [Q]

Middle-top plot (TBN - MNP):
- T/K axis: 450, 400, 350, 300, 250, 200, 150
- X axis: TBN 0.2 0.4 0.6 0.8 MNP
- Labels: [L], [C_F + L], [C_F], [O + C_F], [M + C_F], [M + O], [O], [M]

Middle-bottom plot (NPA - MNP):
- T/K axis: 450, 400, 350, 300, 250, 200, 150
- X axis: NPA 0.2 0.4 0.6 0.8 MNP
- Labels: [L], [C_F + L], [C_F], [C_F + T], [C_F + M], [T + M], [T], [M]

Left-top plot (TBN - NPA):
- T/K axis: 400, 350, 300, 250, 200, 150, 100
- X axis: TBN 0.2 0.4 0.6 0.8 NPA
- Labels: [L], [C_F + L], [O + C_F], [C_F], [T + C_F], [T], [O], [D + T], [O + T], [D]

Left-bottom plot (NPA - NPG):
- T/K axis: 410, 360, 310, 260, 210, 160, 110
- X axis: NPA 0.2 0.4 0.6 0.8 NPG
- Labels: [L], [C_F + L], [C_F]

$\Delta H_m / kJ \cdot mol^{-1}$

Figure: Cubic Lattice Parameter a / Å versus X for four series. Top panel: $TBN_{1-x}NPA_x$, $T = 293$ K (open squares). Second panel: $TBN_{1-x}MNP_x$, $T = 293$ K (filled circles). Third panel: $NPA_{1-x}NPG_x$, $T = 313$ K (open circles). Bottom panel: $NPA_{1-x}MNP_x$, $T = 303$ K (filled triangles).

C_p (a.u.)

0.25 J.K^{-1}.g^{-1}

120   160   200   240   280

T/K

T /K

300   200   100

$\alpha_v \cdot 10^5 /K^{-1}$

0

20

40

60

$T_g \cong 130\ K$

a /Å

8.40

8.60

8.80

9.00

0.70

0.65

0.60

0.55

A   0.2   0.4   X   0.6   0.8   B

A / B	T*/K
□ TBN/NPA	293.2
● TBN/MNP	293.2
△ NPG/PG	356.2
○ NPA/NPG	313.2
▲ NPA/MNP	303.2
+ MNP/NPG	318.2
◇ MNP/PG	358.2
⊠ PG/PE	453.2
✦ AMP/TRIS	378.2

T/K vs X phase diagram. Regions labeled: [Liquid], [L + C$_F$], ODIC Phase [C$_F$]. Y-axis T/K with values 400, 425, 450, 475. X-axis from (CH$_3$)$_2$C(CH$_2$OH)$_2$ to (CH$_3$)C(CH$_2$OH)$_3$.
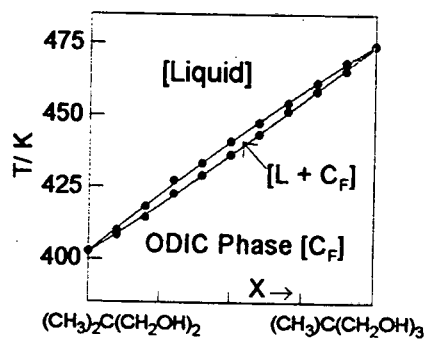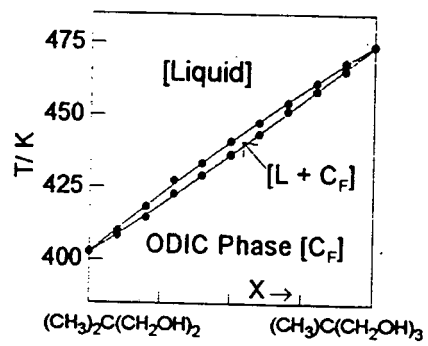
Two-component systems of isomorphous orientationally disordered crystals . Part II: Thermodynamic Analysis.

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Abstract

A thermodynamic analysis was made of a set of two-component systems displaying isomorphous orientationally disordered phases (ODIC). The pure compounds are molecular materials belonging to the series $(CH_3)_{4-n1} C(CH_2OH)_{n1}$ ($n_1=1,2,3$), $(NO_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ ($n_2=0,1$) and $(NH_2)(CH_3)_{3-n3}C(CH_2OH)_{n3}$ ($n_3=2,3$). The Equal-Gibbs-Curve method was used in order to determine the Gibbs excess energy of the orientationally disordered mixed crystals. The excess Gibbs energies of the disordered phases obtained from the disordered-liquid equilibria were used on the analysis of the low-temperature ordered-disordered equilibria. This excess property was correlated for the mentioned chemically coherent group of materials (neopentane derivatives) studied in this work, with a crystallographic parameter, the packing coefficient, which accounts for the steric factors and intermolecular interactions in the disordered mixed crystals.

1.- INTRODUCTION

As noted in previous work [1], so far there has been a reduced set of experimental thermodynamic data on orientationally disordered mixed crystals. In addition, comprehensive thermodynamic studies of two-component systems displaying such disordered phases are scarce and, when available, subject to large uncertainties. One way to underestimate them is to consider a chemically coherent group of materials. Such a procedure enables to find regularities, the similar trends or common characteristics in order to correlate them. These correlations offer the opportunity to check experimental data for their consistency or to estimate physical properties of materials, which have not been or cannot easily be measured. These properties also hold for the excess mixing properties of the chemically group of materials.

In the present communication we report a comprehensive thermodynamic analysis on the two-component systems relating neopentane derivatives which have been previously determined [1]. The compounds belong to the series $(CH_3)_{4-n1} C(CH_2OH)_{n1}$ $(n_1=1(NPA),2(NPG),3(PG))$, $(NO_2)(CH_3)_{3-n2}C(CH_2OH)_{n2}$ $(n_2=0(TBN), 1(MNP))$ and $(NH_2)(CH_3)_{3-n3}C(CH_2OH)_{n3}$ $(n_3=2(AMP), 3(TRIS))$. The structure of this work is as follows: (i) A detailed description of the procedure for the thermodynamic assessment applied to the two-component systems displaying orientationally disordered phases is initially performed. (ii) The obtained results for five two-component systems included in part I of this series of works, together with other previously published [2-7], are sketched. (iii) The last part of the present work gives a simple empirical method for the estimation of the thermodynamic mixing properties in this kind of systems by means of a well-known crystallographic parameter, the packing coefficient of the disordered mixed crystals.

2.- THERMODYNAMIC ANALYSIS PROCEDURE

The thermodynamic properties of a two-component system under isobaric conditions are known if for each phase the Gibbs energy of the pure components, as well as the excess Gibbs energy of the mixtures, are known as a function of temperature for the first one, and as a function of temperature and composition for the second one.

In the thermodynamic analysis that follows A and B represent two pure components displaying isomorphism in α phase giving rise to a continuous series of mixed α crystals. Recalling the general relationship for the Gibbs energy for a mixture of (1-X) mole of A and X mole of B, the temperature and composition dependence can be written as:

$$G^{\alpha}(T,X) = (1-X)\mu_A^{*,\alpha} + X\mu_B^{*,\alpha} + RTLN(X) + G^{E,\alpha}(T,X) \qquad (1)$$

in which $\mu_A^{*,\alpha}$ and $\mu_B^{*,\alpha}$ represent the molar Gibbs energies of pure components A and B respectively, R is the gas constant and $G^{E,\alpha}(T,X)$ stands for the deviation from ideal mixing behaviour, the so-called excess Gibbs energy.

In order to determine the two-phase equilibrium region between two phases (α and β) in a two-component phase diagram the well known equilibrium rule corresponding to the minimum Gibbs energy of the mixed crystal $A_{1-X}B_X$ at each temperature must be applied. Otherwise said, the intersection between both Gibbs energies characterising the phases of the corresponding equilibrium, $G^{\alpha}(T,X)$ and $G^{\beta}(T,X)$ must be determined. To do so, the molar Gibbs energies of the pure compounds A and B as well as the excess properties for each phase are required. Such an information is generally not available in this direct form and several simplifying assumptions concerning the considered thermodynamic properties have to be done.

In the following the Equal-Gibbs-Curve method (EGC) will be used [8]. To analyse the two-phase equilibrium between α and β phases, the difference between their Gibbs energies (eq. (1)) can be written as:

$$\Delta G(T,X) = G^{\alpha}(T,X) - G^{\beta}(T,X) = (1-X)\Delta\mu_A^{*}(T) + X\Delta\mu_B^{*}(T) + \Delta G^{*}(T,X) \qquad (2)$$

where $\Delta\mu_i^{*}$ is $\mu_i^{*,\alpha} - \mu_i^{*,\beta}$ (i=A,B) and $\Delta G^{E}(T,X)$ is the excess Gibbs energy difference between the considered phases, i.e., $G^{E,\alpha}(T,X) - G^{E,\beta}(T,X)$.

The equation $\Delta G^{\alpha \to \beta}(T_{EGC},X)=0$ provides a curve in the TX plane where the α and β phases have equal values of the Gibbs energies (the EGC curve). By assuming that the heat capacities may be ignored, $\Delta\mu_i^{*}(T)$ can be approximately written as $\Delta S_i^{*}(T_i^{\alpha \to \beta}-T)$, being $T_i^{\alpha \to \beta}$ the temperature of the $\alpha \to \beta$ transition for the component i.

The EGC temperature can be then deduced from equation (3) as:

$$T_{EGC} = \frac{(1-X)\Delta H_A^{*} + X\Delta H_B^{*}}{(1-X)\Delta S_A^{*} + X\Delta S_B^{*}} + \frac{\Delta G_{EGC}^{E}(X)}{(1-X)\Delta S_A^{*} + X\Delta S_B^{*}} \qquad (4)$$

The first term of the right side of equation (4) is called T_{ZERO} and represents the zero line, i.e., the EGC temperature for the α-β equilibrium when the excess Gibbs energy difference is zero.

For the orientationally disordered mixed crystals (ODIC)-liquid equilibrium of two-component phase diagrams analysed in this work an additional simplifying assumption has been performed: The liquid state has been taken as an ideal mixture. From this, the excess Gibbs energy difference, ΔG^{E}, can be written as minus $G^{E,ODIC}$, which stands for the excess Gibbs energy of the orientationally disordered state.

This assumption for the liquid state deserves an special mention. The validity of such an *a priori* strong approximation can be reasonably proved for each analysed phase diagram.

Moreover it is well known that the deviation from the ideal behaviour in the liquid state is smaller than in the solid state. By assuming that the excess Gibbs energy provided by equation (4) can be considered in the whole temperature range of the orientationally disordered phase the thermodynamic analysis on the ordered-disordered equilibria can be performed. Such a calculation will be only proved to be satisfactory if the excess Gibbs energy of the orientationally disordered phase has been determined accurately enough. This test will provide the validity to the above considered assumption.

Relating the ordered-disordered equilibria and whatever the two-component system is considered, the two-phase region involving two non-isostructural phases implies the occurrence of a three-phase equilibrium. If the miscibility in the ordered phase cannot be neglected, this region of the phase diagram can be considered as the result of two interfering ordered-disordered loops (crossed isodimorphism). Thus, each kind of ordered mixed crystal will be described by means of a Gibbs energy function. The metastable extension of the ordered-disordered loop ends in the theoretical metastable transition point of the pure substances corresponding to a phase that is assumed to be isomorphous with the phase for which the extension of loop is done. The metastable transition points were obtained as a result of a number of trial and error calculations (for details see references [9-12].

To end with, the thermodynamic assessment has been performed using WINFIT program [13], which is a modification in a windows version of the well-known LIQFIT program [14-16]. In such a framework the description of the excess Gibbs energy was given by a two-parameter function in the form of a Redlich-Kister polynomial:

$$G^E(X) = X(1-X)[G_1 + G_2(1-2X)]$$
(5)

Generally, unless the system presents some strong local anomaly, such simple polynomials of two terms are fairly adequate and physically more understandable than other polynomial forms including more than two terms.

3. RESULTS

The results obtained for the five binary systems by means of the thermodynamic analysis using the described procedure as well as previously two-component systems [2-7] are gathered in Table 1. The corresponding calculated phase diagrams together with the experimental temperature-composition data are drawn in figure 1.

A comparison between the calculated and experimental values for the three-phase equilibria of the systems is given in Table 2. As can be seen from figure 1 the experimental orientationally disordered-liquid equilibria are very well reproduced. On the contrary, the accord between the calculated and experimental data corresponding to the ordered-disordered equilibria is relatively poor in some cases (see Table 2). Two reasons can account for such a disagreement. On the one hand the validity of excess energy function of the orientationally disordered phase for the whole temperature range. On the other hand, the error produced on the analysis of finding the metastable transition points when crossed isodimorphism must be applied [9,10,12]. Nevertheless, although the accuracy of the calculation of the ordered-disordered equilibria is somewhat limited, it may be remarked that, from a thermodynamic point of view, a correct description of the phase diagrams and the thermodynamic properties of the disordered mixed crystals is given. Relating the calculated phase diagrams presented in figure 1, the NPA/NPG ($(CH_3)_3C(CH_2OH)$ / $(CH_3)_2C(CH_2OH)_2$) deserves an special mention. As can be seen the ordered-disordered equilibrium contains only an experimental point, as a consequence of the existence of a glassy state previously determined [1] for the disordered mixed crystals. Thus, the

calculated equilibrium cannot be compared with the experimental, but certainly it

represents the possibly attainable phase equilibrium

4. THERMODYNAMIC EXCESS PROPERTIES *VS.* PACKING OF THE ORIENTATIONALLY DISORDERED MIXED CRYSTALS

The analysis of a set of thermodynamic mixing data corresponding to a series of

structurally and chemically similar compounds allows one to study the general trends and

similarities. Particularly, the behaviour of two-component systems of similar compounds

leading to the formation of continuous mixed crystals enables to account for the influence

of molecular surroundings and leads to an understanding of the orientationally disordered

molecular alloys presented in this work.

The polymorphic behaviour of the considered tetrahedral derivatives of neopentane allows

to analyse the conditions of the mixed crystal formation under two different types of order:

The low-temperature ordered forms and the high-temperature disordered forms. The

factors ruling the formation of mixed crystals are known to be distinguished: (i) The size

and shape of the molecules and the unit-cell dimensions (steric or geometric conditions)

and (ii) the role of the intermolecular interactions in the mixed crystal structures.

Whatever the two-component system considered, the low-temperature region shows a total

or wide non miscibility zone. On the contrary, in the high temperature region

corresponding to the stability domain of the orientationally disordered phases, continuous

solid solutions are found. Such an experimental evidence has been largely explained

[9,17,18] by means of two factors: (i)The considerable difference in the available volume

of a molecule between the ordered solid and the disordered forms and (ii) The easiness to

simulate the symmetry elements of the orientationally disordered host lattice for the guest

molecule due to the existence of a large number of possible energetically feasible orientations. A detailed discussion of these factors can be found in references [17,18].

To analyse the influence of the above mentioned factors which control the thermodynamic excess properties, in particular the excess Gibbs energy in the orientationally disordered phases, several coefficients largely used in other series of mixed crystals are introduced.

Relating to the shape and size of the molecules, a coefficient of geometric similarity ε_K (degree of molecular homeomorphism) was introduced by Kitaigorodsky [19]. This temperature and phase independent coefficient is calculated as $\varepsilon_K = 1 - \Gamma/\Delta$, where Γ is the volume of the non-overlapping parts and Δ that of the overlapping parts when the two molecules are superimposed. It is quite clear that the coefficient, in spite of its validity for other organic mixed crystals [20], falls down when applied to an orientationally disordered phase, because the shape of the molecule is *missing* during the overall tumbling which characterises these phases. As can be seen in Table 1, ε_K varies from 0.83 to 0.98, exceeding the limiting value of 0.85 proposed by Kitaigorodsky in spite of the complete miscibility found for all the studied systems.

To go further on the government of the structural arrangements of the mixed crystals, the concept of degree of isomorphism, ε^i_m, has been recently proposed [21,22]. It accounts, in a excellent way, for the excess properties of organic mixed crystals built up from p-dihalobenzene derivatives [21], n-alkanes [23,24] and alkali halides [25,26]. The ε^i_m coefficient (see Table 1), which is defined in a similar way to ε_K, but superimposing the unit-cells of the isomorphous phases, accounts for the relative difference between the unit-cells. As can be easily seen, these values state the close similarity of the orientationally disordered unit-cells of the series of pure compounds presented and, obviously, the excess Gibbs energy will be hardly probable dependent on the relative mismatch. It must be born

in mind that the success of the ε^i_m parameter has been found in systems where all the interactions between molecules were of van der Waals type, in contrast to the systems of this work in which, in spite of the disordered character, intermolecular hydrogen bonds are present.

The key parameter when the steric factors and intermolecular interactions are considered is revealed to be packing coefficient, defined as the ratio of the volume of the molecules in the crystal-unit cell to its overall volume.

In figure 2 the absolute value of the excess Gibbs energy at the equimolar composition for the orientationally disordered mixed crystals is plotted against the relative packing difference of the pure components of each binary system. In spite of the obvious scatter due to the experimental uncertainties together with the relative small non-ideal behaviour of the disordered mixed crystals, the figure states an strong evidence of the relation between mixing properties and packing coefficient. One of the most relevant evidences, which can be obtained from figure 2, is that the straight line runs across the origin. Such an experimental result states that a binary system relating two components displaying isomorphous orientationally disordered phases with a packing coefficient difference close to zero, will behave, from a thermodynamic point of view, as ideal. Moreover, this result reinforces the idea that strain energies due to the differences in the size and shape of the molecules being mixed are not relevant in this kind of phases.

Another important thermodynamic property which has been used in the thermodynamic analysis is the temperature at which equimolar orientationally disordered and liquid mixtures have equal Gibbs energy, the $T_{EGC}(X=0.5)$ temperature. Figure 3 reveals the strong correlation between this thermodynamic parameter for all the fcc molecular alloys. It must be pointed out that, although the bcc molecular alloys corresponding to the AMP/TRIS ($NH_2(CH_3)C(CH_2OH)_2$ / $NH_2(CH_3)C(CH_2OH)_3$) system follow the trends of

the global correlation, the structural differences seem to be relevant to taken apart the system. The question of whether these structural differences will produce a different correlation between both parameters cannot be answered at present due to the lack of two-component systems displaying isomorphous bcc orientationally disordered lattices.

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Figure Captions

Figure 1.- Calculated phase diagrams and experimental temperature-composition data for the analysed systems. M_i, O and Q refer to the monoclinic, orthorhombic and tetragonal phases. C_F refers to the orientationally disordered face centerd cubic phase. (-·-·-·) Temperature at which packing coefficient was determined. Dotted line in the NPA/NPG system corresponds to the theoretical equilibrium line. (For compound abbreviations see Table 1).

Figure 2 .- Absolute value of the excess Gibbs energy of the orientationally disordered phases at the equimolar composition as a function of the relative packing difference of the pure components (ξ_A and ξ_B). (For compound abbreviations see Table 1).

Figure 3.- EGC temperature as a function of the packing parameter, both at the equimolar composition, for the orientationally disordered fcc (●) abd bcc (O) mixed crystals. (For compound abbreviations see Table 1).

Table 1.- Thermodynamic parameters of the pure components (temperatures T_i and entropy change ΔS^*_i for the melting process) and the excess properties (T_{EGC} and $G^{E,ODIC}$ at X=0.5) together with the crystallographic parameters (packing coefficient of the pure components, ξ_i, for the mixed crystals at X=0.5, ξ(X0.5), isomorphism ε^i_m coefficients, all of them at T^*, and the homeomorphism ε_K. (The lattice symmetry of the mixed crystals is fcc, except for the AMP/TRIS, which is bcc). Compound abbreviations: TBN, $NO_2C(CH_3)_3$; MNP $NO_2C(CH_3)_2(CH_2OH)$; NPA, $(CH_3)_3C(CH_2OH)$; NPG, $(CH_3)_2C(CH_2OH)_2$; PG, $(CH_3)C(CH_2OH)_3$; AMP, $NH_2(CH_3)C(CH_2OH)_2$ TRIS, $NH_2C(CH_2OH)_3$.

System A	B	T_A /K	ΔS^*_A /R	T_B /K	ΔS^*_B /R	T_{EGC}(X=0.5) /K	$G^{E,ODIC}$(X=0.5) /J·mol^{-1}	T^* /K	$\xi_A(T^*)$	$\xi_B(T^*)$	ξ (X=0.5,T*)	ε^i_m (T*)	ε_K
TBN	NPA	298.5	1.034	329.8	1.359	314.1	60.0	293	0.574	0.599	0.585	0.990	0.882
TBN	MNP	298.5	1.034	363.9	1.049	331.5	80.0	293	0.574	≈ 0.615	0.590	0.990	0.935
NPG	PG	402.8	1.297	474.4	1.196	438.2	-31.3	358	0.626	0.661	0.644[a]	0.998	0.941
NPA	NPG	329.8	1.359	402.9	1.297	366.6	85.0	313	0.590	0.636	0.612	0.984	0.938
NPA	MNP	329.8	1.359	363.9	1.049	346.8	25.0	303	0.597	0.612	0.607	0.986	0.904
MNP	NPG	363.9	1.049	402.8	1.297	383.4	107.0[b]	318	0.605	0.637	0.621[c]	0.997	0.889
MNP	PG	363.9	1.049	474.4	1.196	419.2	156.0[b]	358	0.597	0.661	0.626[d]	0.997	0.826
AMP	TRIS	384.7	0.876	442.7	0.870	413.6	11.0[b]	378	0.663	0.689	0.674[e]	0.979	0.939

[a] [2]; [b] [4]; [c] [5]; [d] [6]; [e] [7].

Table 2.- Experimental (E) and calculated (C) temperature and mole fraction characterising the three-phase equilibria for the two-component systems. (For compound abbreviations see Table 1).

System A / B	Invariant		T(K)	X_M	X_N	X_P
TBN / NPA	Eutectoid	E	227.8	0.04	0.87	0.94
		C	228.9	0.095	0.83	0.94
	Pertitectoid	E	217.9	0.03	0.05	0.94
		C	220.0	0.08	0.12	0.93
TBN / MNP	Eutectoid	E	250.0	0	0.13	0.92
		C	245.7	0.08	0.17	0.92
NPG / PG	Eutectoid	E	306.5	0.09	0.14	0.52
		C	307.3	0.08	0.18	0.55
NPA / NPG	Eutectoid	E	---	---	---	---
		C	223.2	0	0.11	1
NPA / MNP	Eutectoid	E	227.4	0	0.08	1
		C	223.8	0	0.10	1