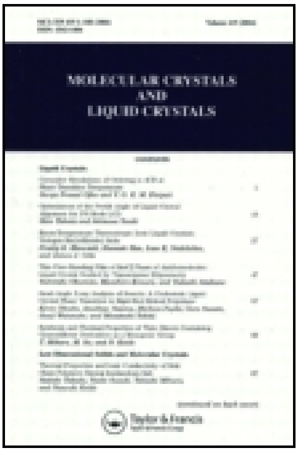

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Syncrystallization in Plastic Phase: Comparison Between Four Cases of Total Miscibility

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Syncrystallization in Plastic Phase: Comparison Between Four Cases of Total Miscibility

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The experimental binary phase diagram between the pure components 2-methyl-2-nitro-1-propanol (MNP) and 2-hydroxymethyl-2-methyl-1,3-propanediol (PG) has been established from 273 K to the liquid state, using thermal analysis and X-ray powder diffraction at several temperatures.

The main features of this phase diagram, such as, the miscibility and the molecular interactions in plastic phase are discussed on the basis of the similarity in shape and size of the molecules. In addition, other binary systems, previously reported by us, between neopentane-like compounds which present a comparable situation are considered.

Keywords: Syncrystallization, plastic phases, isomorphism, molecular alloys

1. INTRODUCTION

Some sixty years ago Timmermans[1] identified a group of molecular crystals with certain well-defined chemical and physical properties. These substances are called plastic crystals or ODIC (Orientationally Disordered Crystals),[2-4] due to the fact that they present at high temperature, as a minimum, an orientational disordered solid form besides the ordered solid form at lower temperature.

The study of the derivatives of the neopentane ($C(CH_3)_4$) and their molecular mixed crystals is of special interest to advance in the syncrystallization problem and, in particular, in the role of the intermolecular interactions in the mixed plastic crystals. In this way, some time ago, we undertook a systematic work on several series of neopentane-like compounds ($X(CH_3)_{3-n}C(CH_2OH)_n$ where $X = —CH_2OH, —NH_2, —NO_2,...$) and on the various binary systems between them.[5-14]

The purpose of the present paper is, on the one hand, to go further into the research on binary mixtures in which one of the pure substances belongs to the series $NO_2(CH_3)_{3-n}C(CH_2OH)_n$ in order to analyse the influence of the nitro group on the molecular alloys. We report here on the experimental binary phase diagram between the 2-methyl-2-nitro-1-propanol (MNP) and the pentaglycerin or 2-hydroxymethyl-2-methyl-1,3-propanediol (PG) (see Figure 1). On the other hand, phase diagrams, previously published by us, relating to neopentane like-compounds and showing similar features will be discussed and compared.

2. EXPERIMENTAL

Thermal measurements have been performed with a Perkin-Elmer DSC-7 using a scanning rate of 2 K.min^{-1} and sample masses of about 6 mg. The samples were hermetically sealed into aluminium crucibles in order to avoid sublimation.

X-ray powder diffraction measurements have been made at constant temperature using a Siemens D-500 vertical diffractometer whose most relevant characteristics have been previously described.[15] The experimental conditions have been consigned in a foregoing work.[14]

The materials used in this study were purchased from Aldrich Chemical Company with purities of 99%. Additional purification was performed for MNP by vacuum sublimation at 333 K and for PG by a drying process at the same temperature.

3. PURE COMPOUNDS

3a. MNP

The low temperature lattice, form II (referred as M), has been reported by us in a recent work[16] as monoclinic with space group $P2_1/c$ and twelve molecules per unit cell ($Z = 12$). At 288 K the lattice parameters determined in this work were $\mathbf{a} = 6.195(3)$ Å, $\mathbf{b} = 19.115(8)$ Å, $\mathbf{c} = 16.601(9)$ Å and $\boldsymbol{\beta} = 90.12(2)°$.

At (312.0 ± 1.0) K this substance undergoes a first order transition between the ordered solid form (form II) and an orientationally disordered solid form (form I, plastic phase) determined as face centered cubic (referred as C_F) with a lattice parameter of 8.857 (10) Å at 356 K. The measured enthalpy variation for this transition was (15.0 ± 0.8) kJ.mol^{-1}.

At (364.0 ± 1.0) K the plastic form melts with an associated enthalpy change of (3.2 ± 0.2) kJ.mol^{-1}.

$$CH_3 - \overset{\overset{NO_2}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2OH \qquad CH_2OH - \overset{\overset{CH_2OH}{|}}{\underset{\underset{CH_3}{|}}{C}} - CH_2OH$$

(MNP) (PG)

FIGURE 1 Molecules of MNP and PG.

3b. PG

The low temperature solid phase, form II (referred as Q) has been determined as body centered tetragonal, space group $I\bar{4}$ with two molecules per unit cell.[17,18] Our measurements of the lattice parameters at 288 K gave $\mathbf{a} = 6.052(2)$ Å and $\mathbf{c} = 8.845(4)$ Å. In this form, the molecules are linked in a similar way as in pentaerythritol, with strong intermolecular hydrogen bonds along the a-axis and weak Van der Waals forces along the c-axis.

At (357.5 ± 1.0) K with an associated enthalpy variation of (21.3 ± 1.0) kJ.mol^{-1}, PG undergoes a solid-solid transition between the ordered solid form (form II) and an orientationally disordered face centered cubic (form I, plastic phase) with a parameter of 8.866(8) Å at 358 K.

At (471.7 ± 1.0) K the substance melts with an enthalpy variation of (5.1 ± 0.3) kJ.mol^{-1}.

4. RESULTS

4a. Thermal Characterization

In order to determine the characteristic temperatures from DSC-thermograms, we have used the "shape factor method".[19,20]

In Figure 2, we present the characteristic thermograms for various samples corresponding to the ordered solid to plastic transition. As one can see in this Figure, there exists a eutectoid invariant at (301.2 ± 1.0) K. The eutectoid composition and the concentration limits have been calculated from the Tammann diagram (see Figure 3), being 0.21 (eutectoid composition), 0.005 (left limit) and 0.87 (right limit). The Tammann diagram has been performed using a method the basis of which has been described by us in a foregoing paper.[14]

In the case of the disordered solid to liquid transition and unlike the solid-solid transition, the temperature of the thermal signals increase continuously with the molar fraction of PG giving rise to a simple two-phase region (loop) between plastic and liquid phases.

In Table I, we give all the experimental characteristic temperatures obtained from DSC-thermograms.

4b. Crystallographic Characterization

Due to the fact that the ordered solid forms (M and Q) of the two pure components are not isostructural, a demixing region $[M + Q]$ must appear below the invariant eutectoid temperature. In order to determine its limits, we have performed X-ray powder measurements at 288 K.

In addition, we are interested in the syncrystallization problem between disordered-solid forms (plastic forms) and in practice, although both plastic phases are isostructurals, the formation of continuous series of solid solutions has to be proved. Due to this fact, we have performed X-ray powder measurements at 358 K, where the samples are in plastic phase.

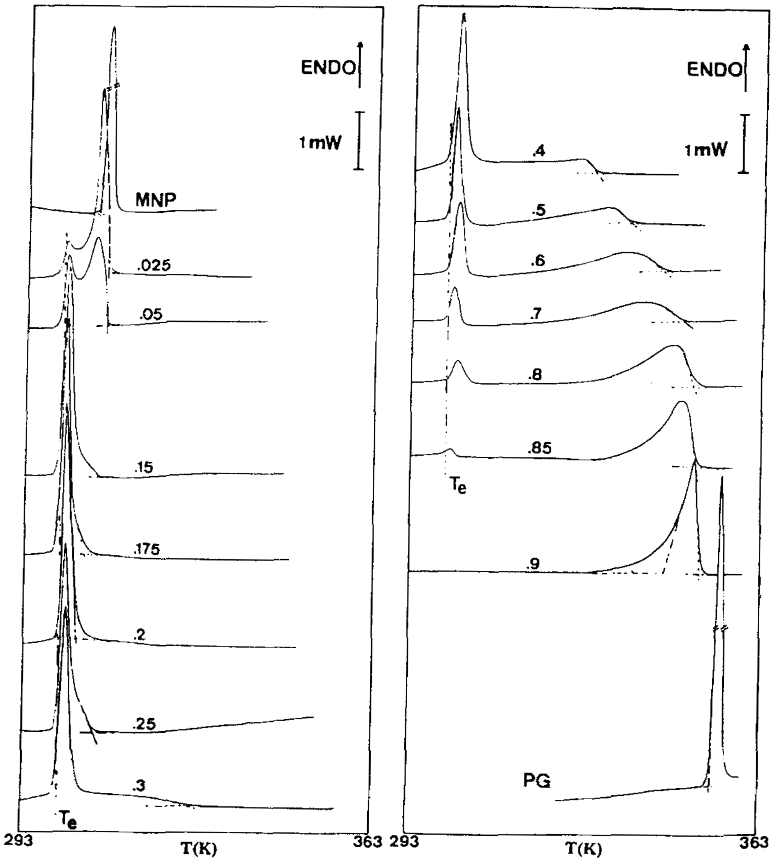

FIGURE 2 Characteristic DSC-Thermograms for the pure components and several molar fractions of PG for the solid-solid transition.

b1) Isothermal study in the low temperature region at 288 K

To determine the limits of the demixing region $[M + Q]$ at 288 K, we have analysed the evolution of the reflections of each form in function of the concentration.

In Figure 4, we show, as examples, the evolution of the (101) and (002) reflections corresponding to the tetragonal form (Q) with the mole fraction of PG. From it, we conclude that the solubility boundary of MNP in PG is $S_B(T = 288\ \mathrm{K}) \approx 0.92$, i.e., the molecular alloy $\mathrm{PG}_{0.92}\mathrm{MNP}_{0.08}$. For the compositions rich in MNP, we have always detected the coexistence of monoclinic (M) and tetragonal (Q) forms, even for the lowest molar fraction analysed, $X = 0.025$. As a consequence, we assume that the solubility boundary of PG in MNP, S_A, is lower than 0.025 ($S_A(T = 288\ \mathrm{K}) < 0.025$).

The cell parameters determined at 288 K for the pure components and their solid solutions (S_A, S_B and $X = 0.95$) are summarized in Table II.

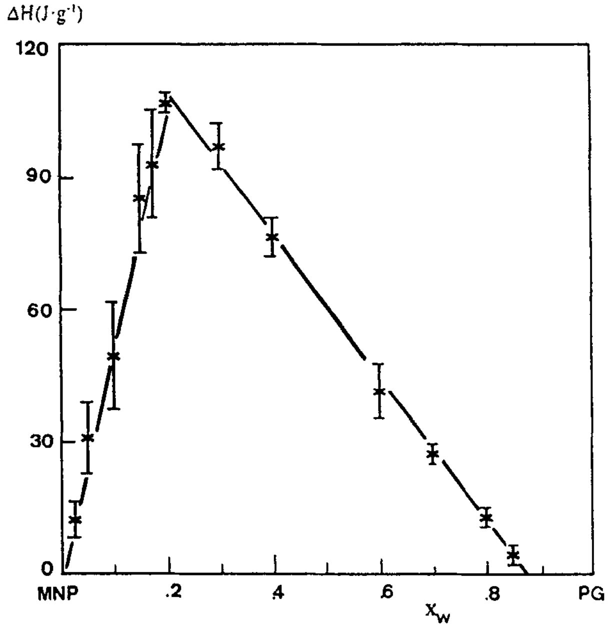

FIGURE 3 Tammann diagram corresponding to the eutectoid transformation.

TABLE I

Equilibrium temperatures corresponding to the ordered solid to plastic transition ($T_{lower\ solvus}$, $T_{eutectoid}$, $T_{upper\ solvus}$) and the melting process ($T_{solidus}$, $T_{liquidus}$)

X	$T_{l\ solvus}$(K)	T_{eut}(K)	$T_{U\ solvus}$(K)	T_{sol}(K)	T_{liq}(K)
0(MNP)	312.0 ± 1.0			364.1 ± 1.0	
0.025		301.6 ± 1.1	310.1 ± 1.0		
0.050		301.6 ± 1.1	309.4 ± 1.4		
0.100		301.5 ± 1.2	308.0 ± 1.4	368.0 ± 2.2	372.7 ± 2.0
0.150		301.2 ± 1.1	307.9 ± 1.7	373.2 ± 2.8	380.4 ± 2.5
0.175		301.2 ± 1.2	306.1 ± 1.3		
0.200		301.7 ± 1.2	304.6 ± 1.8	376.6 ± 2.6	386.2 ± 2.0
0.250		301.1 ± 1.1	307.9 ± 2.7	378.4 ± 1.7	388.1 ± 2.6
0.300		301.2 ± 1.2	322.7 ± 3.5	381.5 ± 1.3	395.3 ± 2.6
0.400		301.1 ± 1.2	329.3 ± 4.0	391.9 ± 3.7	409.1 ± 2.8
0.500		301.0 ± 1.2	338.4 ± 3.5	399.6 ± 2.5	417.4 ± 2.7
0.600		301.1 ± 1.3	344.9 ± 2.7	407.6 ± 3.1	422.9 ± 2.4
0.700		300.5 ± 1.2	348.3 ± 2.6	420.6 ± 4.3	434.6 ± 3.1
0.800		301.2 ± 1.1	350.5 ± 1.9	433.1 ± 2.3	442.6 ± 2.4
0.850		300.2 ± 1.9	350.7 ± 1.5		
0.900	330.1 ± 3.5		353.0 ± 1.5	448.0 ± 3.9	458.0 ± 3.0
1(PG)	357.5 ± 1.0			471.7 ± 1.0	

b2) Isothermal study of plastic molecular alloys at 358 K

The purpose of this study is to assure the existence of plastic mixed crystals in the whole concentration range and, in addition, to analyse the evolution of the lattice parameters versus concentration.

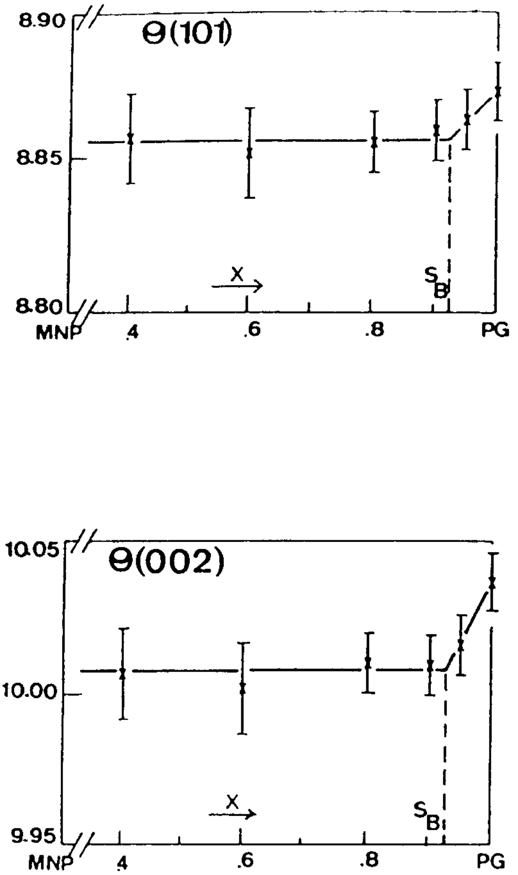

FIGURE 4 Variation of the Bragg's angles with the composition for the (101) and (002) reflections corresponding to the tetragonal form at 288 K.

TABLE II

Lattice parameters of the unit cells of the pure compounds, their alloys and the solubility boundaries at room temperature

X	Form	Parameters			
		a(Å)	b(Å)	c(Å)	β(°)
0(MNP)	M	6.195(3)	19.115(8)	16.601(9)	90.12(2)
S_A	M	6.192(2)	19.071(10)	16.614(14)	89.96(2)
S_B	Q	6.056(2)		8.865(4)	
0.95	Q	6.055(3)		8.863(5)	
1(PG)	Q	6.052(2)		8.845(4)	

In Figure 5, we show, as examples, the evolution of the (111) and (002) reflections versus molar fraction of PG proving doubtless the existence of a continuous series of face centered cubic alloys, the cell parameters of which are presented in Table III.

4c. Phase Diagram

Both thermal and crystallographic characterizations have been used to perform the experimental phase diagram presented in Figure 6.

5. DISCUSSION AND CONCLUSIONS

The main characteristics of the experimental phase diagram MNP/PG are the existence, on the one hand, of a eutectoid invariant and, on the other hand, of a simple loop for the melting phenomenon of the plastic alloys.

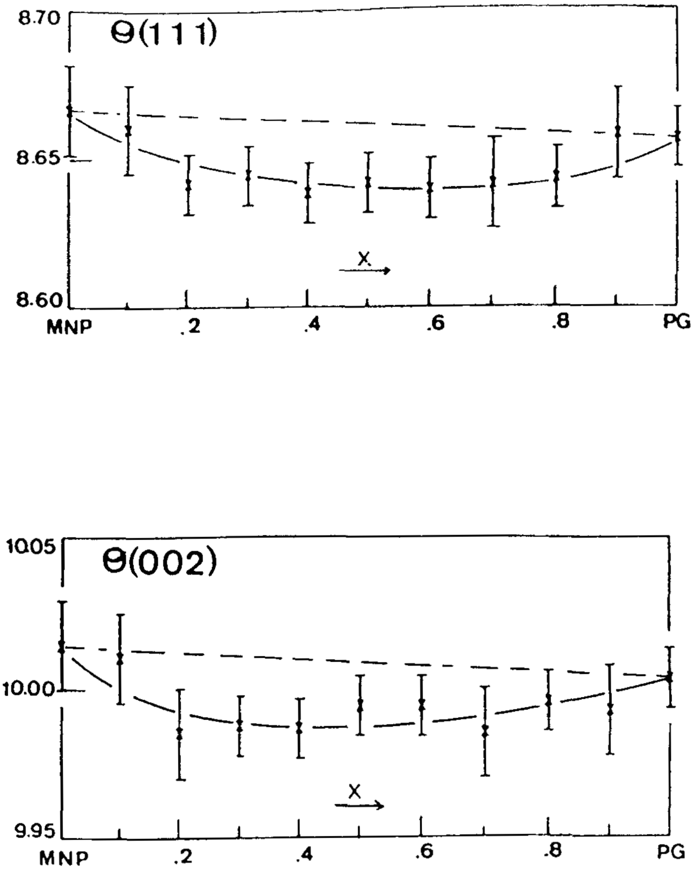

FIGURE 5 Variation of the Bragg's angles with the mole fraction for the (111) and (002) reflections corresponding to the fcc alloys at 358 K.

TABLE III

Lattice parameters for the MNP/PG alloys at 358 K

X	a(Å)
0(MNP)	8.857(10)
0.10	8.862(10)
0.20	8.870(10)
0.30	8.880(10)
0.40	8.884(10)
0.50	8.878(10)
0.60	8.879(10)
0.70	8.883(10)
0.80	8.877(10)
0.90	8.872(10)
1(PG)	8.866(8)

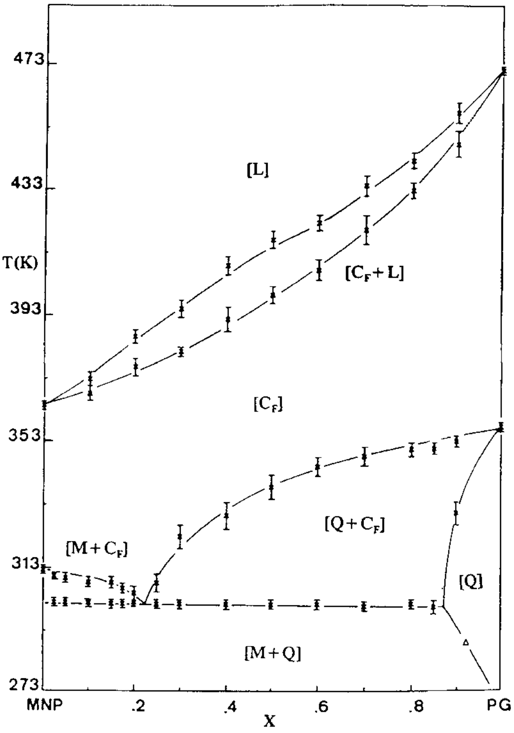

FIGURE 6 Experimental binary phase diagram MNP/PG.

These trends are associated to the existence of a large inmiscibility domain in the low temperature region and to a complete miscibility in the plastic phase. Both features have been found in some previous binary phase diagrams between related compounds determined by us. In Figure 7 we depict four of these diagrams. The basic crystallographic characteristics of the involved compounds are given in the Table IV.

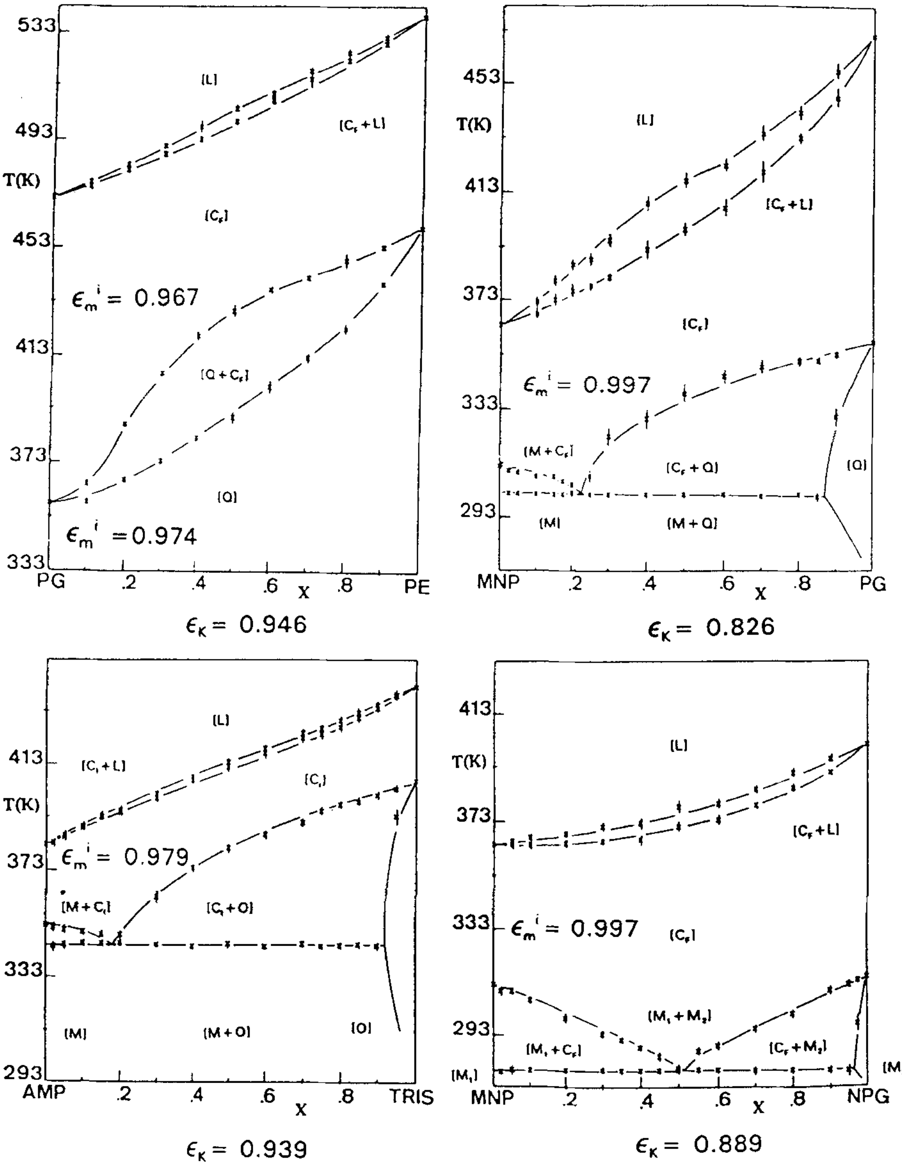

FIGURE 7 Phase diagrams showing total miscibility in plastic phase.

In order to analyse or even to predict the possibilities of the formation of mixed crystals by two organic compounds, the geometrical similarity between the two isolated molecules has to be considered. This similarity in shape and size can be quantified by means of the coefficient ε_K proposed by Kitaigorodsky[22,23] and

TABLE IV

Basic characteristics of compounds involved in the presented phase diagrams of Figure 7[21]

	Compound	Phase	V/Z(Å^3)	T(K)
PG	$(CH_3)C(CH_2OH)_3$	Solid ($\overline{14}$)	162.5	293
		Plastic (fcc)	180.3	453
PE	$C(CH_2OH)_4$	Solid ($\overline{14}$)	162.2	293
		Plastic (fcc)	182.3	453
AMP	$(NH_2)(CH_3)C(CH_2OH)_2$	Solid (Monoclinic)	144.8	293
		Plastic (bcc))	156.2	378
TRIS	$(NH_2)C(CH_2OH)_3$	Solid ($Pn2_1a$)	152.0	293
		Plastic (Im3m)	159.5	378
MNP	$(NO_2)(CH_3)_2C(CH_2OH)$	Solid ($P2_1/c$)	163.8	293
		Plastic (fcc)	171.4	318

defined as:

$$\varepsilon_K = 1 - \frac{\Delta}{\Gamma}$$

where Γ is the volume of the overlapping part and Δ the non-overlapping part when the two molecules are superimposed so as to maximize the intermolecular overlap. ε_K compares exclusively the shape and size of both molecules, the more the molecules are similar the closer ε_K will be to unity and then it is, unfortunately, independent of temperature and intermolecular arragement, i.e., independent of the analysed phase. Thus, ε_K expresses the degree of homeomorphism of two molecules.

To calculate ε_K values we have built up the molecules by means of the standard distances between atoms and Van der Waals radii, the values of which have been taken from references.[22,24,25] To do such a calculation, some simplifying hypotheses have been used: the molecules are rigid bodies (characteristic bond lengths and angles were temperature independent) and tetrahedral symmetry around the central C atom was imposed. Table V summarizes the used values to calculate the molecular volumes.

The values of ε_K are consigned at the bottom of each phase diagram in Figure 7. The values corresponding to the molecular volumes are listed in Table VI.

TABLE V

Values taken for the calculation of molecular volumes and ε_K coefficients[22,24,25]

Van der Waals radii (Å)	Bond lengths (Å)	Bond angles (°)
$R_c = 1.80$	C—C = 1.54	C—C—H = 110.0
$R_H = 1.17$	C—N = 1.47	C—C—O = 107.4
$R_N = 1.57$	C—O = 1.43	O—N—H = 109.5
$R_O = 1.36$	C—H = 1.08	H—N—H = 104.5
	O—H—0.97	C—N—O = 119.0
	N—O = 1.24	O—N—O = 122.0
	N—H = 1.02	C—O—H = 106.1

TABLE VI

Molecular volumes

Compound	Molecular volume (Å^3)
PG	115.3
PE	121.4
AMP	103.6
TRIS	109.9
MNP	103.7

According to the Kitaigorodsky analysis, high similarity of the molecules ($\varepsilon_K > 0.85$) can lead to a continuous miscibility from one pure compound to the other one. In the present case a great similarity exists for the PG/PE($\varepsilon_K = 0.946$) and AMP/TRIS($\varepsilon_K = 0.939$). However, for the latter the differences in the molecular arrangements and intermolecular forces for the two pure compounds in the low temperature solid phase make ε_K unable to account for the miscibility.

For the systems including MNP compound, i.e. MNP/NPG($\varepsilon_K = 0.889$) and MNP/PG($\varepsilon_K = 0.826$) steric hindrance for the formation of the substitutional solid solutions should be important due to the relatively low degree of homeomorphism.

For each one of the four analysed systems we have proved[11,21] the existence of isomorphism between components in the plastic phase, i.e., continuous evolution of the cell parameters and only one curve of the Gibbs energy is required to account for the stability of all the alloys from $X = 0$ to $X = 1$. These experimental results enable us to use the concept of degree of crystalline isomorphism.[26,27] This concept is the result of the whole set of factors that govern the structural arrangements (size and shape of the molecules, intermolecular interactions and the effects of orientational and positional disorder). It is assumed that the lattices of the phases corresponding to the analysed compounds must have the same space group and the same number of molecules per unit cell. So then, the degree of isomorphism is accounted for the ε_m^i, coefficient[27] and defined as:

$$\varepsilon_m^i = 1 - \frac{\Delta_m}{\Gamma_m}$$

where Γ_m is the maximum volume of the overlapping part of the unit cell of both compounds and Δ_m the total volume of the non-overlapping parts.

The values of ε_m^i for the isomorphous phases are presented in the phase diagrams of the Figure 7. As can be seen, a high degree of isomorphism appears in the regions where complete miscibility is found.

It should be mentioned that for the low temperature region in the case of AMP/TRIS, MNP/NPG and MNP/PG the phases are not isomorphous and then, the calculation of ε_m^i has not any sense. In the case of the PG/PE system where total miscibility has been also found in the ordered forms (i.e. we have isodimorphism), a high value of ε_m^i is again obtained.

From the analysis of the ε_K values for the MNP/NPG and MNP/PG systems it can be concluded that the low similarity in shape and size of the molecules does not block the formation of molecular alloys in the whole concentration range in the plastic form due to the fact that in the high temperature forms the entities to be considered are the globular ones (i.e. the dynamical envelope). These facts are in agreement with the high degree of isomorphism in both cases.

To go further into the study of the intermolecular interactions in the plastic phase we have analysed the evolution of the volume occupied by the average molecule (V/Z) of the alloy $A_{1-x}B_x$ as a function of the concentration. This evolution is depicted in Figure 8 for the four systems (the evolution corresponding to the ordered form of the PG/PE system has also been included). The plot has been performed in such a manner as to the B molecule in the $A_{1-x}B_x$ alloys corresponds to the larger molecule (see Table VI). Figure 8 makes evident that whatever the presented system the values of V/Z against the mole fraction are roughly constant. Therefore, when analysing the behaviour of V/Z in the plastic form, it is obvious that the geometrical effect cannot account for the presented evolution, because of the guest molecule (B) is always larger than the substituted host molecule (A). In the particular cases of PG/PE and AMP/TRIS systems the slight increase in V/Z (1.1% and 2.1% respectively) is considerably lower than the increase of the respective molecular volumes when going from $X = 0$ (PG or AMP) to $X = 1$ (PE or TRIS) (5% and 5.8% respectively).

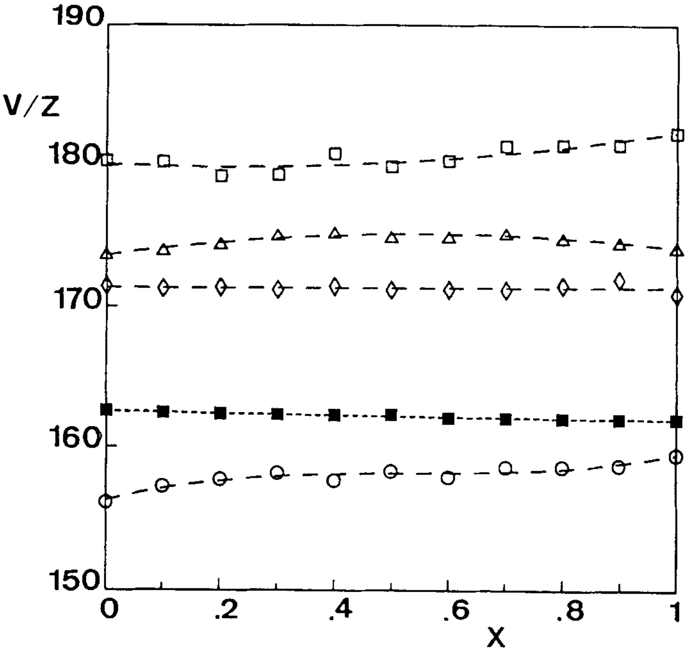

FIGURE 8 V/Z against X for the plastic phases of the four phase diagrams (□ PG/PE, △ MNP/PG, ◇ MNP/NPG, ○ AMP/TRIS) and for the ordered solid form of the PG/PE binary system (■).

Then, to explain the fact that V/Z is almost constant as a function of the molar fraction we have to admit that there exist intermolecular interactions in order to compensate the geometrical effect.

With regard to the ordered solid phase, in the case of the PG/PE system the effect is more remarkable, because of V/Z even decreases (about 0.2%) when X changes from 0(PG) to 1(PE) in spite of the introduction of larger PE guest molecules in the host lattice of PG. For both pure compounds it has been largely proved that the molecules are linked by hydrogen bonds in the (001) planes of the tetragonal structures, this interaction being stronger in PE than in PG, due to the existence of four hydroxy (-CH_2OH) groups in the former in front of three in the latter. Now, we know that this kind of interaction is also present in the molecular alloys.

As a final remark we want to point out the power of the two coefficients, ε_K and ε^i_m, in order to analyse the miscibility between two organic compounds and the usefulness of the molecular alloys to push further in the intermolecular interactions.

Acknowledgements

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