JOURNAL OF Materials CHEMISTRY

Two-component systems of isomorphous orientationally disordered crystals. Part 2† Thermodynamic analysis

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Received 26th October 1998, Accepted 27th January 1999

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 the preceding paper,[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 finding of regularities, 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, or cannot easily be measured. These properties also hold for the excess mixing properties of the chemically similar group of materials.

Here, we report a comprehensive thermodynamic analysis on the two-component system relating to 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 1[1] of this series of work, together with other previously published,[2–7] are presented. (iii) The final part of the present work gives a simple empirical method for the estimation of the thermodynamic mixing properties in this kind of system 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, and as a function of temperature and composition for the second.

In the thermodynamic analysis that follows, A and B represent two pure components displaying isomorphism in the α phase giving rise to a continuous series of mixed α crystals. Recalling the general relationship for the Gibbs energy for a mixture of $(1-x)$ moles of A and x moles 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, *i.e.*, 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 information is generally not available in this direct form and several simplifying assumptions concerning the considered thermodynamic properties have to be made.

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 [eqn. (1)] can be written as:

$$\begin{aligned}\Delta G(T,x)&=G^{\alpha}(T,x)-G^{\beta}(T,x)\\&=(1-x)\Delta\mu_A{}^*(T)+x\Delta\mu_B{}^*(T)+\Delta G^E(T,X)\end{aligned} \qquad (2)$$

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

$$\Delta G^{\alpha\rightarrow\beta}\,(T_{EGC},x)=0 \qquad (3)$$

provides a curve in the T–x plane where the α and β phases have equal values of the Gibbs energies (the EGC curve). By

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†Part 1: ref. 1.

assuming that the heat capacities may be ignored, $\Delta\mu_i^*(T)$ can be approximately written as $\Delta S_i^*(T_i^{\alpha\rightarrow\beta}-T)$, where $T_i^{\alpha\rightarrow\beta}$ the temperature of the α→β transition for the component *i*.

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

$$T_{\mathrm{EGC}}=\frac{(1-x)\Delta H_{\mathrm{A}}^*+x\Delta H_{\mathrm{B}}^*}{(1-x)\Delta S_{\mathrm{A}}^*+x\Delta S_{\mathrm{B}}^*}+\frac{\Delta G_{\mathrm{EGC}}{}^{\mathrm{E}}(x)}{(1-x)\Delta S_{\mathrm{A}}^*+x\Delta S_{\mathrm{B}}^*} \quad (4)$$

The first term of the right hand side of eqn. (4) is denoted 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 $G^{\mathrm{E,ODIC}}$, which stands for the excess Gibbs energy of the orientationally disordered state.

This assumption for the liquid state deserves further 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 eqn. (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 only prove 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 type of ordered mixed crystal can 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).

Finally, the thermodynamic assessment has been performed using the 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 is given by a two-parameter function in the form of a Redlich–Kister polynomial:

$$G^{\mathrm{E}}(x)=x(1-x)[G_1+G_2(1-2x)] \quad (5)$$

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 Fig. 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 Fig. 1 the experimental orientationally disordered–liquid equilibria are very well reproduced. By contrast, the agreement 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 and on the other the error produced in 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 Fig. 1, the NPA–NPG[$(CH_3)_3C(CH_2OH)$–$(CH_3)_2C(CH_2OH)_2$] system deserves 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 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 one 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 analysis of the conditions of 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. By contrast, 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 ease of simulating the symmetry elements of the orientationally disordered host lattice for the guest molecule owing to the existence of a large number of possible energetically feasible orientations. A detailed discussion of these factors can be found in references 17 and 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 $\varepsilon_{\mathrm{K}}=1-\Gamma/\Delta$, 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

Table 1 Thermodynamic parameters of the pure components (temperatures T_i and entropy changes 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 ($x=0.5$), isomorphism ε_m^i coefficients, all of them at T^*, and the homeomorphism ε_K[a]

System													
A	B	T_A/K	$\Delta S^*_A/R$	T_B/K	$\Delta S^*_B/R$	T_{EGC} ($x=0.5$)/K	$G^{E,ODIC}$ ($x=0.5$)/ J mol^{-1}	T^*/K	ξ_A (T^*)	ξ_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[b]	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[c]	318	0.605	0.637	0.621[d]	0.997	0.889
MNP	PG	363.9	1.049	474.4	1.196	419.2	156.0[c]	358	0.597	0.661	0.626[e]	0.997	0.826
AMP	TRIS	384.7	0.876	442.7	0.870	413.6	11.0[c]	378	0.663	0.689	0.674[f]	0.979	0.939

[a] The lattice symmetry of the mixed crystals is fcc, except for the AMP–TRIS system, 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 = $NH_2C(CH_2OH)_3$. [b] Ref. 2. [c] Ref. 4. [d] Ref. 5. [e] Ref. 6. [f] Ref. 7.

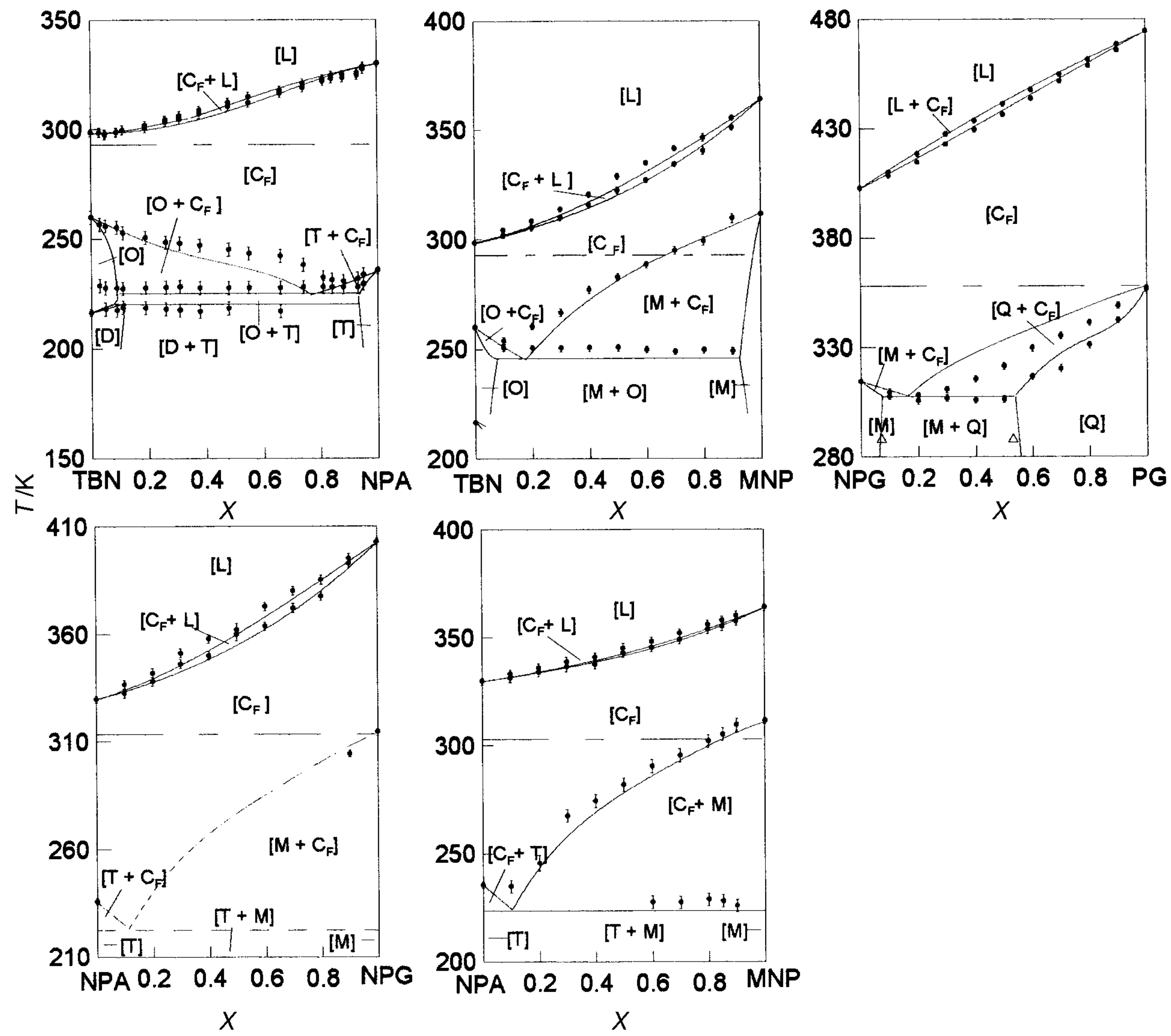

Fig. 1 Calculated phase diagrams and experimental temperature–composition data for the analysed systems. M, O and Q refer to the monoclinic, orthorhombic and tetragonal phases. C_F refers to the orientationally disordered face centred cubic phase. (––) Temperature at which the packing coefficient was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

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

which characterises these phases. As can be seen in Table 1, ε_K varies from 0.83 to 0.94, 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_m^i, has been recently proposed.[21,22] It accounts, in an 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_m^i 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 show the close similarity of the orientationally disordered unit cells of the series of pure compounds presented and, obviously, the excess Gibbs energy will be scarcely dependent on the relative mismatch. It must be borne in mind that the success of the ε_m^i 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 the packing coefficient, defined as the ratio of the volume of the molecules, in the crystal unit cell to its overall volume.

In Fig. 2 the absolute value of the excess Gibbs energy at the equimolar composition for the orientationally disordered mixed crystals is plotted *vs.* the relative packing difference of the pure components of each binary system. In spite of obvious scatter

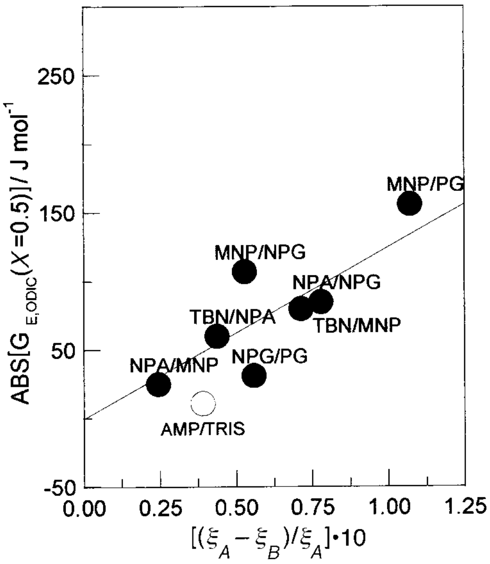

Fig. 2 Absolute value of the excess Gibbs energy of the orientationally disordered phases at the equimolar composition as a function of the relative packing difference of the pure components (ξ_A and ξ_B). (For compound abbreviations see Table 1.)

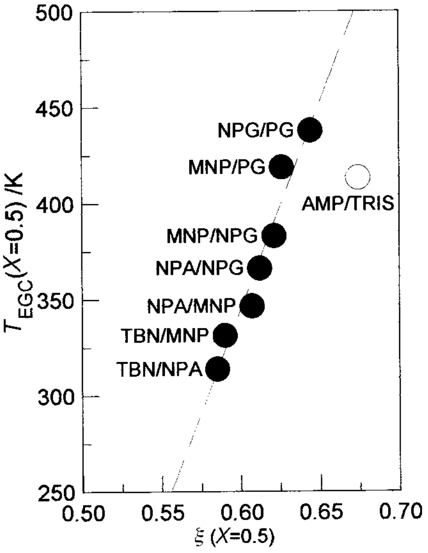

Fig. 3 EGC temperature as a function of the packing parameter, both at the equimolar composition, for the orientationally disordered fcc (●) and bcc (○) mixed crystals. (For compound abbreviations see Table 1.)

due to the experimental uncertainties together with the relative small non-ideal behaviour of the disordered mixed crystals, Fig. 2 shows strong evidence of the relation between mixing properties and packing coefficient. One of the most relevant results is that the straight line runs across the origin. Such an experimental result implies 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 phase.

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 temperature $T_{EGC}(x=0.5)$. Fig. 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 taken apart from the general trend of the system. The question of whether these structural differences will produce a different correlation between both parameters cannot be answered at present owing to the lack of two-component systems displaying isomorphous bcc orientationally disordered lattices.

Acknowledgements

This work has been performed within the framework of the Réseau Européen sur les Aliages Moléculaires (REALM). We acknowledge the financial support of the DGICYT Grant PB95-0032.

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