Uniform Thermodynamic Description of the Orientationally Disordered Mixed Crystals of a Group of Neopentane Derivatives

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The experimental systems considered in this paper are isobaric binary plastic-crystalline mixed crystals of neopentane derivatives, and their properties studied are (i) solid−liquid phase behavior and (ii) the thermodynamic mixing properties, actually the excess enthalpy, entropy, and volume. More in particular, 10 systems are considered, nine being face-centered cubic and one body-centered cubic, and their components are derived from neopentane, $C(CH_3)_4$, by substituting one or more $-CH_3$ groups by one or more $-CH_2OH$ groups and/or one $-NO_2$ or $-NH_2$ groups. The (mean) number of $-CH_2OH$ groups per molecule appears to have a dominating influence with regard to melting temperature and degree of compactness. The values of the excess properties vary from system to system, whereas their quotients are system-independent. For the group of fcc systems, the quotient of excess enthalpy and excess entropy (compensation temperature) has the uniform value of 630 K, and the quotient of excess enthalpy and excess volume the value of about 0.5 GPa.

I. Introduction

Molecular materials composed of spherical or pseudospherical molecules often give rise to a mesostate—between ordered crystalline and liquid—in which the molecules have rotational freedom. The mesostate is referred to as the plastic crystalline state and one speaks of plastic crystals or orientationally disordered crystals, ODICs for short. Well-known examples of such materials are carbon tetrachloride (CCl_4) and neopentane ($C(CH_3)_4$). The transition from ODIC to liquid is characterized by small changes in entropy and volume.

During the last 10 years, the authors have made an extensive thermodynamic and structural study of a group of neopentane derivatives and their binary systems.[1−14] The binary systems invariably involve the formation of mixed crystals—mixed ODICs to be precise. The substances studied fall into three series that are denoted as series I, II, and III. In series I, the substances have the general formula $(CH_3)_{4-n}C(CH_2OH)_n$ (with $n = 0, 1, 2, 3, 4$); an individual member of the series is indicated as I_n. In the case of series II, one of the $-CH_3$ groups is replaced by $-NH_2$ and we have $NH_2(CH_3)_{3-n}C(CH_2OH)_n$ (with $n = 0, 1, 2, 3$) and members II_n. Similarly, for series III: $NO_2(CH_3)_{3-n}C(CH_2OH)_n$ (with $n = 0, 1, 2, 3$) and members III_n. In their ODIC state, the neopentane derivatives are either face centered cubic (C_F) or body centered cubic (C_I). It implies that in part of the binary systems the components are isomorphous—giving rise to a continuous series of mixed crystals—whereas in the remaining part of the systems the components are not isomorphous—with two interrupted series of mixed crystals. In the case of the "isomorphous" binary systems, it is relatively easy to determine the thermodynamic mixing properties of the mixed crystalline state.

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(1) Barrio, M.; Font, J.; López, D. O.; Muntasell, J.; Tamarit, J. Ll.; Chanh, N. B.; Haget, Y. *J. Chim. Phys.* **1990**, *87*, 1835.

(2) Barrio, M.; Font, J.; López, D. O.; Muntasell, J.; Tamarit, J. Ll.; Chanh, N. B.; Haget, Y.; Teisseire, M.; Guion, J.; Alcobé, X. *J. Chim. Phys.* **1992**, *89*, 695.

(3) Barrio, M.; Font, J.; López, D. O.; Muntasell, J.; Tamarit, J. Ll.; Negrier, P.; Chanh, N. B.; Haget, Y. *J. Phys. Chem. Solids* **1993**, *54*(2), 171.

(4) Barrio, M.; Font, J.; López, D. O.; Muntasell, J.; Tamarit, J. Ll.; Negrier, P.; Haget, Y. *J. Phys. Chem. Solids* **1994**, *55*(11), 1295.

(5) Barrio, M.; Font, J.; López, D. O.; Muntasell, J.; Tamarit, J. Ll.; Haget, Y. *J. Chim. Phys.* **1994**, *91*, 189.

(6) López, D. O.; Barrio, M.; Tamarit, J. Ll.; Negrier, P.; Haget, Y. *Mol. Cryst. Liq. Cryst.* **1995**, *268*, 129.

(7) Barrio, M.; López, D. O.; Tamarit, J. Ll.; Negrier, P.; Haget, Y. *J. Mater. Chem.* **1995**, *5*(3), 431.

(8) Barrio, M.; López, D. O.; Tamarit, J. Ll.; Haget, Y. *Mater. Res. Bull.* 1**995**, *5* (3), 431.

(9) Barrio, M.; López, D. O.; Tamarit, J. Ll.; Negrier, P.; Haget, Y. *J. Solid State. Chem.* **1996**, *124*, 29.

(10) Salud, J.; López, D. O.; Barrio, M.; Tamarit, J. Ll.; Oonk, H. A. J.; Negrier, P.; Haget, Y. *J. Solid State.Chem.* **1997**, *133*, 536.

(11) López, D. O.; Van Braak, J.; Tamarit, J. Ll.; Oonk, H. A. J. *Calphad* **1994**, *18*(4), 387.

(12) López, D. O.; Van Braak, J.; Tamarit, J. Ll.; Oonk, H. A. J. *Calphad* **1995**, *19*(1), 37.

(13) Salud, J.; López, D. O.; Barrio, M.; Tamarit, J. Ll. *J. Mater. Chem.* **1999**, *9*, 909.

(14) Salud, J.; López, D. O.; Barrio, M.; Tamarit, J. Ll.; Oonk, H. A. J. *J. Mater. Chem.* **1999**, *9*, 917.

10.1021/cm991178r CCC: $19.00

In this paper, we bring together the results of thermodynamic and structural investigations on the "isomorphous" binary systems—with concentration on the pure constituents of the systems and the equimolar mixtures. The thermodynamic data pertain to the transition from the ODIC to the liquid state. The data allow the influence of the (number of) substituents in the molecules on the solid−liquid phase behavior to be studied and the excess enthalpy (H^E) and excess entropy (S^E) of the mixed ODIC state at equimolar composition to be calculated. The structural information is on the ODIC state as such, and the original data have been used to calculate the molar volumes and packing coefficients of the constituents and excess volumes (V^E) of the equimolar mixtures. The principal aim of the paper is to examine to what extent the available data will allow a uniform thermodynamic description of the ensemble of substances and binary systems. To that end, the possibility is studied of making correlations—between different thermodynamic properties, and between thermodynamic properties and nonthermodynamic parameters.

In more detail, the actions to be taken are the following—starting with correlations between different thermodynamic properties. From a comparison of the H^E and S^E values of the equimolar mixtures it can be derived to what extent the group of systems is a class of similar systems in terms of enthalpy−entropy compensation.[15] A class of similar mixed-crystalline systems is characterized by a uniform value of the ratio H^E/S^E. This ratio, having the dimension of temperature, is referred to as compensation temperature—to indicate that for that temperature H^E and S^E compensate for one another, such that the excess Gibbs energy G^E ($= H^E - TS^E$) becomes zero, or rather goes through zero. On the same lines of thought, one may infer, from a comparison of H^E and S^E values, to what extent the group of systems gives rise to a uniform value of the ratio H^E/V^E. It could imply the existence of a compensation pressure, at which the excess internal energy U^E ($= H^E - pV^E$) goes through zero, and so for the whole group of systems at the same value of pressure p.

After having established what the uniform characteristics of the group of systems are, the next step is to explore to what extent the nonuniform properties of the individual members of the group can be related to an elementary feature (by means of which the members can be distinguished from one another). In our case the nonuniform properties in particular are melting temperature and excess enthalpy (to which the other excess quantities are related through compensation temperature and pressure). With regard to the elementary feature to distinguish between the members of the group, we may refer to the mixed-crystalline rotator state in binary normal alkane systems.[16,17] By taking the number n of carbon atoms in the molecules as the elementary feature, one can observe that the melting temperatures are related to n, and the excess enthalpies to $\Delta n/\bar{n}$, i.e., the relative difference in number of carbon atoms in the molecules of the constituent substances. On these lines it is worthwhile—for the underlying systems with their varying numbers of hydrogen bonding ($-$OH and $-$NH$_2$) groups—to study the possibility of relating the nonuniform properties to the number of hydrogen bonding groups, or to otherwise rationalize the results in terms of hydrogen bonding.

II. Thermodynamic Formulation and Data

The essentials of the thermodynamic treatment are enumerated as follows. At constant pressure, the molar Gibbs energy of a homogeneous mixture in the system {(1 − X) mole of substance A + X mole of substance B} usually is given as the following function of thermodynamic temperature (T) and mole fraction (X)

$$G(T,X) = (1 - X)G^*{}_A(T) + XG^*{}_B{}^*(T) + RT\{(1 - X)\ln(1 - X) + \mathrm{X}\ln X\} + G^E(T,X) \quad (1)$$

where $G^*{}_A$ and $G^*{}_B$ are the molar Gibbs energies of the pure constituents; R, the gas constant ($R = 8.31451$ J K^{-1} mol^{-1}); and G^E, the excess Gibbs energy. There exists one Gibbs energy function of the type of eq 1 for each different state. Substances that form mixed crystals, generally, are so much alike that their liquid mixtures are virtually ideal ($G^{E,liq} = 0$). The excess Gibbs energy of mixed crystals (ODIC in our case) are almost linear functions of temperature and are, for our purposes, conveniently represented by the following formula with three system-dependent constants:[11,12,18,19]

$$G^{E,ODIC}(T,X) = A\left(1 - \frac{T}{\theta}\right) X(1 - X)\,[1 + B(1 - 2X)] \quad (2)$$

The constant A expresses the magnitude of the excess function; B is a measure of its asymmetry; and θ is the temperature at which the function changes sign. The corresponding formulas for the excess enthalpy (H^E) and the excess entropy (S^E) are

$$H^{E,ODIC}(T,X) = H^{E,ODIC}(X) = AX(1 - X)[1 + B(1 - 2X)] \quad (3)$$

$$S^{E,ODIC}(T,X) = S^{E,ODIC}(X) = \left(\frac{A}{\theta}\right)X(1 - X)[1 + B(1 - 2X)] \quad (4)$$

The fact that the excess Gibbs energy, eq 2, is a linear function of temperature implies that the excess enthalpy (the heat of mixing) and the excess entropy are independent of temperature.

Generally, information on the above-mentioned excess properties is obtained by studying the solid (ODIC) to liquid transition as a function of composition. In most cases, the experimental method is thermal analysis, which, at the same time, gives the phase diagram and the heat of melting as a function of composition. The heat of melting, in a direct manner, yields the excess enthalpy function of the solid-state taking into consideration that the liquid state is considered as an ideal

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[15] Boots, H. M. J.; Bokx, P. K. *J. Phys. Chem.* **1989**, *93*, 8240.
[16] Oonk, H. A. J.; Mondieig, D.; Haget, Y.; Cuevas-Diarte, M. A. *J. Chem. Phys.* **1998**, *108*(2), 715.
[17] Mondieig, D.; Espeau, P.; Robles, L.; Haget, Y.; Oonk, H. A. J.; Cuevas-Diarte, M. A. *J. Chem. Soc. Faraday Trans.* **1997**, *93*(18), 3343.
[18] Calvet, M. T. Thesis, University of Barcelona, 1990.
[19] Calvet, M. T.; Cuevas-Diarte, M. A.; Haget, Y.; Van der Linde, P. R.; Oonk, H. A. J. *Calphad* **1991**, *15*(3), 225.

Table 1. For the Binary Systems Considered, Their ODIC Form, Melting Point and Heat of Melting of Pure Components and, for the Equimolar Mixture, Ideal Enthalpy and Entropy Change for the Solid−Liquid Transition, Temperatures of Zero Line and Equal Gibbs Curve, Excess Gibbs Energy, Excess Enthalpy, Excess Entropy and the Quotient of Excess Enthalpy and Excess Entropy[a]

		pure components				equimolar mixture							
system A + B	form	T^o_A	T^o_B	ΔH^*_A	ΔH^*_B	ΔH^*	ΔS^*	T_{ZERO}	T_{EGC}	$G^{E,ODIC}$	$H^{E,ODIC}$	$S^{E,ODIC}$	$H^{E,ODIC}/S^{E,ODIC}$
$III_0 + I_1$	C_F	298.5	329.8	2560	3730	3145	9.94	316.3	310.3	60 ± 10	125 ± 23	0.21 ± 0.11	597
$III_0 + III_1$	C_F	298.5	363.9	2560	3200	2880	8.68	331.6	322.4	80 ± 20	160 ± 21	0.24 ± 0.12	667
$I_1 + III_1$	C_F	329.8	363.9	3730	3200	3465	10.05	344.7	342.2	25 ± 10	58 ± 25	0.09 ± 0.10	639
$I_1 + I_2$	C_F	329.8	402.6	3730	4330	4030	11.03	365.3	357.6	85 ± 20	214 ± 28	0.35 ± 0.13	611
$III_1 + I_2$	C_F	363.9	402.6	3200	4330	3765	9.77	385.2	374.2	107 ± 20	265 ± 30	0.41 ± 0.13	646
$III_1 + I_3$	C_F	363.9	474.4	3200	4720	3960	9.37	422.6	406.0	156 ± 25	420 ± 30	0.63 ± 0.13	667
$I_2 + I_3$	C_F	402.6	474.4	4330	4720	4525	10.35	437.1	440.1	−31 ± 12	−145 ± 35	−0.26 ± 0.11	558
$I_2 + I_4$[b]	C_F	402.6	539.0	4330	5200	4765	10.20	467.2					
$I_3 + I_4$	C_F	474.4	537.0	4720	5200	4960	9.80	506.1	502.6	31 ± 10	151[c]	0.24[c]	630[c]
$II_2 + II_3$	C_I	384.9	442.7	2800	3200	3000	7.25	413.7	412.2	11 ± 7	−48 ± 30	−0.14 ± 0.07	343

[a] All quantities in SI units. [b] The values for the system $I_2 + I_4$ are calculated, see text. [c] These values have been calculated by means of WINIFIT and eq 2 by assuming $\theta = 630$ K.

Table 2. For the Binary Systems Considered and Pure Components, Survey of Volume and packing coefficient (ξ) Data[a]

		pure components				equimolar mixture		
system A + B	T (K)	V^*_A (cm^3 mol^{-1})	V^*_B (cm^3 mol^{-1})	ξ_A	ξ_B	V (cm^3 mol^{-1})	V^E (cm^3 mol^{-1})	$\xi(X = 0.5)$
$III_0 + I_1$	293	102.3	103.1	0.573	0.599	103.3	0.6 ± 0.4	0.585 ± 0.002
$III_0 + III_1$	293	102.3	101.6	0.573	0.615	102.6	0.7 ± 0.4	0.590 ± 0.003
$I_1 + III_1$	303	103.2	101.7	0.599	0.614	102.5	0.0 ± 0.4 (2.5×10^{-3})[b]	0.607 ± 0.003
$I_1 + I_2$	313	104.4	103.1	0.592	0.639	104.1	0.6 ± 0.4	0.612 ± 0.002
$III_1 + I_2$	318	103.0	102.9	0.606	0.637	103.1	0.2 ± 0.4	0.621 ± 0.006
$III_1 + I_3$	358	105.0	104.7	0.595	0.663	105.4	0.6 ± 0.4	0.626 ± 0.006
$I_2 + I_3$	358	105.1	104.7	0.624	0.663	104.9	0.0 ± 0.4 (−0.035)[b]	0.644 ± 0.003
$I_2 + I_4$[c]	453	111.4	109.8	0.589	0.666			
$I_3 + I_4$[c]	358	104.7	106.0	0.663	0.690			
$II_2 + II_3$	378	94.1	96.1	0.663	0.689	95.4	0.3 ± 0.4	0.674 ± 0.004

[a] T is the temperature for which the data are measured or calculated. [b] These values are indicative of the sign of V^E. [c] For these two systems there are no experimental data on volume as a function of composition.

mixture (which implies $H^{E,Liq} = 0$). The excess Gibbs energy function is derived, in an indirect manner, from the solid−liquid phase diagram by means of a procedure which is directed by the Equal-G Curve (EGC).[20] The EGC is a curve in the TX plane that represents the solution of the equation

$$\Delta G(T,X) = G^{Liq}(T,X) - G^{ODIC}(T,X) = 0 \qquad (5)$$

In other words, at the EGC, which is a curve in the phase diagram running between the solidus and the liquidus curves, solid and liquid mixtures of the same composition have equal Gibbs energies. From eq 5, it is easy to prove that the temperature of the EGC, T_{EGC}, as a function of X, can be given by the (implicit) relation

$$T_{EGC}(X) = \frac{\Delta H^*(X)}{\Delta S^*(X)} - \frac{G^{E,ODIC}(T = T_{EGC},X)}{\Delta S^*(X)} \qquad (6)$$

where $\Delta H^*(X)$ and $\Delta S^*(X)$ are short notations for $\{(1 - X)\ \Delta H^*_A + X\ \Delta H^*_B\}$ and $\{(1 - X)\Delta S^*_A + X\Delta S^*_B\}$, respectively. The ratio $\Delta H^*(X)/\Delta S^*(X)$ is called T_{ZERO} (it represents, more or less, the straight line between the melting points of the pure components and may be denoted by ZERO line). In practice, the Gibbs function is calculated by means of the computer program LIQFIT[21] or its version for Windows which is named WINIFIT:[22] an iterative procedure of phase diagram computations, of which the output is the optimized phase diagram together with the excess Gibbs energy of the solid-state along the EGC.

The output of the thermochemical research and phase diagram assessments is given in Table 1 for the equimolar compositions of the systems studied. It must be emphasized that the numerical data given are calculated values provided by the statistical procedures. The thermochemical data have been verified and completed by isothermal X-ray diffraction as a function of composition. In all cases the existence of a continuous series of ODIC mixed crystals was confirmed.[13]

The cubic lattice parameter a has been determined as a function of composition, and the data were used to calculate the equimolar excess volumes and packing coefficients ξ (the ratio of the volume of one molecule and the volume of the material per molecule). The relevant data to the present paper are given in Table 2.

III. Results and Discussion

A. Correlation of Excess Properties. From eqs 3 and 4 it follows that for an individual system, the value of the constant θ is obtained as the quotient of the

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(20) Oonk, H. A. J. *Phase Theory, The Thermodynamics of Heterogeneous Equilibria*; Elsevier: Amsterdam, 1981.

(21) Jacobs, M. H. G.; Oonk, H. A. J. *LIQFIT*. A Computer Program for the Thermodynamic Assessment of T−X Liquidus or Solidus data. Utrecht University, 1990.

(22) López, R.; López, D. O. *WINIFIT*. A Windows Computer Program for the Thermodynamic Assessment of T−X Phase Diagrams using the C.I.C. (Crossed Isopolymorphism Concept). Polythecnic University of Catalonia, 1998.

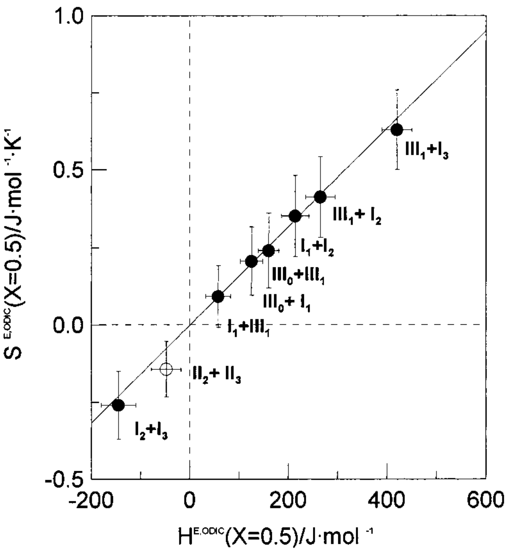

Figure 1. For the binary systems between neopentane derivatives, equimolar excess entropy versus equimolar excess enthalpy. Filled circles indicate the C_F systems; empty circle, the C_I system $II_2 + II_3$.

equimolar excess enthalpy and excess entropy. The individual values, which are shown in the last column of Table 1, are in the vicinity of 600 K, with the exception of the value obtained for the C_I system. In Figure 1 the excess enthalpy and the excess entropy values are plotted against one another. Despite the experimental uncertainties, see Table 1, we conclude that the seven C_F systems are characterized by a uniform compensation temperature (θ) of 630 ± 30 K.

In this respect, the plastic crystalline neopentane derivatives show a behavior that has been observed earlier for mixed crystals of alkali halides[23] (NaCl structure, $\theta = 2565$ K), of *p*-dihalobenzenes[18,19] (monoclinic, $\theta = 500$ K), and of *n*-alkanes[16,17] (form rotator I, $\theta = 320$ K). From these data and data on isolated systems (such as argon + krypton,[24] $\theta = 190$ K, and MgO + CaO,[25] $\theta = 6650$ K) it can be inferred that the compensation temperature is, generally, above the melting temperature. This general observation that the compensation temperature is above the melting temperature is accentuated in Figure 2 by the division into an *ordinary region* (compensation temperature above melting temperature seems to be a common fact) and an *extraordinary region* (melting temperature above compensation temperature is a less-common fact but possible). The empirical observations can be put in the following expression

$$\frac{\log \theta}{\log[T_{EGC}(X = 0.5)]} = 1.10 \pm 0.05 \qquad (7)$$

For the seven C_F systems this relationship is well respected; the mean of the quotient of logarithms is 1.09. The conclusion, therefore, is justified that, despite the small values of the excess properties and their relatively large experimental uncertainties, the set of C_F data is internally consistent, and in line with the properties displayed by other (groups of) mixed crystalline materials.[16,17,24−31]

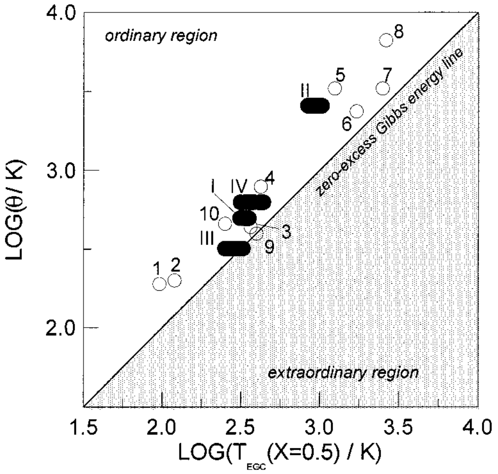

Figure 2. log−log representation of compensation temperature (θ) versus equimolar EGC temperature ($T_{EGC}(X = 0.5)$) for a given system or family. Empty circles are isolated systems: 1, Ar + Kr (24); 2, Kr + Xe (24); 3, *d*-carvoxime + *l*-carvoxime (26); 4, 1,2,4,5-tetrachlorobenzene+1,2,4,5-tetrabromobenzene (27); 5, Ni + Au (28); 6, Pd + Au (29); 7, SrO + BaO (25); 8, MgO + CaO (25); 9, $CBr_4 + C_2Cl_6$ (30); 10, $CCl_4 + C(CH_3)_4$ (31). Shadow marks: I, *p*-dihalobenzene family (18,19); II, common ion alkali halide family (23); III, *n*-alkane family (16,17); IV, the class of neopentane derivatives.

From a phenomenological point of view and by analogy with the proportionality of excess enthalpy and excess entropy, it is interesting to examine if there is such a relationship between excess enthalpy and excess volume. If that would be the case, one could speak of a characteristic pressure for the group of systems: a pressure at which H^E and V^E “compensate” for one another, such that the excess internal energy (U^E) changes sign, as $U^E = H^E - pV^E$. From the experimental evidence, displayed in Figure 3, taking into account the large experimental uncertainties, we tend to conclude that the C_F systems are characterized by a compensation pressure of the order of 0.5 GPa.

B. Substance-Dependent Properties. To begin with, we consider the melting characteristics of substances and binary systems pertaining to series I. From the pure-substance data in Table 1, it clearly follows that the melting temperatures and heats of melting are substance-dependent properties. The entropies of melting, on the other hand, change but slightly from substance to substance: on the average they are about 1.25*R*—a value which is typical for the entropy of melting of metals.

A revealing figure, Figure 4, is obtained when the melting temperatures of the pure substances and the

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(23) Van der Kemp, W. J. M.; Blok, J. G.; Van Genderen, A. C. G.; Van Ekeren, P. J.; Oonk, H. A. J. *Thermochim. Acta* **1992**, *196*, 301.

(24) Walling, J. F.; Halsey, G. D. *J. Phys. Chem.* **1958**, *62*, 756.

(25) Van der Kemp, W. J. M.; Blok, J. G.; Van der Linde, P. R.; Oonk, H. A. J.; Schuijff, A.; Verdonk, M. L. *Calphad* **1994**, *18*, 225.

(26) Calvet, M. T.; Oonk, H. A. J. *Calphad* **1995**, *19*, 49.

(27) Van Genderen, M. J.; Mondieig, D.; Haget, Y.; Cuevas-Diarte, M. A.; Oonk, H. A. J. *Calphad* **1992**, *16*, 301.

(28) Sellers, C. M.; Maak, F. *Trans. Metall. Soc. AIME* **1966**, *236*, 457.

(29) Okamoto, H.; Massalsky, T. B. *Bull. Alloy Phase Diagrams* **1985**, *6*, 229.

(30) Van Braak, J.; López, D. O.; Salud, J.; Tamarit, J. Ll.; Jacobs, M. H. G.; Oonk, H. A. J. *J. Cryst. Growth* **1997**, *180*, 315.

(31) Salud, J.; López, D. O.; Van Braak, J.; Barrio, M.; Jacobs, M. H. G.; Tamarit, J. Ll.; Oonk, H. A. J. *XXIV Jounées des Equilibres entre Phases*; Kuhnast, F. A., Kuntz, J. J., Eds.; 1998; Nancy, France, p 261.

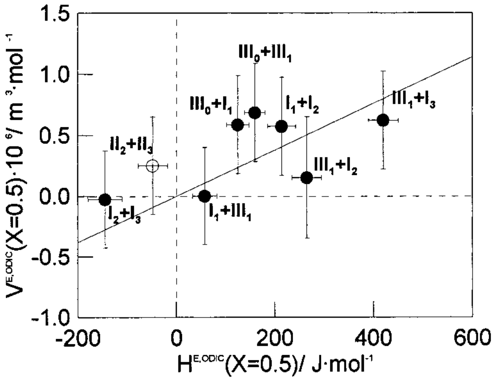

Figure 3. For the binary systems between neopentane derivatives, equimolar excess volume versus equimolar excess enthalpy.

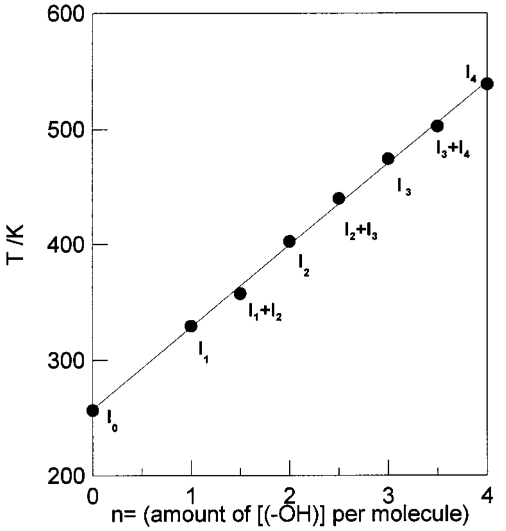

Figure 4. For pure substances in the series **I** ($(CH_3)_{4-n}C(CH_2OH)_n$), and equimolar mixtures, (mean) melting temperatures as a function of the (mean) value of number of −OH groups per molecule.

equimolar EGC temperatures (say about the mean temperature of the melting range) are plotted against the (mean) number of −OH groups per molecule. The figure includes I_0 which is neopentane and whose melting point (in the C_F form) is 256.8 K. Going from I_0, via I_1, I_2, and I_3, to I_4, the melting temperature is more than doubled, the change per extra −OH group being about 70 K (the corresponding change in heat of melting is about 0.5 kJ mol^{-1}). The EGC temperatures of the equimolar mixtures are in almost perfect line with the melting temperatures of the pure substances. It means that the formers are close to the corresponding ZERO lines, or, in other words and in agreement with the data in Table 1, that the excess Gibbs energies are small.

It clearly follows from Figure 4 that the (mean) number *n* of −OH groups per molecule is the leading parameter for indicating the melting temperature. A linear fit of the points in the figure gives the relationship

$$T/\mathrm{K} = 257.6 + 71.0n \qquad (8)$$

with a mean absolute deviation of the individual points of 3.25 K (which is but 1.3% of the temperature range for which the equation is valid). In a simplistic manner, one may add that the mean temperature of the melting range of a sample composed of I_0, I_1, I_2, I_3, and I_4 in arbitrary proportions but with given mean number of −OH groups per molecule is approximated by eq 8—provided that the ODIC + liquid equilibrium is not overruled by another one.

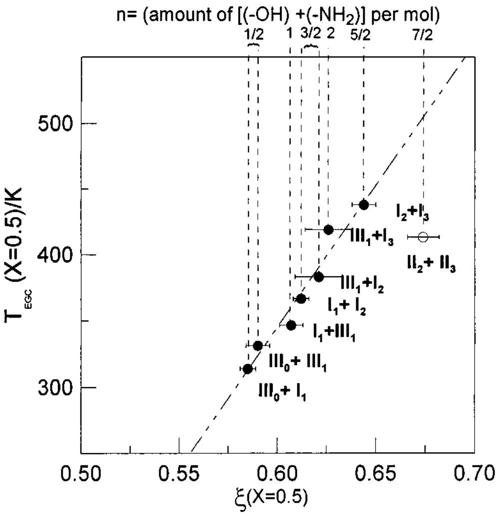

Figure 5. For binary systems between neopentane derivatives, the temperature at which equimolar ODIC and liquid mixtures have equal Gibbs energy ($T_{EGC}(X = 0.5)$) as a function of $\xi(X = 0.5)$.

With regard to the series of substances II and III, for each of the two there are just three data points, and they pertain to the systems $II_2 + II_3$ and $III_0 + III_1$, respectively. In both cases the three points show a behavior more or less parallel to the behavior shown by the points in Figure 4.

Another system-dependent property, which is clearly related to the number of −OH groups, is the packing coefficient. Just like the melting temperatures, the packing coefficient increases—the ODIC state becomes more compact—with increasing *n*—the mean number of −OH groups and $-NH_2$ groups per molecule. The fact that melting temperature and packing coefficient have the same origin is clearly demonstrated by Figure 5, where the two properties are plotted against one another.

C. Excess Properties and Mismatch. At this point we know that the C_F systems can be regarded as a set of similar systems in terms of enthalpy−entropy compensation (and that there is not enough reason to include the C_I one). Let us now suppose that we are asked to predict in an accurate manner (i.e., better than the approximation that can be made on the basis of eq 8) the solid−liquid phase diagrams of the remaining systems shared by substances I_1, I_2, I_3, I_4, III_0, and III_1.

To carry out such predictions it is necessary to have a recipe for the excess enthalpies of the binary systems (the excess entropy and the excess Gibbs energy are then also known via the compensation temperature). In comparable studies, such a recipe is constructed by considering the relation between excess enthalpy and a certain mismatch parameter. For a given binary system, a mismatch parameter is, for a certain property, the relative difference between the values shown by the two pure components of the system. As a rule, the mismatch parameter has a geometric nature, such as $\Delta V/\bar{V}$ (difference in molar volume divided by mean molar

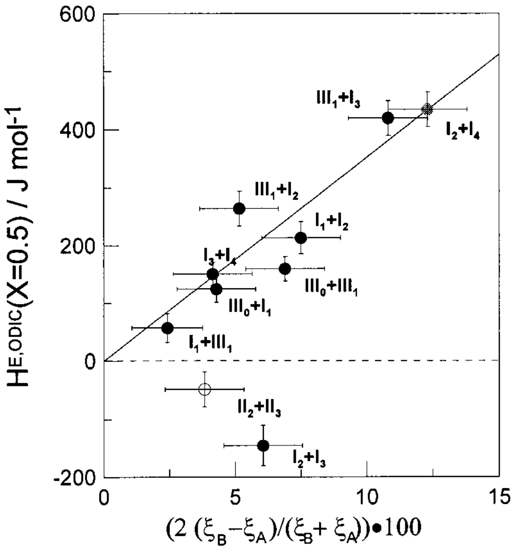

Figure 6. For the equimolar mixed plastic crystals having C_F structure, the excess equimolar enthalpy plotted against the packing mismatch parameter, defined by eq 9. The figure also includes system $I_2 + I_4$ (●), for which excess enthalpy has been calculated by means of eq 10, in which *m* parameter has been obtained from packing coefficients of I_2 and I_4 given in Table 2.

volume, and used for alkali-halide systems[23]), or $\Delta n/\bar{n}$ (relative difference in chain length, used for *n*-alkane systems[16,17]). For the underlying systems, mismatch in terms of volume, or a related property, is not a good choice: the variation in molar volume is just a few percent.

As a matter of fact, the most discriminating parameter of the underlying substances is the number *n* of hydroxyl groups—as expressed by melting temperature and packing coefficient; see above. A logical choice of mismatch parameter *m*, therefore, is the following one, based on packing coefficient ξ:

$$m = \frac{2(\xi_B - \xi_A)}{\xi_A + \xi_B} \quad \text{with } \xi_B > \xi_A \tag{9}$$

In Figure 6 the equimolar excess enthalpies of the individual systems are plotted against their mismatch parameters. Before addressing the question, whether the evidence displayed in Figure 6 will be a suitable basis for making predictions, we will make some observations. From the point of view of hydrogen bonding, the substituents $-CH_3$ and $-NO_2$ have a minor influence and it would mean that (i) the binary systems $I_n + III_n$ should not show large excess properties, and (ii) the excess properties of the systems I_n + B and III_n+ B should be more or less the same. Indeed, these demands are respected: (i) the system $I_1 + III_1$ shows the smallest deviation from ideal mixing behavior, and (ii) the behavior of $I_1 + I_2$ and $III_1 + I_2$, and that of $I_1 + III_0$ and $III_1 + III_0$ are very much alike. In addition, for the three systems having III_1 as a common component, there is a regular sequence: in order of increasing excess enthalpy $(III_1 + I_1) \rightarrow (III_1 + I_2) \rightarrow (III_1 + I_3)$.

Despite these observations, it follows from Figure 6 that the complete group of mixed ODICs does not correspond to a unique family of mixed crystals. In particular the systems $II_2 + II_3$ and $I_2 + I_3$ are deviating. In the case of the former of these systems, the deviating position could be the result of its form (C_I).

The remaining seven C_F systems of the group show a more or less common trend; the trend which is represented by the straight line

$$H^E(X = 0.5) = \{3526\ \mathrm{m}\}\ \mathrm{J\ mol^{-1}} \tag{10}$$

The relationship (eq 10) is such that the positive excess property (caused by a "repulsive" effect between the molecules of the substances A and B: attraction between A and B is smaller than the mean of attractions between A and A and B and B) increases with increasing value of the mismatch parameter. It is the kind of behavior found for families of systems of which the components belong to a chemically coherent group of substances (alkali-halides, *n*-alkanes). Supposing that the relationship between H^E and mismatch parameter makes sense, then in the case of $I_2 + I_3$ there must be an effect of an attractive nature that overcompensates the repulsive effect due to mismatch (in this respect, $I_2 + I_3$ would resemble 2-methylnaphthalene + 2-chloronaphthalene and 2-methyl naphthalene + 2-bromonaphthalene,[32] with the difference, however, that for $I_2 + I_3$ any additional evidence is lacking).

As a result, therefore, we have to conclude that (even) the group of C_F systems does not reveal a unique behavior—such that the excess properties unambiguously can be predicted in terms of a mismatch parameter.

D. The System $I_2 + I_4$. To end with and to assist the reader in his/her judgment of the significance of the results disclosed in this paper, we consider the system $I_2 + I_4$, of which we determined the TX phase diagram.[33] The experimental data reveal the existence of one peritectic and one metatectic three-phase equilibrium (caused by the interference of the (C_F + liquid) equilibrium and the (C_F + Q) equilibrium), the temperatures of which are at about 430 K and about 425 K, respectively. In Figure 7, two calculated phase diagrams are shown. The diagram displayed in Figure 7a corresponds to ideal-mixing behavior—not only in the liquid, but also in the plastic crystalline state (let us say with the mean melting temperature provided by eq 8). In the case of Figure 7a, the two equilibria between two phases do not interfere. The diagram shown by the Figure 7b was calculated with the same input as for the other diagram (Figure 7a), with the exception of the excess Gibbs energy of the mixed ODIC state, for which we took

$$G^{E,ODIC}(T,X) = 1740\left(1 - \frac{T}{630\ \mathrm{K}}\right)X(1 - X)\ \mathrm{J\ mol^{-1}} \tag{11}$$

This expression satisfies the compensation temperature of 630 K and its numerical value of 1740 J mol^{-1} is based on eq 10. The mismatch parameter of the system $I_2 + I_4$ is $m = (12.3 \pm 1.5) \times 10^{-2}$, so that from eq 10 the equimolar excess enthalpy is calculated as 435 J mol^{-1} and four times this value is 1740 J mol^{-1}.

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[32] Calvet, T.; Cuevas-Diarte, M. A.; Haget, Y.; Mondieig, D.; Kok, I. C.; Verdonk, M. L.; Van Miltenburg, J. C.; Oonk, H. A. J. *J. Chem. Phys.* **1999**, *110* (10), 4841.

[33] López, D. O. Ph.D. Thesis, Autonomous University of Barcelona, 1990.

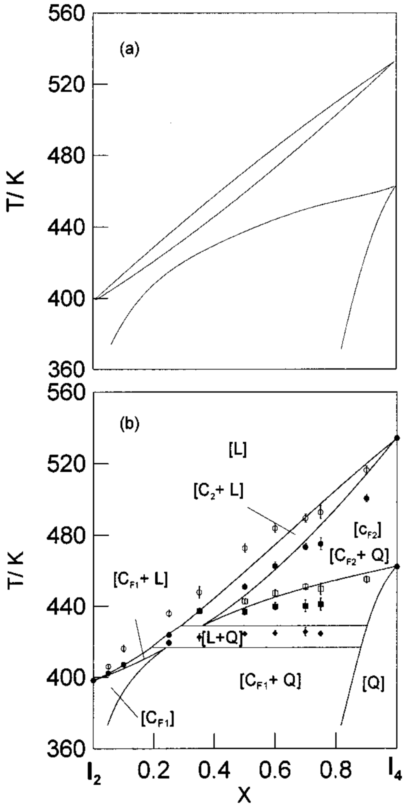

Figure 7. The system $I_2 + I_4$: (a) calculated phase diagram for ideal behavior in liquid and plastic crystalline state; and (b) calculated phase diagram and experimental data. Calculations are based on eq 12 for the plastic crystalline state. Experimental data: ○ liquidus temperature; ● solidus temperature; □ temperature at the two phase equilibria curve; ■ metatectic temperature; ♦ peritectic temperature.

This time, i.e., with eq 11, the calculated phase diagram is in agreement with the experimental data to the extent that not only the individual data points, but also the two three-phase equilibria are well reproduced.

IV. Conclusions

In the mixed plastic crystalline state, the binary systems of neopentane derivatives studied show relatively small deviations from ideal mixing behavior. The search for a uniform thermodynamic description has resulted in the following characteristics:

- The group of systems of which the components fall in series I [$(CH_3)_{4-n}C(CH_2OH)_n$] and series III [$NO_2(CH_3)_{3-n}C(CH_2OH)_n$] and crystallizing in the form C_F constitute a class of similar systems in terms of excess enthalpy—excess entropy compensation, its characteristic temperature being about 630 K.

Accordingly, the excess Gibbs energies of the nine C_F systems are given by

$$G^E(T,X) = A\left(1 - \frac{T}{630\ \mathrm{K}}\right)X(1 - X)[1 + B(1 - 2X)] \quad (12)$$

where A is a system-dependent constant (the influence of the "asymmetry parameter" B is negligible for the present systems).

- There is evidence that another system-independent property is found in the quotient of excess enthalpy and excess volume. This property with dimension of pressure, has a value of about 0.5 GPa.
- The upper limit on the temperature scale of the region of existence of the plastic crystalline state is largely determined by the value of n, the number of substituted −OH groups in the molecules. In a first approximation, this limit—for pure substances and mixtures in series **I**—is given by eq 8.

For a fine-tuning of the temperature limit, it is necessary to have a recipe for the system-dependent constant A in eq 12. In a tentative way, a recipe is proposed in terms of a mismatch parameter based on packing coefficients, eqs 9 and 10.

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