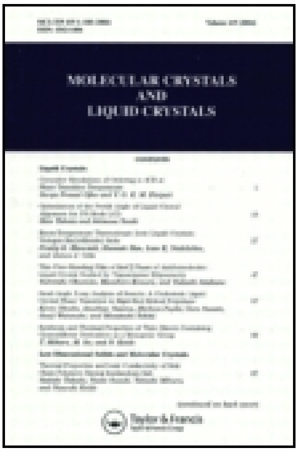

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Binary Mixtures of n-Alkanes. Phase Diagram Generalization: Intermediate Solid Solutions, Rotator Phases

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Binary Mixtures of n-Alkanes. Phase Diagram Generalization: Intermediate Solid Solutions, Rotator Phases

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At "low temperatures", the binary mixtures of the consecutive [even-numbered: even-numbered]; [even-numbered: odd-numbered] and [odd-numbered: odd-numbered] *n*-alkanes ($19 < n < 27$) do not form a continuous homogeneous solid solution. This study shows the existence of terminal solid solutions which have the pure *n*-alkanes structures and many intermediate solid solutions, denoted β'_n and β''_n ($n = 1$ or 2): these intermediate phases have an orthorhombic cell as the odd-numbered *n*-alkanes, but they are not isostructural with the pure *n*-alkanes nor with their terminal solid solutions. On the basis of powder X-ray diffraction photographs, the phases β'_1 and β'_2 are indistinguishable in all the binary systems. The X-ray behavior of the phases β''_n is also identical. The succession of the solid solutions is described when varying the concentration. With increasing temperature, the intermediate phases undergo the same solid-solid transitions as the odd-numbered *n*-alkanes (*n*-tricosane), and the rotator phases appear at "high temperatures" below the solidus line. The phase diagrams of n–C_{22}: n–C_{23}, n–C_{23}: n–C_{24}, n–C_{22}: n–C_{24} and n–C_{24}: n–C_{26} are presented.

Keywords: Alkanes, binary mixtures, phase diagrams, phase transitions, solid phase sequence rules, rotator

1. INTRODUCTION

In our laboratory, we are currently pursuing joint studies of calorimetry and X-ray diffraction on the liquid-solid and solid-solid equilibria occuring in the pure *n*-alkanes[1–3] and in binary mixtures of consecutive [even-numbered: even-numbered], [even-numbered: odd-numbered] *n*-alkanes (here after denoted by C_n).[4–9] Recently Jouti *et al.*[10] have measured certain properties of [odd-numbered: odd-numbered] C_n [C_{23}:C_{25}]. We aime to determine their behavior when varying the molar concentration and temperature. For simplify odd-numbered and even-numbered will be called odd and even. Achour *et al.*[6–8] and Sabour *et al.*[9–10] have established the phase diagrams of the binary systems (Fig. 1): [C_{22}:C_{24}];[6-7] [C_{24}:C_{26}];[8] [C_{23}:C_{24}][9] and [C_{22}:C_{23}] (11) and Jouti *et al.* (10) have determined the structural behavior of [C_{23}:C_{25}] mixtures at "low temperature". In spite of what is generally found in the literature[12-25] two consecutive [even: even] or [odd: odd] C_n do not form a continuous homogeneous solid solution at "low temperatures". For instance, many phase diagrams of the type [even: even][12,14] have been presented with an orthorhombic continuous solid solution S_β even if the two pure compounds are triclinic or monoclinic, this is not compatible with Palatnik and Landau's rule[26] on the adjacent phase domains.

Our studies[6,6-11] show (Fig. 1) the existence of limited terminal solid solutions, which have the structures of the pure C_n, and many orthorhombic intermediate phases, whose structures are similar to those of odd C_n.

In 1957, Smith[27] was the first to highlight two orthorhombic intermediate phases in the [C_{24}: C_{26}] binary mixtures of 1:1 and 2:1 stoichiometry respectively. More recently, the structure of one of these two phases was determined by Gerson and Nyburg.[28] In 1972, H. Luth *et al.*[29] published the [C_{20}: C_{22}] phase diagram with three orthorhombic intermediate solid solutions. In 1993, Achour *et al.*[8] showed the similarity between this system and both of the [C_{22}: C_{24}] and [C_{24}: C_{26}] systems that we have studied, except for the "high temperature" domain just below the solidus line. With increasing temperature, the orthorhombic intermediate phases undergo the same solid-solid transitions as those observed in the odd pure C_n[5-9] (C_{23} or C_{25}, for example) from the solid phase, appearing above the transition δ,[30] to the melting point:[31-45]

←"LOW TEMPERATURE" | "HIGH TEMPERATURE"→

$$\beta_0(C_{23} \text{ or } C_{25}) \text{ ——transition } \delta \rightarrow \beta'_0 \rightarrow \beta-\text{RI} \rightarrow \alpha-\text{RII} \rightarrow \text{LIQUID}$$

Notations

- Crystal phases at "low temperature"

β_0: orthorhombic phase with the space group Pbcm.[46]
β'_0: orthorhombic phase which appears above the transition δ.[21,30]

- Plastic or Rotator phases of "high temperature"

β-RI: orthorhombic Rotator phase with the space group Fmmm.[20,35]
α-RII: rhombohedral Rotator phase: space group R$\bar{3}$m.[20,35]
A new Rotator phase RV has been highlighted by SIROTA *et al.*[45] in C_n ($20 < n < 33$).

Our purpose is to show the structural identity between the orthorhombic intermediate phases in the binary systems ([even: even]; [odd: even]; [odd: odd]) and thus corresponding to generalize the thermodynamic and structural behaviors of these mixtures.

2. EXPERIMENTAL METHOD

The *n*-alkanes were purchased from ALDRICH Chemical Company: their purity grade is 99 mole per cent for the even C_n (hereafter denoted by C_{2p}) and over 99 mole per cent for the odd C_n (hereafter called C_{2p+1}) as determined by gas chromatography and mass spctrometry analysis. Mixtures were prepared by weighing together the solid components, melting then thorough mixing. The homogeneous liquid solution thus obtained was quenched in a crystallizing dish maintained at a very low temperature in a Dewar vessel with liquid air. Such rapid cooling ensured a uniform steric concentration of each component in the solid state.

The X-ray diffraction experiments were carried out on powder samples with a Guinier De Wolff Nonius camera, using a focussed monochromatic beam (λCu Kα). The calibration was obtained with spectroscopic pure gold as standard. The line positions were determined with an accuracy of 0.25 millimeter for distances ranging from 10.5 to 125 millimeters.

The phase diagrams (Fig. 1) have been determined by combined thermodynamic and structural studies which have been described earlier.[4-10] For our measurements, the powder photograph method seemed more appropriate than the X-ray diffractometer charts to show the evolution of the reflection lines as a function of the mixture composition at a temperature of 293 K. With increasing temperature, we used both X-ray diffraction and differential thermal analysis (D.T.A.) to determine the phase changes in the binary systems. The D.T.A. analysis showed solid-solid transitions and melting temperatures and indicated the temperature ranges of the transformations. These ranges were explored by X-ray diffraction analysis. The X-ray diffractometer (C.G.R. theta 60) analyses were performed at different temperatures by means of a heated sample holder. Heating of the samples is based on the Peltier effect, with a precision of the sample temperature within ± 0.2 K around the set point. These X-ray diffraction experiments have been realized with increasing temperature at equilibrium state. The differential thermal analyses were performed using a SETARAM DSC 111 calorimeter. The samples were heated from 281 K to just above the liquidus point at a rate of $0.5\,\mathrm{K \cdot mn^{-1}}$.

3. STRUCTURAL BEHAVIOR OF THE BINARY MIXTURES AT "LOW TEMPERATURES"

The phase diagrams (Fig. 1), the observations of Smith,[27] Gerson and Nyburg,[28] Luth *et al.*[29] and our X-ray patterns (Fig. 2) allow us to describe the sequence of the solid phases, observed or predicted when the concentrations vary at "low temperatures", in the binary mixtures of the consecutif [even: even], [even: odd] and [odd: odd] C_n (Fig. 3).

3.1 Terminal Solid Solutions

The limited terminal solid solutions have the structures of the pure C_n, denoted γ_0 for the triclinic even C_{2p} and β_0 for the orthorhombic odd C_{2p+1}. The terminal solid solution range of the short chain in the long C_n structure is larger than the solubility domain of the long chain C_n in the short $C_{n'}$ ($n' < n$): the structural disorder is more

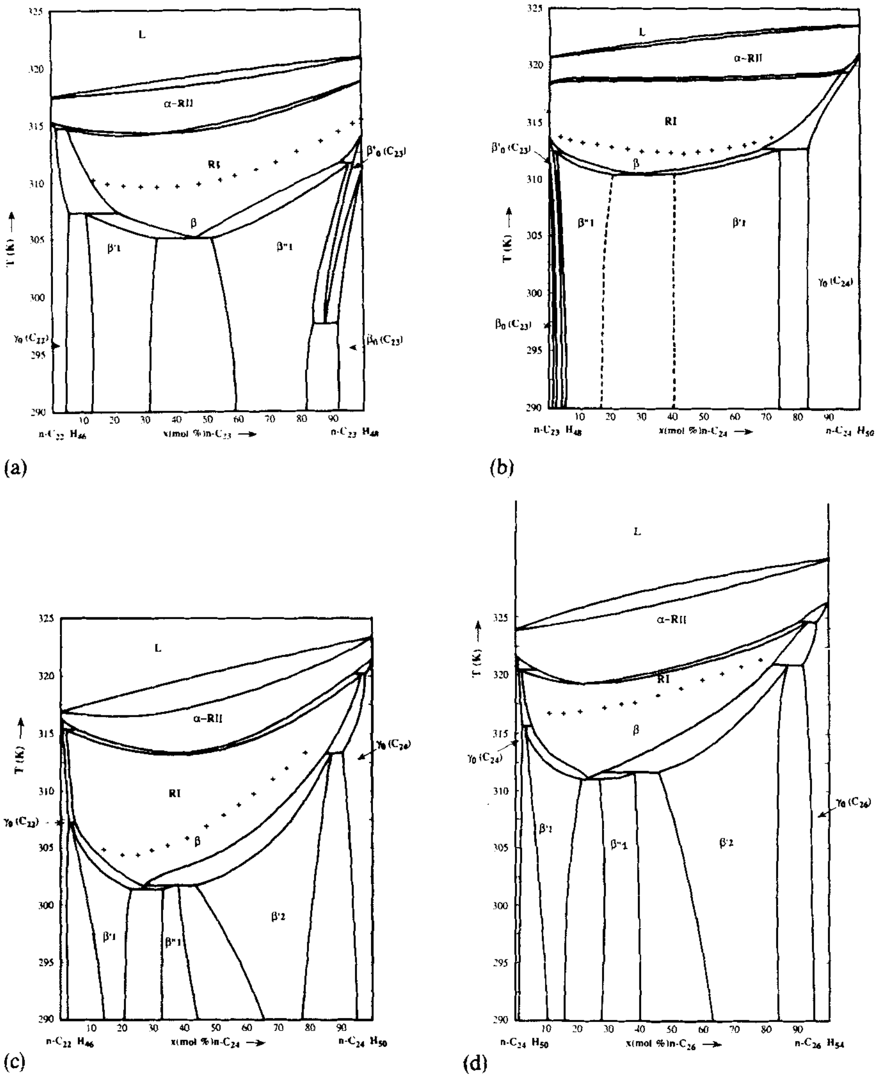
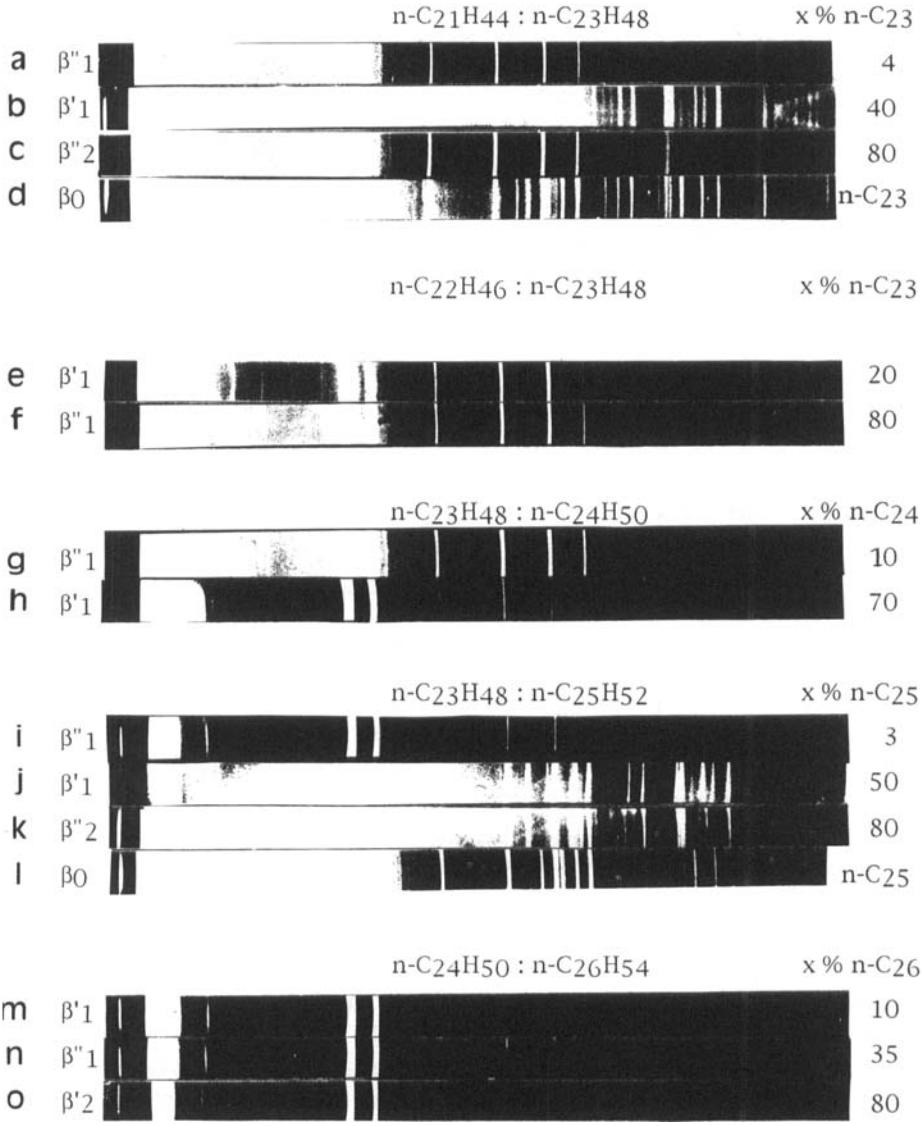


FIGURE 1 Phase diagrams of consecutive [even: odd] (a), [odd: even] (b) and [even: even] (c & d) *n*-alkanes, The + + + line between β and α-RII indicates the beginning of the second-order transition which affects the parameters *a* and *b* of the phase β; the other lines show the equilibria boundaries between the single-phase and two-phase domains according the Palatnik and Landau's rule (26).

important in the last case (Fig. 1). For instance, C_{24} is soluble into the triclinic structure γ_0 (C_{22}) upto 2.5% molar of C_{24} and C_{22} into the triclinic structure γ_0 (C_{24}) up to 5% molar of C_{22} (Fig. 1.c); the behavior is identical with the other systems (Figs. 1.a, 1.b, 1.d) and with the system [C_{23}: C_{25}] which has been recently studied by Jouti *et al.*.[10] Moreover the solubity range into the structure of a same C_n decreases with increasing the carbon number of the solute, for example: C_{23} and C_{24} are soluble respectively up to 5 molar % of C_{23} and 2.5 molar % of C_{24} into the terminal solid solution γ_0 (C_{22}) (Figs. 1.a & 1.c); it is same for the solubility of C_{22} and C_{24} into β_0 (C_{23}) (Figs. 1.a & 1.b).



FIGRE 2 Powder X-ray diffraction patterns (λ Cu Kα) of orthorhombic intermediate phases with GUINIER-de WOLFF camera. x = molar percent. i) the X-ray pictures of the intermediate phases, denoted β'_n ar indistinguishable (b, e, h, j, m, o) in all these binary systems. ii) it is same for the phases called β''_n (a, c, f, g, i, k, n).

The terminal solid solutions β'_0 of the [odd: even] and [odd: odd] C_n mixtures (Figs. 1.a, 1.b) have the structure β'_0 of the pure odd C_{2p+1} (for instance C_{23} and C_{25}) which appears above the transitions δ with increasing temperature:[30] an increase in the disorder of the crystallographic structure of the odd C_{2p+1} is induced by a few percent of an other (odd or even) C_n which can therefore be said to have the same effect as temperature.

TERMINAL SOLID SOLUTIONS	INTERMEDIATE SOLID SOLUTIONS	TERMINAL SOLID SOLUTIONS
	TWO EVEN-NUMBERED N-ALKANES	
$\gamma_0\,(C_{2p})$ $n\text{-}C_{2p}H_{4p+2}$	…./ β'_1 /…./ β''_1 /…./ β'_2 /…./ $\xrightarrow{\quad\quad}$ $x\ (n\text{-}C_{2p+2})$	$\gamma_0\,(C_{2p+2})$ $n\text{-}C_{2p+2}H_{4p+6}$
	EVEN-NUMBERED AND ODD-NUMBERED N-ALKANES	
$\gamma_0\,(C_{2p})$ $n\text{-}C_{2p}H_{4p+2}$	…./ β'_1 /…./ β''_1 /…./ $\xrightarrow{\quad\quad}$ $x\ (n\text{-}C_{2p+1})$	$\beta'_0(C_{2p+1})$/…./$\beta_0\,(C_{2p+1})$ $n\text{-}C_{2p+1}H_{4p+4}$
$\beta_0(C_{2p-1})$/…./$\beta'_0(C_{2p-1})$ $n\text{-}C_{2p-1}H_{4p}$	…./ β''_1 /…./ β'_1 /…./ $\xrightarrow{\quad\quad}$ $x\ (n\text{-}C_{2p})$	$\gamma_0\,(C_{2p})$ $n\text{-}C_{2p}H_{4p+2}$
	TWO ODD-NUMBERED N-ALKANES	
$\beta_0(C_{2p-1})$/…./$\beta'_0(C_{2p-1})$ $n\text{-}C_{2p-1}H_{4p}$	…./ β''_1 /…./ β'_1 /…./ β''_2 /…./ $\xrightarrow{\quad\quad}$ $x\ (n\text{-}C_{2p+1})$	$\beta'_0(C_{2p+1})$/…./$\beta_0\,(C_{2p+1})$ $n\text{-}C_{2p+1}H_{4p+4}$
	FOR INSTANCE	
$n\text{-}C_{22}H_{46}$	../ β'_1 /../ β''_1 /../ β'_2 /../	$n\text{-}C_{24}H_{50}$
$n\text{-}C_{22}H_{46}$	../ β'_1 /../ β''_1 /../	$n\text{-}C_{23}H_{48}$
$n\text{-}C_{23}H_{48}$	../ β''_1 /../ β'_1 /../	$n\text{-}C_{24}H_{50}$
$n\text{-}C_{23}H_{48}$	../ β''_1 /../ β'_1 /../ β''_2 /../	$n\text{-}C_{25}H_{52}$
	$\xrightarrow{\quad x \quad}$	

FIGURE 3 Sequences of the solid solution domains versus the concentration of the longer n-alkane in the binary systems of consecutive [even: even], [even: odd] and [odd: odd] alkanes at "low temperatures". /···/ two-phase regions.

With increasing temperature, the solid-solid transition (for instance $\beta_0(C_{23}) \rightarrow \beta'_0(C_{23})$) is accompanied by a small enthalpy effect[9] and the following evolutions of X-ray diffractions:[9,10] the lines $d = 0.229$ nm (1 0 24), 0.1765 nm (2 1 23) of the phase β_0 disappear, the lines $d = 0.237$ nm, 0.1675 nm appear and the intensity of the BRAGG diffraction $d = 0.221$ nm (1 3 0) increases. The same structural evolutions have been observed in the binary systems [C_{23}: C_{24}],[9] [C_{23}: C_{25}][10] and [C_{23}: C_{22}][11] at 293 K with increasing solute concentration into the pure C_{23}. However in the binary systems, this phase β'_0 is not always detected, because it may undergo an eutectoïd transition ($\beta'_0 \leftrightarrow \beta_0 + \beta''_n$) above the room temperature as observed by Sabour[9] (Fig. 1.a) and also by Jouti *et al.*.[10]

3.2 Intermediate Solid Solutions

Earlier[4,7,9,10] we have observed the structural behaviors of these binary mixtures versus concentration at 293 K and we have already described the differences between the X-ray diffraction patterns of all the phases.[4–10]

The intermediate solid solutions have always the orthorhombic cell analogous to that of the odd C_{2p+1} (Figs. 2.d & 2.1) and denoted β'_n or β''_n with an index n ($n = 1$ or 2) to identify isostructural phases of different stoichiometries in one binary system. Nevertheless these intermediate phases are not isostructural with the orthorhombic terminal solid solutions $\beta_0(C_{2p+1})$ or $\beta'_0(C_{2p+1})$.

We measured the unit cell parameters. They are listed in Table I and compared with those of three odd pure C_{2p+1}:[47] C_{21}, C_{23}, C_{25}.

Remark: The structure of one of these intermediate phases was determined by Luth *et al.*[29] ($Bb2_1m$, Bb2b, Bbm2 or Bba2) in the [C_{20}: C_{22}] system and by Gerson and Nyburg[28] in the [C_{24}: C_{26}] system ($Bb2_1m$). But the composition that they have studied (0.25 of n-$C_{22}H_{46}$[29] and 0.23 of n-$C_{26}H_{54}$)[28] correspond both to the middle of two-phase regions $\beta'_1 + \beta''_1$ (Fig. 1.d and (29)).

3.3 A Generalization of Structural and Thermodynamic Behaviors of Consecutive C_n Binary Mixtures at "Low Temperature"

On the basis of powder X-ray diffraction photographs (Fig. 2; Table I), the following results are established:

TABLE I

Crystalline parameters of the orthorhombic intermediate phases and three odd-numbered pure n-alkanes (n-C_{21}; n-C_{23}; n-C_{25})

	Phase	x (mol.%)	a (nm)	b (nm)	c (nm)
n-$C_{21}H_{44}$	$\beta_0(n\text{-}C_{21})$	*	0.497	0.7463	5.7089
			0.497	0.746	5.717
n-$C_{21}H_{44}$: n-$C_{23}H_{48}$	β''_1	4	0.497	0.746	5.806
	β'_1	30	0.497	0.746	5.981
	β''_2	80	0.496	0.745	6.186
n-$C_{23}H_{48}$	$\beta_0(n\text{-}C_{23})$	*	0.4968	0.7441	6.237
			0.494	0.745	6.23
n-$C_{22}H_{46}$: n-$C_{23}H_{48}$	β'_1	20	0.496	0.742	6.08
	β''_1	80	0.496	0.743	6.213
n-$C_{22}H_{46}$: n-$C_{24}H_{48}$	β'_1	18	0.499	0.748	6.112
	β''_1	40	0.499	0.748	6.27
	β'_2	67.5	0.499	0.748	6.42
n-$C_{23}H_{48}$: n-$C_{24}H_{50}$	β''_1	10	0.496	0.745	6.3
	β'_1	60	0.497	0.746	6.39
n-$C_{23}H_{48}$: n-$C_{25}H_{52}$	β''_1	3	0.494	0.745	6.288
	β'_1	30	0.495	0.745	6.484
		50	0.495	0.745	6.656
	β''_2	80	0.495	0.745	6.712
n-$C_{25}H_{52}$	$\beta_0(n\text{-}C_{25})$	*	0.496	0.744	6.724
			0.496	0.745	6.75
n-$C_{24}H_{50}$: n-$C_{26}H_{54}$	β'_1	10	0.5	0.745	6.665
	β''_1	35	0.498	0.752	6.83
	β'_2	80	0.496	0.748	7.03

* By Gerson *et al.*.[47]
x = molar percent of the higher n-alkane.

i) The intermediate phases of all the binary systems, denoted β'_n ($n = 1$ or 2) are indistinguishable (Figs. 2.b, 2.e, 2.h, 2.j, 2.m,2.o) and thus they are isostructural.
ii) It is same for the phases called β''_n ($n = 1$ or 2) (Figs. 2.a, 2.c, 2.f, 2.g, 2.i, 2.k, 2.n).

Both literature data[27-29] and our laboratory results (Figs. 1 & 3) about the mixtures of two consecutive [even-even], [even-odd] or [odd-odd] C_n^{4-11} allow us to determine the following rule of the solid phase sequences at "low temperature" when the second C_n concentration increases:

i) From an even C_{2p}: $\gamma_0(C_{2p})$, β'_1, β''_1
ii) From an odd C_{2p+1}: $\beta_0(C_{2p+1})$, $\beta'_0(C_{2p+1})$, β''_1, β'_1
iii) On the one hand the structural behavior is "symmetrical" on both sides of the last intermediate phase of the above sequences if the solute C_n has the same parity as the solid solvent (Fig. 3); this structural behavior is normal because the second C_n becomes the solvent beyond the last intermediate phase and the rule of the solid phase sequences is applied in the inverse direction. For instance:
   - In the system [C_{22}: C_{24}] (Fig. 1.c) this sequence is: $\gamma_0(C_{22})$, β'_1, β''_1, β'_2, $\gamma_0(C_{24})$ when the C_{24} molar concentration increases. It is same for the binary system [C_{24}: C_{26}] (Fig. 1.d).
   - In the system [C_{23}: C_{25}][10] the sequence is: $\beta_0(C_{23})$, $\beta'_0(C_{23})$, β''_1, β'_1, β''_2, $\beta_0(C_{25})$. Certainly the phase $\beta'_0(C_{25})$ undergoes an eutectoïd transition above the temperature $T = 293$ K, as the phase $\beta'_0(C_{23})$ of the system [C_{22}: C_{23}] (Fig. 1.a).

On the other hand, if the two *n*-alkanes do not have the same parity, the terminal solid solutions of the second C_n appear next to the last intermediate phase of the above sequences (Fig. 3), for example:

- In the system [C_{22}: C_{23}] (Fig. 1.a): $\gamma_0(C_{22})$, β'_1, β''_1, $\beta'_0(C_{23})$, $\beta_0(C_{23})$.
- In the system [C_{23}: C_{24}] (Fig. 1.b): $\beta_0(C_{23})$, $\beta'_0(C_{23})$, β''_1, β'_1, $\gamma_0(C_{24})$; this sequence is the opposite of the above sequence.

According to the Palatnik and Landau's rule,[26] a two-phase domain is always adjacent to each single-phase domain, characterized by its crystalline structure.

3.4 Notations

γ : Triclinic structures
β : Orthorhombic structures
Index 0 : Alloted to the pure C_n and their limited terminal solid solutions.
β'_n or β''_n : Orthorhombic intermediate solid solutions with the index n ($n = 1$ or 2) to identify isostructural phases of different stoïchiometries in a same binary system. The phases called β'_1 and β'_2 are isostructural in all these mixtures; it is same for the phase β''_1 or β''_2.

4. STRUCTURAL BEHAVIOR VERSUS TEMPERATURE

With increasing temperature, all the orthorhombic intermediate phases β'_n and β''_n undergo the same solid-solid transitions as the odd pure C_{2p+1}[5,9] above their transition δ^{30} up to their melting point. Many authors[5,31–45] characterized these solid phase transitions in the odd and even C_n. The solid phase sequence from "low" to "high temperatures" for the β'_n or β''_n phases corresponds to the following diagram:

$$\begin{array}{lclc}
\longleftarrow & & \longrightarrow & \\
\text{Low Temperatures} & | & \text{High Temperatures} & \\
\beta''_n \text{ or } \beta'_n & \rightarrow & \beta-\mathrm{RI} \rightarrow \alpha-\mathrm{RII} & \rightarrow \text{Liquid}
\end{array}$$

Remark: The space groups Fmmm of the orthorhombic rotator phase β-RI R$\bar{3}$m of the rotator phase $\alpha-\mathrm{RII}$ have been determined by Ungar,[35] and Ungar and Masic.[20] Gerson and Nyburg[28] attributed the space group Fmmm to the phase which appears above the intermediate solid solutions in the $[C_{20}: C_{22}]$ system: this phase is certainly the rotator phase $\beta-\mathrm{RI}$.

The occurrence of the phase $\beta-\mathrm{RI}$ is accompanied by a considerable increase in the unit cell base area $(\vec{a},\vec{b})$[5,6,35] and an important enthalpy effect;[1,5,9] this is a first-order transition.[20,35] However our experimental means did not allow us to observe the new rotator phase RV which has been highlighted by Sirota *et al.*[45] in the *n*-alkanes $(20 < n < 33)$.

All the intermediate phases β'_n or β''_n undergo peritectoïd decompositions when the temperature increases (Fig. 1):

i) The first intermediate phases which appear next to the terminal solid solutions undergo the following decompositions:
   - In the systems [even: even] (Figs. 1.c & 1.d) or [even: odd] (Fig. 1.b)

$$\beta'_{1\text{ or }2} = \gamma_0 + \beta-\mathrm{RI}$$

   - In the system [odd: odd] or [odd: even] (Fig. 1b)

$$\beta''_{1\text{ or }2} = \beta''_0 \quad \text{or} \quad \beta_0 + \beta-\mathrm{RI}$$

ii) The second intermediate phases present the following transformations:
   - In the systems [even-even] (Figs. 1.c, 1.d)

$$\beta''_1 = \beta'_2 + \beta-\mathrm{RI}$$

   - In the systems [odd: odd]

$$\beta'_1 = \beta''_2 + \beta-\mathrm{RI}$$

Note Bene: all the peritectoid transitions of the systems [odd: odd] are predicted.

With increasing temperature, on the one hand, this phase $\beta-\mathrm{RI}$ does not undergo any crystalline parameter evolutions in a small temperature range (Fig. 1); on the other hand, the parameter ratio b/a of this phase increasing progressively: the beginning of the transition is observed by X-ray diffraction when the peak (0 2 0) moves towards the line (111) but the X-ray diffraction line intensities do not change significantly and we have not observed the appearance of a second phase which characterizes a first-order transformation in the binary systems.[5–7,9] This phenomenon, which is accompanied by an abnormal and continuous enthalpy consumption[5,7–9] is probably a second-order transition[20,34–38] which characterizes the rotator RI state of the phase β (Fig. 1). Next, when the subcell is hexagonal ($b/a = \sqrt{3}$), the mixtures undergo a further weak first-order transition into the rotator phase $\alpha-$RII (R$\bar{3}$m), just a few degree below the solidus line: the stacking mode along the long *c* axis of the chains is ABCABC[35] instead of ABAB as in the $\beta-$RI structure (Fmmm). This transition provokes a very small enthalpy effect,[9] and leads to a two-phase domain (RI + $\alpha-$RII) (Fig. 1); when the phase $\beta-$RI does not exist in the pure C_n, this one undergoes the following peritectoïd decomposition ($\beta-\text{RI} = $ terminal solid solution $(C_n) + \alpha-$RII) or a peritectic melting ($\beta-\text{RI} = \text{liquid} + \alpha-$RII). The binary mixtures can form continuous homogeneous rotator solution domains at "high temperature" below the solidus line, provided the same rotator phase (RI or $\alpha-$RII) exists in the two pure *n*-alkanes (Fig. 1).

With decreasing temperature from the "low temperature" domain the intermediate phases β'_n and β''_n may undergo eutectoïd decompositions:[9,11]

– In the systems [even: even]:

$$\beta'_{1\text{ or }2} = \gamma_0 + \beta''_1 \quad \text{then} \quad \beta'_1 = \gamma_0(n-C_{2p}) + \gamma_0(n-C_{2p+2})$$

– In the systems [odd: odd]:

$$\beta''_{1\text{ or }2} = \beta_0 + \beta'_1 \quad \text{then} \quad \beta'_1 = \beta_0(n-C_{2p-1}) + \beta_0(n-C_{2p+1})$$

4.1 Remarkable Observations

i) The structural behaviors of the two-phase diagrams [C_{22}: C_{23}] and [C_{23}: C_{24}] (Figs. 1.a, 1.b) are "symetrical" in relation to the pure C_{23}.

ii) The similar phase diagrams of two consecutive even C_{2p}[C_{22}: C_{24}] and [C_{24}: C_{26}] (Figs. 1.c, 1.d) present a "symetrical" behavior on both sides of the intermediate phase β''_1.

iii) The phase diagram [C_{22}: C_{24}] (Fig. 1.d) can be described as the addition of the two diagrams [C_{22}: C_{23}] + [C_{23}: C_{24}] (Figs. 1.a & 1.b) when the terminal solid solutions $\beta_0(C_{23})$ and $\beta'_0(C_{23})$ have been eliminated.

iv) It will be same for the diagram [C_{23}: C_{25}] from the two phase diagrams [C_{23}: C_{24}] + [C_{24}: C_{25}] with the deletion of the terminal solid solution $\gamma_0(C_{24})$.

5. CONCLUSIONS

The literature references[4–10,27–29] and the experiments performed on the binary mixtures of the consecutive [even: even], [even: odd] and [odd: odd] *n*-alkanes ($19 < n < 27$) allow us to give a general description of the structural and thermodynamic behaviors of these systems which are real molecular alloys similar to metallic alloys as other binary organic components mixtures.[48–51] Recently Yamamoto *et al.*[52] highlighted the solid-state diffusion of C_{23} into the crystal of C_{21} which explains the solid-solid transitions and the existence of the intermediate solid solutions.

At "low temperatures", these systems show the presence of many orthorhombic intermediate solid solutions, isostructural to one of the two phases denoted β'_1 and β''_1.

At "high temperatures" below the solidus line, the rotator phases β-RI (Fmmm), next α-RII ($R\bar{3}m$) or other rotator phases[45] appear; it is possible that the mixtures form continuous homogeneous rotator solutions when the same rotator phases exist in the two pure *n*-alkanes.

The orthorhombic intermediate solid solutions undergo a peritectoïd decomposition at "high temperatures" and also an eutectoid decomposition at "low temperatures".

We think that the same behavior occurs in other binary systems of consecutives *n*-alkanes that we have not studied with transition temperature varying versus the carbon number of the *n*-alkanes. In all the cases, below the rotator phases domains these binary systems of consecutive *n*-alkanes do not form a continuous homogeneous solid solution and it is probably not possible with the binary mixtures of *n*-alkanes whose carbon number difference is greater than two as predicted by Kravchenko.[53]

The existence of the intermediate solid solutions accounts for the anomalies observed in these binary systems,[22] particularly a remarkable phenomenon detected in our laboratory:[2,3] the addition of one long *n*-alkane to a shorter one increases the solubility of the latter in organic solvents.

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References

1. P. Barbillon, L. Schuffenecker, J. Dellacherie, D. Balesdent and M. Dirand, *J. Chim. Phys.*, **88**, 91 (1991).
2. P. M. Goghomu, J. Dellacherie and D. Balesdent, *J. Chem. Thermody.*, **21**, 925 (1989).
3. P. M. Goghomu, J. Dellacherie and D. Balesdent, *Thermochimica Acta.*, **21**, 241 (1990).
4. N. Hasnaoui, J. Dellacherie, L. Schuffenecker, M. Dirand and D. Balesdent, *J. Chim. Phys.*, **85**(2), 153 (1988).
5. N. Hasnaoui, J. Dellacherie, L. Schuffenecker, M. Dirand and D. Balesdent, *J. Chim. Phys.*, **85**(6), 675 (1988).
6. Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, *Thermochim. Acta.*, **204**, 187 (1992).
7. Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, *J. Chim. Phys.*, **89**, 707 (1992).
8. Z. Achour, J. B. Bourdet, M. Bouroukba and M. Dirand, *J. Chim. Phys.*, **90**, 325 (1993).
9. A. Sabour, J. B. Bourdet, M. Bouroukba and M. Dirand, *Thermochim. Acta.*, **249**, 269 (1995).
10. B. Jouti, J. B. Bourdet, M. Bouroukba and M. Dirand, *Mol. Cryst. Liq. Cryst.*, (to be published).
11. A. Sabour, *Ph.D. Thesis I.N.P.L.-Nancy*, (1994).
12. W. M. Mazee, *Am. Chem. Soc., Meeting Symp. of Div. Pet. Chem.*, Chicago 93 (1958).
13. R. T. Edwards, **49**, 740 (1957).
14. W. M. Mazee, *Erdol und Kohle* **13**(2), 88 (1960).
15. R. M. Butler and D. M. Mc Lerd, *Can. J. Chem. Eng.*, 53 (1961).
16. G. A. Holder and J. Winckler, *J. Inst. Petrol*, **51**, 228 (1965).
17. W. R. Turner, *Ind. Eng. Chem. Prod. Res. Dev.*, **10**(3), 238 (1971).
18. I. Denicolo, A. F. Craievich, J. Doucet, *J. Chem. Phys.*, **80**(12), 6200 (1984).
19. J. J. Retief, D. Wengel and E. G. Boonstra, *J. Appl. Cryst.*, **18**, 156 (1985).
20. G. Ungar and G. Masic, *J. Phys. Chem.*, **80**, 1036 (1985).
21. M. Maroncelli, H. L. Strauss and R. G. Snyder, *J. Phys. Chem.*, **89**, 5260 (1985).
22. Y. Kim, H. L. Strauss and R. G. Snyder, *J. Phys. Chem.*, **93**, 485 (1989).
23. D. L. Dorset, *Macromolécules*, **23**, 623 (1990).
24. I. Basson and E. C. Reynhardt, *J. Chem. Phys.*, **95**(2), 1215 (1991).
25. S. P. Srivastava, J. Handoo, K. M. Agarwal and G. S. Joshi, *J. Phys. Chem. Solids.*, **54**(6), 639 (1993).

26. L. S. Palatnik and A. I. Landau, *Phase equilibria in multicomponent systems*, Holt, Rinhart and Winston, New York (1964).
27. A. E. Smith, *Acta Cryst.*, **10**, 802 (1957).
28. A. R. Gerson and S. G. Nyburg, *Acta. Cryst.*, **B50**, 252 (1994).
29. H. Luth, S. C. Nyburg, P. M. Robinson and H. G. Scott, *Mol. Crys. Liq. Cryst.*, **22**, 337 (1972).
30. R. G. Snyder, A. F. Maroncelli, S. P. Qi and H. L. Strauss, *Science*, **214**(9), 188 (1981).
31. J. Doucet, I. Denicolo and A. Craievich, *J. Chem. Phys.*, **75**(3), 1523 (1981).
32. J. Doucet, I. Denicolo, A. Craievich and A. Collet, *J. Chem. Phys.*, **75**(10), 5125 (1981).
33. A. Holz, J. Naghizadeh and D. T. Virgen, *Phys. Rev.*, **B27**(1), 512 (1983).
34. I. Denicolo, J. Doucet and A. F. Craievich, *J. Chem. Phys.*, **78**(3), 1465 (1983).
35. G. Ungar, *J. Phys. Chem.*, **87**, 689 (1983).
36. J. Doucet, I. Denicolo, A. F. Craievich and G. Germain, *J. Chem. Phys.*, **80**(4), 1647 (1984).
37. J. Doucet and A. J. Dianoux, *J. Chem. Phys.*, **81**(11), 5043 (1984).
38. I. Denicolo, A. F. Craievich and J. Doucet, *J. Chem. Phys.*, **80**(12), 6200 (1984).
39. S. K. Filatov, E. N. Kotelnikova and E. A. Alek Sandrova, *Zeitsch für Krist.*, **172**, 35 (1985).
40. R. S. Cantor and K. A. Dill, *Macromol.*, **18**, 1875 (!985).
41. J. P. Ryckaert, M. I. Klein and I. R. MacDonald, *Phys. Rev. Letters*, **58**(7), 698 (1987).
42. I. A. M. Royaud, P. J. Hendra, W. Maddams, C. Passingham and H. A. Willis, *J. of Mol. Struct.*, **239**, 83 (1990).
43. R. D. Heyding, K. E. Russell, T. L. Varty and D. St Cyr, *Powder Dif.*, **5**(2), 93 (1990).
44. A. Toda, H. Miyaji, Y. Ogawa and K. Takamizawa, *J. of Mat. Sci.*, **26**, 2793 (1991).
45. E. B. Sirota, H. E. King Jr, D. M. Singer and H. H. Shao, *J. Chem. Phys.*, **98**, 5809 (1993).
46. A. E. Smith, *J. Chem. Phys.*, **21**, 2229 (1953).
47. A. R. Gerson, K. J. Roberts and J. N. Sherwood, *Acta. Cryst.*, **B47**, 280 (1991).
48. N. B. Chanh and Y. Haget-Bouillaud, *Acta. Cryst.*, **B28**, 3400 (1972).
49. Y. Haget, J. Housty, A. Maiga, L. :Bonpunt, N. B. Chanh, M. A. Cuevas-Diarte and E. Estop, *J. Chim. Phys.*, **81**(3), 197 (1984).
50. M. Barrio, J. Font, J. Muntasell, J. L. Tamarit, N. B. Chanh and Y. Haget, *J. Chim. Phys.* **87**(255), 1835 (1990).
51. Y. Haget, *J. Chim. Phys.*, **90**, 313 (1993).
52. T. Yamamoto and K. Nozaki, *Polymer.*, **35**(15), 3340 (1994).
53. V. Kravchenko, *Acta. Phys.*, (Russia) **21**, 335 (1946).