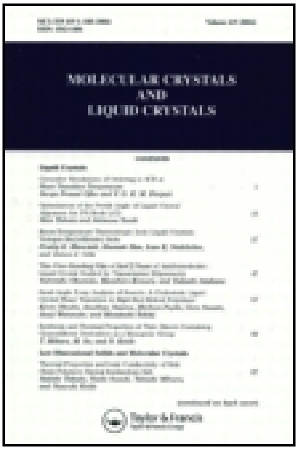

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Isothermal Sections of Ternary Mixtures: n-docosane + n-tricosane + n-tetracosane

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Isothermal Sections of Ternary Mixtures: *n*-docosane + *n*-tricosane + *n*-tetracosane

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The crystallographic long *c* parameter of the binary and ternary β'_1, β'_2, β''_1, intermediate solid solutions (n-$C_{22}H_{46}$ + n-$C_{23}H_{48}$ + n-$C_{24}H_{50}$) is approximately equal to the average *c* parameter of mixture equivalent orthorhombic pure *n*-alkanes: this finding shows that the longer *n*-alkane chain is not straight in unit cell of the mixture, but flexible near the chain end, as earlier observed from spectroscopy analyses by other authors. Four ternary isothermal sections were determined at 305 K, 308 K, 311 K and 313 K from binary diagram data and differential scanning calorimetry and X-ray diffraction analyses of thirty ternary mixtures: the ternary intermediate solid solutions undergo the same first-order solid – solid equilibrium transitions as those of binary alloys with the observation of β(Fmmm)-RI and α($R\bar{3}m$)-RII Rotator states below the solidus point.

Keywords: *n*-docosane; *n*-tricosane; *n*-tetracosane; solid solutions; Rotator states

1. INTRODUCTION

Binary phase diagrams of the systems *n*-docosane + *n*-tricosane (n-$C_{22}H_{46}$ + n-$C_{23}H_{48}$) [1], *n*-tricosane + *n*-tetracosane (n-$C_{23}H_{48}$ + n-$C_{24}H_{50}$) [2] and *n*-docosane + *n*-tetracosane (n-$C_{22}H_{46}$ + n-$C_{24}H_{50}$) [3] were established by means of structural and differential scanning calorimetry analyses. The structural behavior of ternary mixtures (n-$C_{22}H_{46}$ + n-$C_{23}H_{48}$ + n-$C_{24}H_{50}$)

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was determined in the isothermal section at 293 K [4]: this study indicates the existence of limited terminal solid solutions close to the three pure *n*-alkanes (here after denoted by C_n) and three domains of intermediate solid solutions, identical to those observed in the binary systems and called β'_1, β'_2, β''_1 (Fig. 5a).

Our purpose is to study the thermodynamic and structural behavior of these ternary mixtures ($C_{22} + C_{23} + C_{24}$) according to temperature and to present four ternary isothermal sections at 305, 308, 311 and 313 K respectively.

2. EXPERIMENTAL

The three pure C_n were purchased from ALDRICH Chemical Company: their purity grade is 99 mol% for C_{22} and C_{24} and over 99 mol% for C_{23} as determined by chromatography. The mixtures were prepared by weighing together, melting and thorough mixing the solid components. The homogeneous liquid solution thus obtained was quenched in a crystallizing dish maintained at a low temperature in a Dewar vessel filled with liquid air. Such rapid cooling ensured a uniform steric concentration of each component in the mixture.

X-ray diffraction experiments were carried out on thirty powder samples (Tab. I), using $\lambda_{K\alpha}$ copper radiation, with:

(i) a CGR diffractometer (Theta 60): the X-ray diffraction analyses were performed at different temperatures with the help of a heated sample holder; heating or cooling of the sample holder was based on the PELTIER effect: the accuracy of the sample temperature was within ± 0.2 K around the set point and the line positions were measured with an accuracy of 0.05° for each value of BRAGG angles; the calibration was done with pure copper, of which the sample holder was made, as standard.

(ii) a GUINIER-de WOLFF Nonius camera: the line positions were determined with an accuracy of 0.25 millimeters for distances ranging from 10.5 to 125 millimeters; the calibration was obtained with spectroscopic pure gold as standard. This X-ray diffraction device was put in a compartment whose temperature was controlled: this technique allows us to compare simultaneously the structural behavior of four different mixtures at the same temperature (ranging from 293 to 343 K).

TABLE I Molar % concentrations and structural equilibrium state of ternary mixtures at 305, 308, 311 and 313 K

Molar concentration in n-alkanes		*Phases observed by*	*Samples*
(% in n-C_{23}*)*	*(% in n-*C_{24}*)*	*X-ray diffraction*	*No.*
Section 1 ⇒ $T = 305$ K			
17.5	65.5	β'_2	9
33.3	33.3	$\beta''_1 + \beta'_2 + \beta$(Fmmm)	15
15	38.5	$\beta'_2 + \beta$(Fmmm)	17
27.5	27	$\beta''_1 + \beta$(Fmmm)	22
10	25	β(Fmmm)	24
20.5	20.5	β(Fmmm)	25
29.5	15	$\beta'_1 + \beta$(Fmmm)	26
23	12	$\beta'_1 + \beta$(Fmmm)	29
17.5	17.5	β(Fmmm)	32
40.25	39.25	$\beta''_1 + \beta'_2$	42
55.5	15	β''_1	45
48.5	3.5	$\beta''_1 + \beta'_1$	46
28.5	43	$\beta''_1 + \beta'_2$	48
13	33	β(Fmmm)	49
34.5	17.5	$\beta''_1 + \beta'_1 + \beta$(Fmmm)	51
Section 2 ⇒ $T = 308$ K			
14.5	71.5	$\beta'_2 + \beta$(Fmmm)	6
26.5	67	β'_2	7
17.5	65.5	$\beta'_2 + \beta$(Fmmm)	9
40	47	$\beta'_2 + \beta$(Fmmm)	13
33.3	33.3	β(Fmmm)	15
10	25	β-RI	24
40.25	39.25	$\beta'_2 + \beta$(Fmmm)	42
55.5	15	β(Fmmm)	45
34.5	17.5	β(Fmmm)	51
Section 3 ⇒ $T = 311$ K			
10	82	$\gamma_0 + \beta'_2$	4
14.5	71.5	$\beta'_2 + \beta$(Fmmm)	6
26.5	67	$\beta'_2 + \beta$(Fmmm)	7
17.5	65.5	β(Fmmm)	9
40	47	β(Fmmm)	13
Section 4 ⇒ $T = 313$ K			
10	82	β(Fmmm)	4

The focused monochromatic beam was obtained with a filament intensity of 10 mA at 48 kV.

The differential thermal analyses (DTA) were performed using a SETARAM DSC 111 calorimeter of the Tian Calvet type. The samples were first melted and cooled at equilibrium state in the measuring crucible and were then heated from room temperature to above the liquidus point at a rate of 0.5 K min^{-1}. The temperature of transition peaks was determined with a precision of ± 0.5 K.

3. STRUCTURAL BEHAVIOR OF ORTHORHOMBIC INTERMEDIATE SOLID SOLUTIONS *VERSUS* TEMPERATURE

The pure C_n and mixtures consisting of 2, 3, 4 and 5 C_n have been the subject of numerous structural and physico-chemical investigations [1–64]. More particularly the intermediate solid solutions, which have been observed in C_n binary and ternary mixtures [1–4, 21–49, 57–64], are isostructural with two phases only, called β'_n and β''_n. The index $n = 1$ or 2 allows the identification of isostructural phases of different stöchiometries on both sides of the middle intermediate solid solution in the same binary or ternary system.

At "low temperatures", these intermediate β'_n and β''_n phases present orthorhombic unit cells, whose space groups have not yet been precisely determined [21, 28, 31, 39]. Table II and Figure 1 show the crystallographic parameter variations as a function of the average carbon atom number of binary and ternary mixtures ($C_{22}-C_{23}-C_{24}$) and compare their long c parameters with those of orthorhombic pure C_n, using the following linear expression:

$$c\,(\text{nm}) = 0.2545\,n + 0.3842 \quad \text{(in nanometer)}$$

$$\text{with a correlation factor } R^2 = 0.9993$$

c(nm): crystallographic c parameter (in nanometer) of the pure C_n whose unit cells are orthorhombic.

n: atom carbon number of pure C_n chain.

TABLE II Comparison between the average carbon atom $\bar{n}$ number of binary and ternary mixtures and the equivalent carbon atom $\bar{n}_c$ number, calculated from the variation equation $\bar{n}_c = \frac{c(nm)-0.3842}{0.2545}$ of orthorhombic pure C_n c parameters

Molar %	$\bar{n} = \Sigma x_i * n_i$	$a_{exp}(nm)$	$b_{exp}(nm)$	$c_{exp}(nm)$	$\bar{n}_c$	$\Delta\bar{n}$
				Binary mixtures		
C_{22}:20% C_{23}	22.2	0.498	0.752	6.15	22.6	0.5
C_{22}:70% C_{23}	22.7	0.497	0.741	6.23	23	0.3
***pure n*-C_{23}**	23	0.497	0.747	6.24	23	0
C_{23}:10% C_{24}	23.1	0.497	0.747	6.24	23	−0.1
C_{23}:50% C_{24}	23.5	0.496	0.722	6.35	23.4	−0.1
C_{22}			***Ternary mixtures***			
17.5% C_{23}:65.5%C_{24}	23.5	0.498	0.750	6.53	24.1	0.6
55.5% C_{23}:15%C_{24}	22.9	0.499	0.750	6.29	23.2	0.3
27.5% C_{23}:27%C_{24}	22.8	0.499	0.746	6.26	23.1	0.3
13% C_{23}:33%C_{24}	22.8	0.502	0.750	6.22	22.9	0.1
24.3% C_{23}:61.3%C_{24}	23.5	0.492	0.750	6.51	24.1	0.6

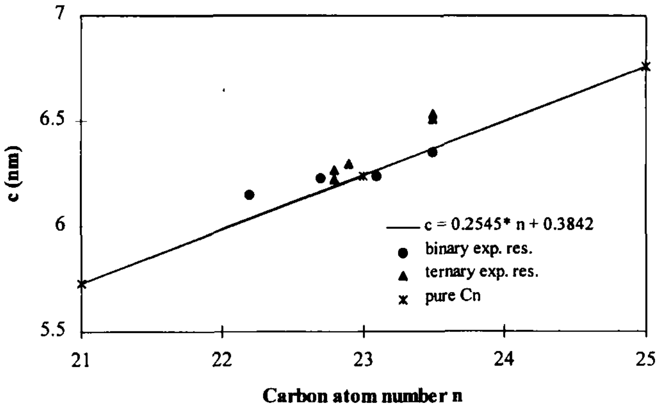

FIGURE 1 Comparison between the long c parameters of pure C_n and those of binary and ternary intermediate solid solutions (C_{22} + C_{23} + C_{24}).

This linear variation expression of the crystallographic c parameter as a function of the carbon atom n number has been determined by optimization from the structural data in the literature [12] on eighteen pure C_n whose unit cells are orthorhombic ($12 < n < 61$).

The long c parameter of each mixture is associated with a chain length of a hypothetical orthorhombic pure C_n whose equivalent carbon atom $\bar{n}_c$ number is calculated from the following linear variation equation:

$$\bar{n}_c = \frac{c\,(\mathrm{nm}) - 0.3842}{0.2545}$$

Table II compares the equivalent carbon atom $\bar{n}_c$ number, calculated from the experimental values of c parameters, to the average carbon atom $\bar{n}$ number obtained from the C_n binary and ternary mixture x_n molar fractions.

$$\bar{n} = \sum x_n \cdot n$$

x_n: molar fraction of each C_n in mixture. n: carbon atom number of each C_n chain in mixture.

According to the results of Table II and Figure 1, the long c parameter corresponds to a hypothetical orthorhombic C_n chain length whose equivalent carbon atom $\bar{n}_c$ number is equal to the average carbon atom $\bar{n}$ number of the mixture with an excess value lower than 0.6. This experimental finding shows that the longer C_n is flexible near its chain end in the unit cell of the mixture, as observed by Clavell-Grunbaum *et al.* [48] from Raman and infrared spectrometry analyses on mixtures consisting of 2, 3 and 4 C_n.

With increasing temperature, all the β'_n and β''_n solid solutions undergo the same first-order solid–solid transitions as the orthorhombic (Pbcm) pure C_{23} [13–19, 28, 39] above the δ transition [65] up to its melting point (Fig. 2):

$$\beta'_n \text{ or } \beta''_n \rightarrow \beta(\text{Fmmm})\text{-RI} \rightarrow \alpha(\text{R}\bar{3}\text{m}) - \text{RII}$$

$\rightarrow$: first-order solid – solid transitions

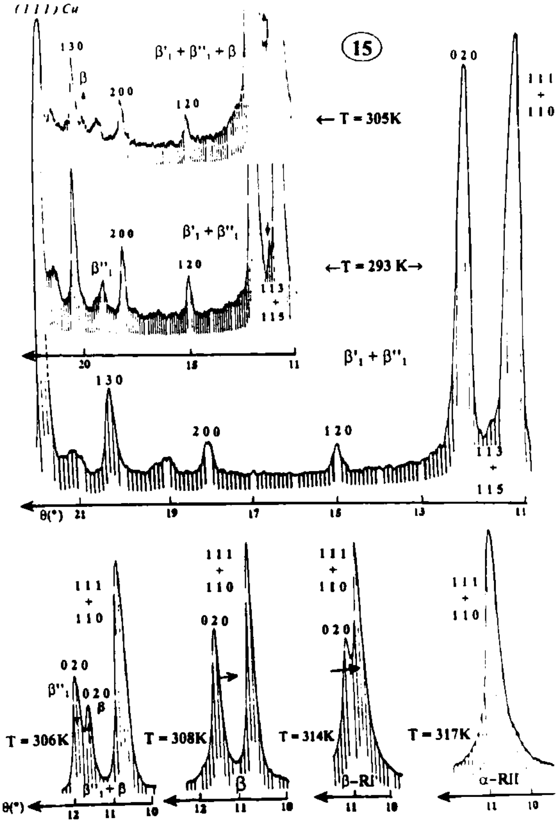

FIGURE 2 Structural behavior of the ternary equimolar mixture (1/3 C_{22} + 1/3 C_{23} + 1/3 C_{24}) with increasing temperature.

(i) the occurrence of the β(Fmmm) phase is characterized by:

  - the disappearance of all the diffraction peaks ($h\ k\ \ell$) whose indices do not have the same parity.
  - an important shift of the (0 2 0) diffraction towards small BRAGG angles, that corresponds to an increase of crystallographic b parameter and of the base area (a, b) of the unit cell. (Figs. 2a, b).

  At first, the crystalline parameters of the β(Fmmm) phase do not evolve in a small temperature range; then, the crystallographic parameter b/a ratio of this phase increases progressively: the beginning of the phenomenon is observed by X-ray diffraction when the (0 2 0) line moves toward the (1 1 1) diffraction peak (Fig. 2); however, the X-ray diffraction line intensities do not change significantly and the appearance of a second phase, which characterizes a first-order transition in the binary, ternary or multicomponent systems [66], is not seen. This phenomenon is accompanied by an abnormal and continuous consumption of enthalpy without changing of the Fmmm space group of the crystallographic structure nor of the β phase composition: it corresponds to a second- or higher-order transition, which defines the RI-Rotator state of this β(Fmmm) phase.

(ii) when the (0 2 0) and (1 1 1) diffraction lines coincide (Fig. 2), the symmetry of the base (ab) of the unit cell becomes hexagonal ($b/a = \sqrt{3}$) and the mixtures undergo a further weak first-order transition into the rhombohedral α-RII Rotator phase whose R$\bar{3}m$ space group has been determined by Ungar *et al.* [14, 15]: the stacking mode of the chains along the crystallographic long c-axis corresponds to the crystalline plane ABCABC rhombohedral sequence instead of the ABABAB orthorhombic (or hexagonal) sequence as in the orthorhombic β(Fmmm) structure [13–19, 39].

This depiction confirms that of Ungar [14, 15]; Doucet *et al.* [13, 16, 17]; Craievich *et al.* [18, 19] and Gerson *et al.* [39], who accurately determined the crystallographic structures of all these "high temperatures" phases.

Nota Bene

Our experimental means did not allow us to observe the other Rotator phases RIII, RIV, RV... which have been highlighted by Sirota *et al.* [41, 42] and Robles *et al.* [50] in pure C_n ($n > 24$). Generally, they were not observed at equilibrium state and some authors have given different names to the same phase: at equilibrium state, a solid phase is defined by its crystallographic structure and more specifically by its space group which is the physical constant of the solid phase. According to Palatnik and Landau [66], the name of the phase does not change in the course of a second- or higher-order transition in which the space group is retained.

RESULTS

First the peaks, observed on the D.T.A. curves (Fig. 3), showed solid–solid transitions and melting points of the mixtures and indicated the temperature

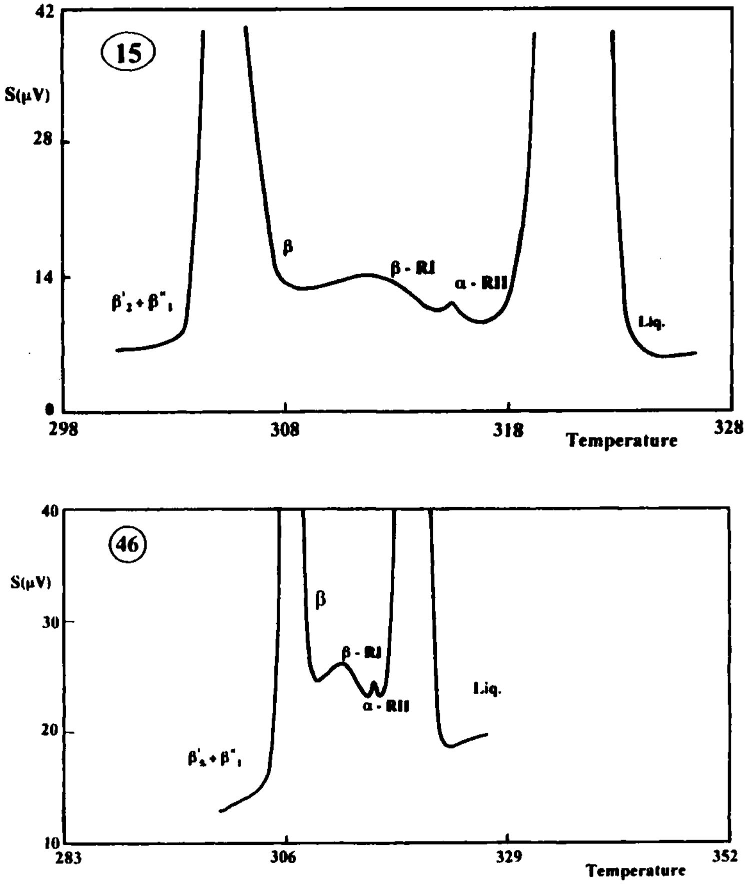

FIGURE 3 D.T.A. curves ternary mixtures No. 15 (1/3C_{22} + 1/3C_{23} + 1/3C_{24}) and No. 46 (0.48C_{22} + 0.485C_{23} + 0.035C_{24}).

domains of following first-order solid–solid and solid–liquid equilibrium transitions (Tab. III):

(i) the first peak: β'_n or $\beta''_n \rightarrow \beta$(Fmmm)
(ii) the small peak just below solidus point: β(Fmmm)$\rightarrow \alpha$(R$\bar{3}m$)-RII.
(iii) the last peak: α(R$\bar{3}m$)-RII$\rightarrow$liquid

Note: As it was said before, the RI-Rotator state of the β(Fmmm) phase is characterized by an abnormal and continuous consumption of enthalpy between the first peak (β'_n or $\beta''_n \rightarrow \beta$) and the small peak below the solidus point ($\beta \rightarrow \alpha$-RII) (Fig. 3): in this temperature range, a second phase is not seen and the Fmmm space group of the β phase is retained [13–19, 28, 39, 58] (Figs. 2 and 3): this observation does not correspond to a first-order solid–solid transition [14].

Further, the temperature domains on both sides of the peaks of the solid–solid transition on the DTA curves (Fig. 3) were explored by X-ray diffraction analysis (Figs. 2 and 4) in order to characterize the structural state of ternary mixtures in several isothermal sections (305, 308, 311 and 313 K, Tab. I).

The ternary isothermal sections (Fig. 5) are established from the binary diagram data (Fig. 5a) [1–4] and experimental results obtained on the

TABLE III Temperatures of first- order solid-solid transition → determined by DSC (± 0.5 K) and by X-ray diffraction (± 0.2 K) with increasing temperature

samples No.	*T(K)*	*Transition*
9	306.5	$\beta'_2 \rightarrow \beta'_2 + \beta$
	309.0	$\beta'_2 + \beta \rightarrow \beta$
	313.0	β-RI: beginning
	317.0	β-RI $\rightarrow \alpha$-RII + β-RI
	317.0	α-RII + β-RI $\rightarrow \alpha$-RII
	321.5	α-RII $\rightarrow \alpha$-RII + Liq.
	322.0	α-RII + Liq. $\rightarrow$ Liq.
46	305.0	$\beta''_1 + \beta'_1 \rightarrow \beta''_1 + \beta$
	306.0	$\beta''_1 + \beta \rightarrow \beta$
	310.0	β-RI: beginning
	315.0	β-RI $\rightarrow \alpha$-RII + β-RI
	315.8	α-RII + β-RI $\rightarrow \alpha$-RII
	318.0	α-RII $\rightarrow \alpha$-RII + Liq.
	319.0	α-RII + Liq. $\rightarrow$ Liq.
49	303.0	$\beta''_1 \rightarrow \beta''_1 + \beta$
	304.0	$\beta''_1 + \beta \rightarrow \beta$
	308.0	β-RI: beginning
	314.5	β-RI $\rightarrow \alpha$-RII + β-RI
	315.0	α-RII + β-RI $\rightarrow \alpha$-RII
	318.5	α-RII $\rightarrow \alpha$-RII + Liq.
	319.0	α-RII + Liq. $\rightarrow$ Liq.

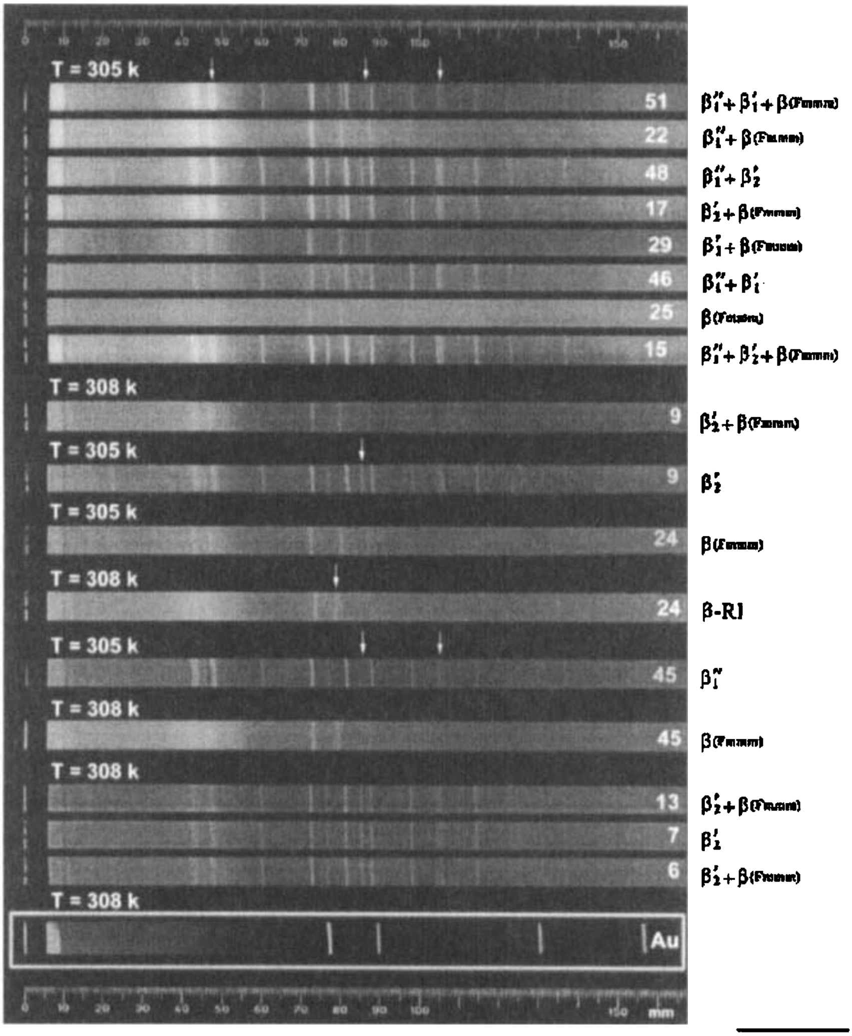

FIGURE 4 X-ray diffraction patterns carried out in Guinier-de Wolff camera at different temperatures, (λCu Kα).

ternary mixtures (Tabs. I and III). According to the Palatnik and Landau's rules [66] on the adjacent phase domains in multicomponent systems, the two-phase areas are situated between two single-phase domains and the three-phase triangular regions, whose vertices are adjacent to the single-phase domains, between three two-phase areas.

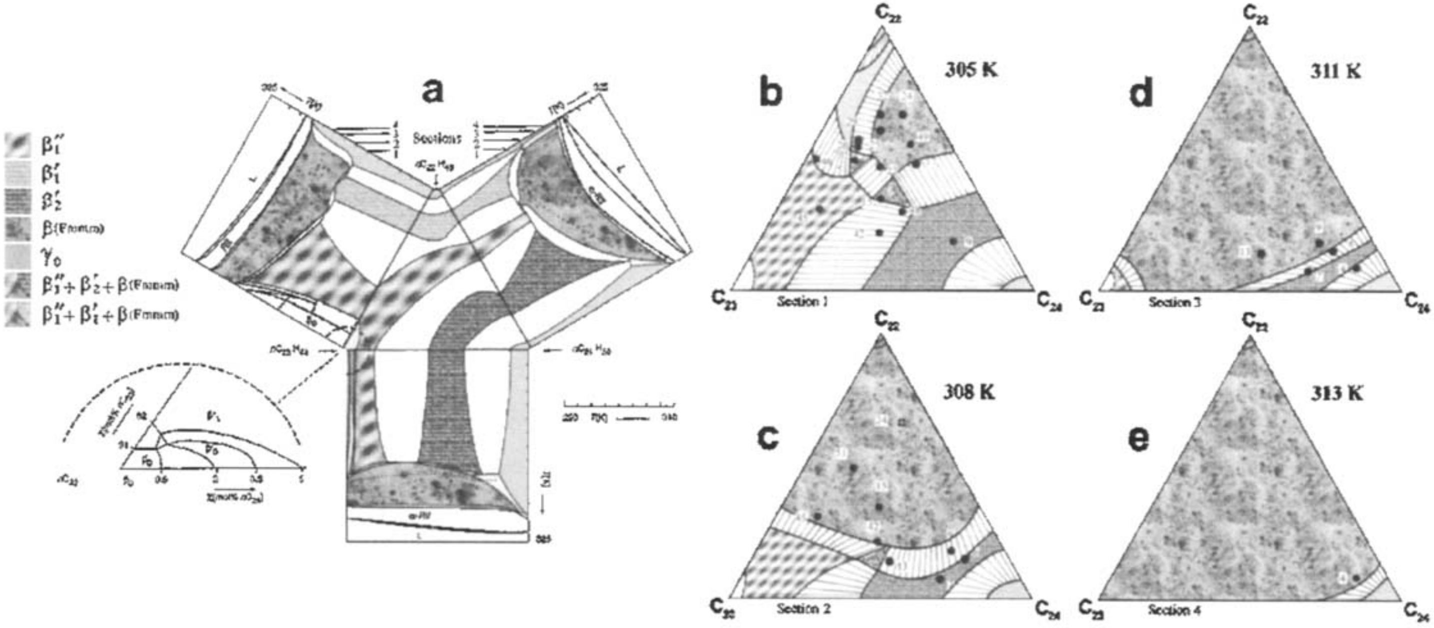

FIGURE 5 Binary phase diagrams and ternary section at 293 K (5-a), ternary sections at 305 K (5-b), 308 K (5-c), 311 K (5-d) and 313 K (5-e).

CONCLUSION

The isothermal sections of $C_{22} + C_{23} + C_{24}$ mixtures were determined at 305, 308, 311 and 313 K respectively. This study shows that the β'_1, β'_2, β''_1 intermediate solid solutions undergo the same first-order solid–solid transitions as those observed in the binary systems of the consecutive C_n, [28–33, 36–40, 43–50, 55–64], as temperature increases.

The long *c* parameter of these intermediate phases is approximately equal to the average *c* parameter of equivalent orthorhombic pure C_n, of mixtures (Tab. II, Fig. 1): this finding shows that longer C_n chain is bend in the unit cell of the mixture, as earlier observed by Clavell-Grunbaum *et al.* [48] from spectroscopy analyses on equimolar mixtures consisting of 2, 3 and 4 C_n.

These isothermal equilibria diagrams show:

(i) eight single-phase domains of the:

  - three limited terminal solid solutions close to the three pure C_n.
  - three β'_1, β''_1, β'_2 intermediate solid solutions.
  - two β(Fmmm) and α(R$\bar{3}$m)-RII "high temperatures" phases.

(ii) two-phase fields between two single-phase domains.

(iii) three-phase triangular areas between three two-phase areas and three single-phase domains.

It is thus possible to observe one, two or three phases in these ternary mixtures as a function of C_n concentrations, as also noted earlier by Clavell-Grunbaum *et al.* [48].

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