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Diagram of the *n*-tricosane–*n*-tetracosane mixtures: Corrections

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Abstract

Following the rules of solid phase sequence in binary mixtures of *n*-alkanes, a new orthorhombic intermediate phase is observed in the rich *n*-tetracosane concentration range, situated near the triclinic terminal solid solution $\gamma_0(C_{24})$. The joint calorimetric (D.T.A) and structural studies, realized on thirty-nine samples, complement the *n*-tricosane : *n*-tetracosane diagram. © 1997 Elsevier Science B.V.

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1. Introduction

Following the works of our laboratory [1] on the solid phase sequences at 'low temperature' in the binary systems of consecutive (even-numbered : even-numbered and odd-numbered : odd-numbered) *n*-alkanes (hereafter denoted by C_n), the studies on C_{23} : C_{24} mixtures [2] are due to be done again.

Indeed when the second consecutive even-numbered C_n concentration increases from the other pure even-numbered C_{2p}, Achour et al. [3–6] showed that the solid phase sequence is as follows: γ_0 (C_{2p}), β'_1 and β''_1 which are the two first intermediate phases near the terminal solid solution γ_0 (C_{2p}). In the binary systems of the consecutive odd-numbered C_{2p+1}, Jouti et al. [7,8] determined the following sequence when the second consecutive odd-numbered C_n concentration increases from the other pure odd-numbered C_{2p+1} : two terminal solid solutions (β_0 (C_{2p+1}) and β'_0 (C_{2p+1}))and the two first intermediate phases (β''_1 and β'_1). The intermediate solid solutions, denoted $\beta'_{1 \text{ or } 2}$, are isostructural in all the binary mixtures; it is same with the intermediate solid solutions, called $\beta''_{1 \text{ or } 2}$ [1]. The aim of this work is to show that the solid phase succession from the odd-numbered C_{23} is β_0 (C_{23}), β'_0 (C_{23}), β''_1, β'_1 (as the system C_{23} : C_{25} [8]) when the consecutive C_{24} concentration increases and vice versa, that the sequence from the even-numbered C_{24} is γ_0 (C_{2n}), β'_1, β''_1 (as the system C_{22} : C_{24} [3]) with the raising of the C_{23} concentration. Thus, a solid phase is missing in the phase diagram C_{23} : C_{24}, which was determined by Sabour et al. [2] and which needs correction.

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2. Notations

at "low temperature"

γ:	triclinic structures of even-numbered C_{2p}
β:	orthorhombic structures.
index 0:	allotted to the pure C_n and their terminal solid solutions.
β'_n or β''_n:	orthorhombic intermediate phases with the index n (n=1 or 2) to identify isostructural phases on both side of the middle intermediate solid solution in the same binary system. All the phases called β'_1 or β'_2 are isostructural in all binary systems of consecutive C_n; it is same for the phase β''_1 or β''_2.

at "high temperature"

β:	orthorhombic phase with the space group Fmmm which appears above the first important enthalpic effect with increasing temperature.
RI:	Rotator state of the phase β (Fmmm) which corresponds to a second order transition [9].
α-RII:	Rotator phase with the space group R$\bar{3}$m [9].

3. Experimental method

The mixtures were obtained by melting appropriate proportions of tricosane C_{23} and tetracosane C_{24}. The two pure C_n and the experimental methods were same as those described by Sabour et al. [2].

At 'low temperature', the X-ray diffraction experiments were carried out on thirty-nine powder samples with a Guinier de Wolff Nonius chamber, using a copper anti-cathode X-beam, obtained with a 10 mA filament intensity at 50 kV voltage. This experimental technique allows to determine the structural behaviour with increasing concentration from 10% up to 95% molar of C_{24} at 293 K:

1. in the single-phase range, the peak intensities are constant; only the diffraction line positions, particularly (0 0 1), change with the cell parameters, especially with the long axis c, which is sensitive to concentration variations.
2. in the two-phase regions, the parameters are constant; but the relative intensities of the diffraction peaks, distinguished in each phase, evolves in function of their respective proportion which changes with increasing concentration in the mixtures where two phases are present.

When the temperature increases, on the one hand the differential thermal analysis (D.T.A) experiments were performed on the samples to detect the solid–solid transitions and the melting and to determine the corresponding temperatures, using a DSC 111 G calorimeter of the Tian–Calvet type, manufactured by SETARAM. On the other hand, the structural solid–solid transitions were identified with the help of the X-ray diffractometer (CGR theta 60) which had been equipped with a heated sample holder, based on the Peltier effect.

4. Experimental results: corrections of the C_{23} : C_{24} diagram

4.1. Structural behaviour versus C_{24} concentration at 293 K

In the concentration range from pure C_{23} up to 15% molar of C_{24}, which have been particularly explored by Sabour et al. [2], the same structural behaviour is observed with the following sequence of the solid phases when the C_{24} concentration increases:

1. β_0 (C_{23}) Fig. 1(a): terminal solid solution with the orthorhombic structure of the pure C_{23} (Pbcm) [10].
2. β'_0 (C_{23}): terminal solid solution with the orthorhombic structure that appears above the δ transition [11] in the pure C_{23}; this phase had been called β' by Sabour et al. [2].
3. an orthorhombic intermediate solid solution, formerly called β'_1 by Sabour et al. [2], that we now denote β''_1. Indeed the powder X-ray patterns of this phase (Fig. 1(b)) are indistinguishable with those obtained by Jouti et al. [7,8] in the rich

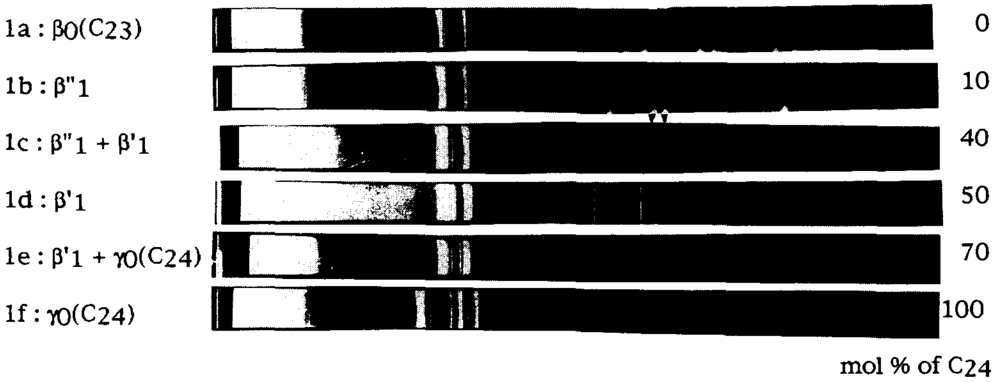

Fig. 1. X-ray diffraction patterns made with a Guinier de Wolff Nonius chamber for C_{23} : C_{24} mixtures when the molar concentration of C_{24} increases at 293 K.

C_{23} concentration domain, situated near the phase β'_0 (C_{23}) of the C_{21} : C_{23} [7] and C_{23} : C_{25} [8] systems respectively; the X-ray line modifications (Table 1) between the β_0 (C_{23}) and this intermediate phase are identical to those described between β_0 (C_{23}) and β''_1 in the two binary systems of the odd-numbered C_n [7,8]. Moreover, this intermediate solid solution is also isostructural to the phase β''_1, observed by Achour et al. in the two even-numbered C_n binary mixtures C_{22} : C_{24} [3] and C_{24} : C_{26} [6].

When the C_{24} concentration increases still, new modifications of the X-ray diffraction are highlighted (Fig. 1(c,d) and Table 1). These structural evolutions are similar to modifications observed by Jouti et al. [7,8] and Achour et al. [4,5] between the two intermediate phases, which are denoted respectively as β''_1 and β'_1 in the binary systems C_{21} : C_{23} [7], C_{23} : C_{25} [8], C_{22} : C_{24} [3] and C_{24} : C_{26} [6]. Moreover the X-ray diffraction photograph (Fig. 1(d)) is indistinguishable with those observed on the β'_1 phase of these four binary systems. According to the rules of the phase sequence established for the binary mixtures of the consecutive C_n [1], this phase β'_1 is the first intermediate solid solution which appears near the domain of the terminal solid solutions of the even-numbered C_{2p} : γ_0 (C_{22}), γ_0 (C_{24}) or γ_0 (C_{26}) when the second consecutive C_n concentration increases.

Thirty-nine mixtures have been studied at 293 K from 10% up to 95% molar of C_{24} to determine the single-phase and two-phase regions (Table 2).

4.2. Structural behaviour with increasing temperature

The differential thermal analyses were performed on binary mixtures heated at a rate of 0.5 K min^{-1} from 309 K to above the liquidus, as already described by Sabour et al. [2]. With increasing temperature, the solid–solid transitions, observed from the intermediate solid solutions particularly, correspond to the following sequence:

$$\beta''_1 \text{ or } \beta'_1 \rightarrow \beta(\text{Fmmm})\text{-RI} \rightarrow \alpha\text{-RII}(\text{R}\bar{3}\text{m})$$

For the three mixtures, whose concentrations are 20, 25 and 30% molar of C_{24} respectively, the start temperature of the first peak (Fig. 2) is constant and equal to 310.25 K; this observation shows the pre-

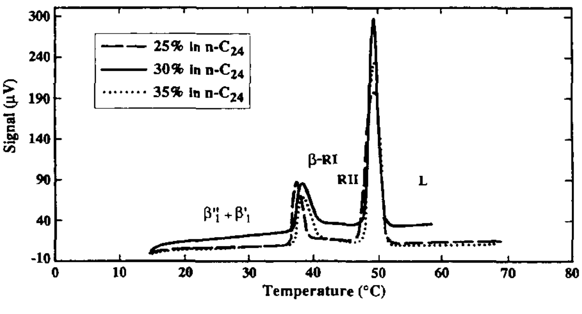

Fig. 2. D.T.A curves of C_{23} : C_{24} mixtures with 25%, 30% and 35% molar of C_{24}. The temperature of the start of the first peak is constant for the three mixtures and corresponds an eutectoïd equilibrium.

Table 1
Experimental lattice spacings, (h k l) index of reflexion planes and observed and calculated intensities

Phase β_0 α=90° a=0.497 nm (n-tricosane) β=90° b=0.741 nm (Pbcm) γ=90° c=6.2350 nm					Phase β''_1 a=0.497 nm (10% in n-C_{24}) b=0.741 nm $\alpha=\beta=\gamma$=90° c=6.2350 nm			Phase β'_1 a=0.4959 nm (50% in n-C_{24}) b=0.722 nm $\alpha=\beta=\gamma$=90° c=6.3472 nm		
h k l	d_{exp} (nm)	d_{calc} (nm)	I_{obs} (nm)	I_{calc} (nm)	d_{exp} (nm)	d_{calc} (nm)	I	d_{exp} (nm)	d_{calc} (nm)	I
0 0 6	1.0424	1.0392	W	1.7	1.0430	1.0467	W	1.0740	1.0579	W
0 0 8	0.7789	0.7794	W	0.9	0.7880	0.7850	W	0.8055	0.7934	W
0 0 10	0.6221	0.6235	W	0.5	0.6279	0.6280	W	0.6505	0.6347	W
1 1 0	0.4134	0.4136	VS	38.4	0.4136	0.4129	VS	O.4134	0.4123	VS
1 1 1	0.4134	0.4127		100	0.4136	0.4120		0.4134	0.4115	
1 1 3	0.4078	0.4058	S	10.2	0.4043	0.4051	M	0.4064	0.4047	S
1 1 5	0.3910	0.3926	M	3.1	0.3933	0.3923	W	0.3953	0.3922	M
0 2 0	0.3709	0.3736	S	12.2	0.3730	0.3730	S	0.3728	0.3711	S
0 2 1	0.3709	0.3729		32.5	0.3730	0.3723		0.3728	0.3705	
0 2 3	0.3671	0.3677	M	3.4	0.3654	0.3672	M	0.3580	0.3562	W
0 2 5	0.3562	0.3578	W	1.2	0.3529	0.3576	W	0.3528	0.3526	W
0 2 7	0.3444	0.3445	W	0.5	0.3442	0.3444	M	0.3258	0.3435	W
1 2 0	0.2978	0.2985	W	1.5	0.2980	0.2981	W	0.2978	0.2971	W
2 0 0	0.2478	0.2484	S	9.4	0.2479	0.2479	S	0.2486	0.2480	S
*#	—	—	—	—	0.2376	—	W	0.2382	—	W
2 1 0	0.2352	0.2358	W	0.8	0.2354	0.2353	W	0.2360	0.2352	W
1 0 24*	0.2288	0.2302	M	3.3	—	—	—	—	—	—
1 3 0	0.2214	0.2226	S	9.4	0.2215	0.2223	S	0.2260	0.2214	S
0 2 23*	0.2188	0.2200	W	0.7	—	—	—	—	—	—
1 1 24	0.2188	0.2194		2.4	—	—	—	—	—	—
*#	—	—	—		0.2152	—	M	—	—	—
0 2 24	0.2120	0.2133	M	3.4	0.2122	0.2142	W	0.2132	0.2154	M
*#	—	—	—		0.2104		M	—	—	—
2 2 0	0.2063	0.2068	S	1.7	0.2064	0.2065	S	0.2068	0.2062	M
2 2 1	0.2063	0.2067		4.5	0.2064	0.2064		0.2068	0.2061	
1 2 23*	0.2003	0.2007	W	1.0	—	—	—	—	—	—
*#	—	—	—	—	0.1978		W	—	—	—
1 2 24*	0.1952	0.1960	W	0.6	—	—	—	—	—	—
1 2 25*	0.1904	0.1914	W	0.7	—	—	—	—	—	—
#	—	—	—	—	—	—	—	0.1913		W
*#	—	—	—	—	0.1886		M	—	—	—
0 4 0	0.1858	0.1868	W	0.4	0.1859	0.1865	W	0.1855	0.1856	M
0 4 1	0.1858	0.1867		0.9	0.1859	0.1864		0.1855	0.1855	
2 1 23*	0.1769	0.1779	M	2.8	—	—	—	—	—	—
2 3 1	0.1757	0.1758	W	1.9	0.1756	0.1755	W	0.1754	0.1751	W
2 1 24	0.1742	0.1746	W	1.86	0.1732	0.1750	W	0.1742	0.1745	W
1 3 23*	0.1705	0.1720	M	3.6	—	—	—	—	—	—
2 1 25	0.1705	0.1713		2.1	—	—	—	—	—	—
*#	—	—	—	—	0.1695		W	—	—	—
#	—	—	—	—	—	—		0.1679		W
*#	—	—	—	—	0.1673		W	—	—	—
1 3 25*	0.1652	0.1661	M	2.8	—	—	—	—	—	
2 2 24	0.1612	0.1618	W	1.3	—	—	—	—	—	—
3 1 0	0.1612	0.1616		0.33	0.1612	0.1614	M	0.1615	0.1614	W
3 1 1	0.1612	0.1616		0.9	—	—	—	—	—	—
#	—	—	—		—	—	—	0.1530		W
0 4 24	0.1507	0.1517	M	3.3	0.1511	0.1519	W	0.1513	0.1510	W
2 4 1	0.1485	0.1492	W	0.4	0.1489	0.1490	W	0.1488	0.1489	W
2 3 24*	0.1449	0.1456	W	2	—	—	—	—	—	—
1 5 1	0.1422	0.1430		0.1	0.1425	0.1428	W	0.1424	0.1423	W
#	—	—	—		—	—	—	0.1410	0.1410	W
3 0 24	0.1389	0.1396	W	0.3	0.1374	0.1397	W	0.1378	0.1380	W

Table 2
Domains of existence of solid solutions versus *n*-tetracosane concentration at 293 K

Molar concentration (% in *n*-C_{24})	Solid solution	Molar concentration (% in *n*-C_{24})	Solid solution
9.95	β''_1	55	β'_1
14.99	β''_1	60.01	β'_1
15.25	β''_1	61	β'_1
15	$\beta''_1+\beta'_1$	63	β'_1
17	$\beta''_1+\beta'_1$	63.25	β'_1
18	$\beta''_1+\beta'_1$	63.53	$\beta'_1+\gamma_0$
20	$\beta''_1+\beta'_1$	63.75	$\beta'_1+\gamma_0$
25	$\beta''_1+\beta'_1$	64	$\beta'_1+\gamma_0$
30	$\beta''_1+\beta'_1$	64.5	$\beta'_1+\gamma_0$
40	$\beta''_1+\beta'_1$	65	$\beta'_1+\gamma_0$
41	$\beta''_1+\beta'_1$	68	$\beta'_1+\gamma_0$
42.5	$\beta''_1+\beta'_1$	70.01	$\beta'_1+\gamma_0$
43	$\beta''_1+\beta'_1$	80	$\beta'_1+\gamma_0$
43.5	$\beta''_1+\beta'_1$	81	$\beta'_1+\gamma_0$
44.01	$\beta''_1+\beta'_1$	82.5	$\beta'_1+\gamma_0$
44.5	$\beta''_1+\beta'_1$	83	$\beta'_1+\gamma_0$
45	$\beta''_1+\beta'_1$	90	γ_0
45.5	$\beta''_1+\beta'_1$	95	γ_0
50	β'_1		

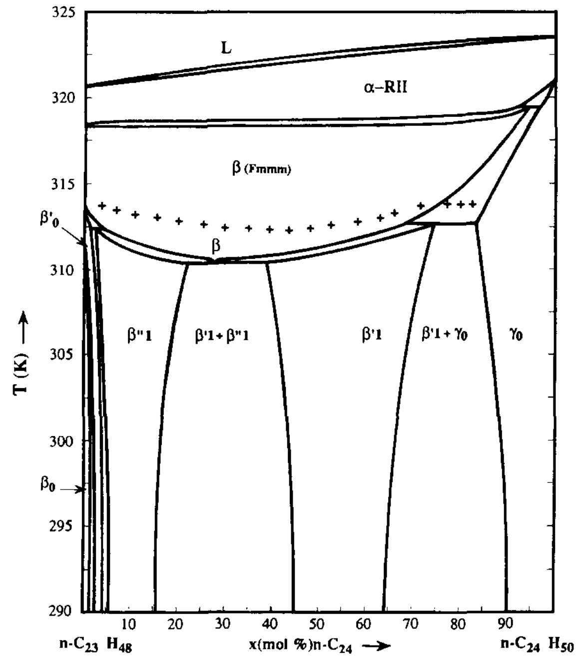

Fig. 3. Corrected phase diagram of *n*-$C_{23}H_{48}$: *n*-$C_{24}H_{50}$ mixtures.

sence of an invariant solid–solid transition. According to the X-ray diffraction experiments, these three mixtures are situated in the two-phase range (Fig. 3) ($\beta''_1+\beta'_1$); thus this invariant transformation is an eutectoïd equilibrium that demonstrates well the existence of the two intermediate phases:

$$\beta''_1+\beta'_1 \rightarrow \beta(\mathrm{Fmmm})$$

5. Conclusion

These joint calorimetric (D.T.A) and structural studies complement the diagram $C_{23}:C_{24}$, determined by Sabour et al. [2], in the concentration range from 10% to 95% molar of C_{24}. They highlight a new intermediate solid solution and confirm that, when the second consecutive C_n (n = even or odd-numbered) concentration increases, the sequence of the first solid phase is the following:

1. from a pure odd-numbered C_{2p+1} : β_0 (C_{2p+1}), β'_0 (C_{2p+1}), β''_1, β'_1;
2. from a pure even-numbered C_{2p} : γ_0 (C_{2p}), β'_1, β''_1.

The results obtained on thirty-nine samples allow to determine the phase diagram of $C_{23}:C_{24}$ mixtures (Fig. 3).

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