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Mixtures of numerous different *n*-alkanes: 1. Structural studies by X-ray diffraction at room temperature—Correlation between the crystallographic long *c* parameter and the average composition of multi-alkane phases

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Abstract

Two quaternary equimolar alloys ($C_{22}/C_{26}/C_{30}/C_{34}$ and $C_{24}/C_{28}/C_{32}/C_{36}$) and three commercial products, which respectively consist of 23 and 33 consecutive *n*-alkanes with chain lengths between 20 and 52 carbon atoms, are studied by X-ray diffraction analyses. A single orthorhombic solid solution, identical to one of the two intermediate phases seen in binary *n*-alkane systems, is observed in two commercial products and in their 50–50 wt% mixture. The *n*-alkane molar concentrations and the long crystallographic *c* parameters have been determined and allow us to demonstrate that the molecule layer stacking periodicity is quasi-equal to the average length of *n*-alkane chains of these complicated mixtures: this periodicity corresponds to that of a hypothetical orthorhombic pure *n*-alkane whose equivalent carbon atom number is quasi-equal to the average carbon atom number of commercial multi-*n*-alkane mixtures. Discontinuous distributions of chain lengths lead to the observation of two or three orthorhombic phases in the quaternary alloys and the presence of an orthorhombic solid solution and of an amorphous solid in the third commercial multi-*n*-alkane product.

Keywords: *n*-alkane; Multi-alkane solid solution; X-ray diffraction

1. Introduction

The crystallization of normal paraffin hydrocarbons in middle distillate fuels and in petroleum cuts has been shown to be at the origin of real problems for refiners and diesel-fuel consumers in very cold regions; thus the normal alkanes and mixtures of 2, 3, 4 and 5 *n*-alkanes have been the subject of many structural and physicochemical investigations [1–41].

Particularly in our laboratory, we are currently pursuing joint thermodynamic and structural studies on the liquid–solid and solid–solid equilibria occurring in pure *n*-alkanes (hereafter denoted by C_n) [42–45], in binary mixtures of consecutive (even: even-numbered) [46–51], (even: odd-numbered) [52,53] and (odd: odd-numbered) [54,55] C_n and in the ternary system ($C_{22}/C_{23}/C_{24}$) [56,57].

From all these results [46–55], Dirand and coworkers [58,59] generalized the thermodynamic and structural behaviour of the binary consecutive C_n systems ($19 < n < 27$) with the following results.

1. At 'room temperature', the existence of two limited terminal solid solutions with the pure C_n structures and many intermediate solid solutions with orthorhombic unit cells as determined by many authors [3,13,20, 31,39,40,46–55,60–64]: in all these binary systems, they are isostructural with two phases only, called β_n' and β_n''; but they are not isostructural with the pure C_n structures nor with their terminal solid solutions.
2. The rules of solid phase sequences when the composition varies.
3. For the two orthorhombic intermediate solid solutions β_n' and β_n'', an identical behaviour to the pure odd-numbered C_{2p+1}, when the temperature increases, with the appearance of 'rotator' states of the phases β-RI and α-RII, whose space groups are (Fmmm) and ($R\bar{3}m$) respectively [9–11].

Nouar and coworkers [56,57] showed that these orthorhombic β_n' and β_n'' intermediate solid solutions are present in the ternary mixtures $C_{22}/C_{23}/C_{24}$ and Clavell-Grunbaum

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et al. [39] highlighted crystalline solid solutions in several equimolar mixtures of 2, 3 and 4 C_n: particularly, they observed orthorhombic (room temperature) and hexagonal (high temperature) structures in quaternary mixtures consisting of C_n with chain length differences of four carbon atoms.

X-ray diffraction patterns of plant waxes, composed of complicated mixtures of aliphatics, esters, ketones, paraffins, fatty acids and fatty alcohols with undetermined compositions, were studied earlier in the literature [60–63]: their structures are lamellar with a single molecule stacking spacing when the wax components have similar chain lengths; if not, several lamellar periodicities appear. The comparison between plant and insect waxes and refined petroleum products was recently made by electron diffraction [40]: however, these refined petroleum products, whose compositions were not defined, were described as an aggregate of five paraffin chain lengths between C_{26} and C_{30}, and the samples that were obtained by evaporation of dilute solutions onto carbon-film-covered electron microscope grids probably do not correspond to the initial and real state of these waxes and petroleum products.

McCrorie [64] also observed a single lamellar spacing in six dental modelling waxes whose main constituents were paraffin wax and beeswax; but the accurate nature of components and the composition of these six waxes were not defined.

Our purpose is:

1. to determine the structural and thermodynamic state of two quaternary molecular alloys ($C_{22}/C_{26}/C_{30}/C_{34}$ and $C_{24}/C_{28}/C_{32}/C_{36}$) and three commercial products which consist of numerous consecutive C_n—23 and 33 *n*-alkanes respectively—with continuous distributions of chain lengths between 20 and 52 carbon atoms and whose concentrations are defined hereafter;
2. to study the influence of the composition on the structural behaviour of mixtures.

2. Experimental method

The *n*-alkanes were purchased from Aldrich Chemical Company: their purity grade is 99 mol% as determined by gas chromatography. The synthesis equimolar samples were prepared by weighing together the solid pure C_n, melting and thorough mixing. Then the homogeneous liquid solution was quenched in a crystallizing dish maintained at a very low temperature in a Dewar vessel with liquid air: the high velocity of the cooling ensured a uniform steric concentration in each solid mixture: then the mixtures were ground in order to obtain a powder for the X-ray analyses.

The X-ray diffraction analyses using a copper anticathode X-beam ($\lambda CuK\alpha$) were carried out on the samples with:

1. a Guinier-de Wolff Nonius camera: the positions of lines were determined with an accuracy of 0.25 mm for distances ranging from 10.5 to 125 mm. The calibration was obtained with spectroscopic pure gold as standard.
2. an X-ray diffractometer (CGR Theta 60): the calibration was carried out with the sample holder which is made of pure copper.

The commercial products were examined in their initial state without any treatment. However, in order to obtain preferential crystallographic orientations and thus to increase the intensity of the diffraction lines (0 0 *l*), some samples were melted and low-cooled on a water surface.

Six samples have been studied with the following notation.

1. Samples 1 and 2: two equimolar mixtures of four C_n, respectively $C_{22}/C_{26}/C_{30}/C_{34}$ and $C_{24}/C_{28}/C_{32}/C_{36}$.
2. Samples 3 and 4: two commercial products, purchased from PROLABO, respectively called paraffin 52–54°C and 60–62°C.
3. Sample 5: a 50–50 wt% mixture of the two commercial products (Sample 3 + Sample 4).

Table 1
Mol% concentrations of multi-C_n Samples 3, 4 and 5: Sample 5 is a 50–50 wt% mixture of commercial products 3 and 4 and their molar fractions in mixture 5 are $x_3 = 0.576$ and $x_4 = 0.424$ respectively

	Sample 3 (mol%)	Sample 4 (mol%)	Sample 5 (mol%)
C20	0.070	0.038	0.056
C21	0.812	0.182	0.0546
C22	4.778	0.678	3.046
C23	13.057	2.078	8.419
C24	20.360	4.254	13.556
C25	18.464	6.594	13.450
C26	14.594	8.476	12.009
C27	9.236	10.615	9.819
C28	6.568	11.756	8.760
C29	4.682	11.722	7.656
C30	3.351	10.376	6.318
C31	2.051	8.807	4.905
C32	1.050	6.702	3.438
C33	0.424	5.072	2.388
C34	0.198	3.572	1.623
C35	0.104	2.594	1.156
C36	0.062	1.831	0.809
C37	0.045	1.419	0.626
C38	0.030	1.039	0.456
C39	0.029	0.639	0.286
C40	0.014	0.489	0.215
C41	0.014	0.318	0.142
C42	0.007	0.246	0.108
C43	–	0.161	0.068
C44	–	0.113	0.048
C45	–	0.068	0.029
C46	–	0.058	0.025
C47	–	0.033	0.014
C48	–	0.024	0.010
C49	–	0.016	0.007
C50	–	0.015	0.006
C51	–	0.008	0.003
C52	–	0.007	0.003

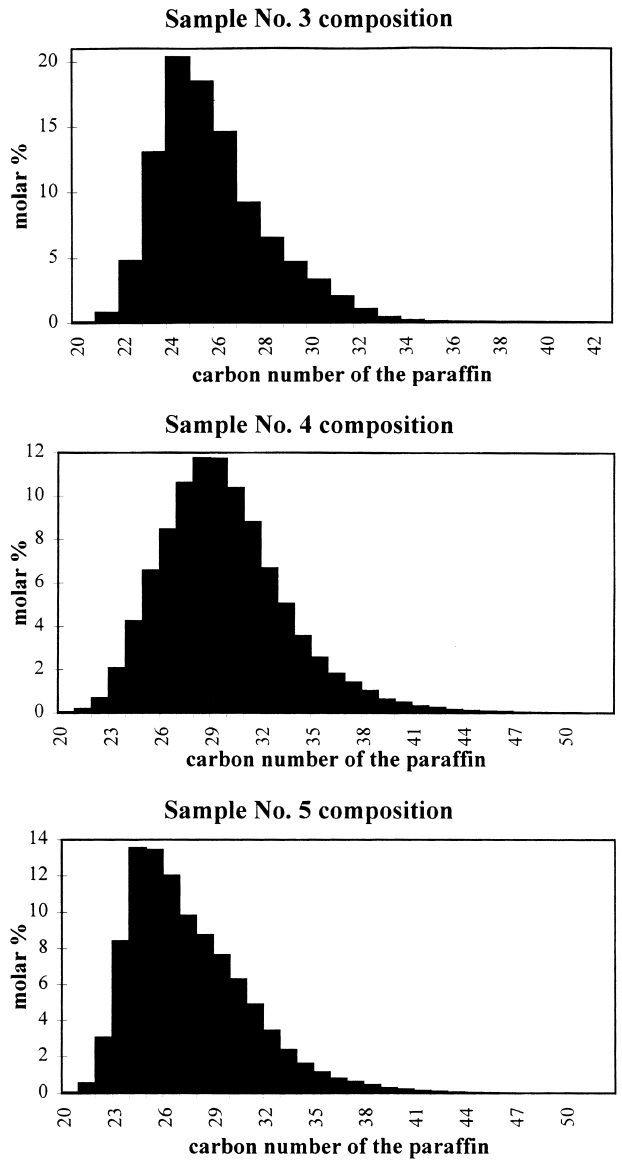

Fig. 1. Concentration distributions of *n*-alkanes in commercial products 3 and 4 and in their 50–50 wt% mixture (Sample 5).

4. Sample 6: a dental modelling wax, purchased from Dentaurum Company: the maquettes of this wax are used for the mould production of prosthondontics.

The *n*-alkane concentrations of samples 3, 4 and 5 were determined by gas chromatography: they are shown in Table 1 and Fig. 1. Sample 6 consists mainly of C_n, as observed by gas chromatography (Fig. 2) and mass spectrography.

3. Results

The experiments, carried out on each sample by X-ray diffraction analyses (Fig. 3), show characteristic diffraction peaks of orthorhombic solid solutions as observed for the β_n' and β_n'' orthorhombic intermediate phases of binary [3,13,20,31,39,47–55] and ternary [56,57] alloys of C_n. The examination of diffractograms leads to the following results.

1. Two and three families of diffraction lines (0 0 *l*) are respectively observed in the region of small Bragg's angles for two quaternary equimolar mixtures 1 and 2 ($C_{22}/C_{26}/C_{30}/C_{34}$ and $C_{24}/C_{28}/C_{32}/C_{36}$): they respectively define two and three crystallographic long *c* parameters, and thus these results show the presence of two orthorhombic solid solutions (Fig. 3c) in Sample 1 and three orthorhombic phases in Sample 2 (Fig. 3d) as observed by Clavell-Grunbaum et al. [39].
2. A single series of diffraction peaks (0 0 *l*) appears on the diffractograms (Fig. 3e, f and g) of commercial multi-C_n products 3,4 and 5: this observation demonstrates the existence of a single molecule layer stacking periodicity along the long *c*-axis and thus the presence of a single orthorhombic crystalline phase in these multi-C_n products which have a continuous and regular distribution of these numerous consecutive C_n ($19 < n < 53$), (Table 1, Fig. 1).
3. An amorphous solid and an orthorhombic crystalline phase are both present in dental modelling wax Sample 6 (Fig. 3h) where the distribution of consecutive C_n is not regular: the concentrations of even-numbered C_{2p} are higher than those of odd-numbered C_{2p+1} (Fig. 2).

4. Discussion

The orthorhombic phases, which are observed in two quaternary equimolar mixtures, Samples 1 and 2, are necessarily intermediate solid solutions, since the crystalline structures of pure even-numbered C_{2p}, of which they are composed, are triclinic or monoclinic [1–8].

It is possible to establish a relation between the average composition in C_n of all the commercial products studied here and the crystallographic long *c* parameter of these multi-C_n orthorhombic solid solutions, using the following linear expression (Fig. 4):

$$c(\text{nm}) = 0.2545n + 0.3842$$

with a correlation factor $R^2 = 0.9993$

where *c*(nm) is the crystallographic *c* parameter (in nm) of the pure C_n whose unit cells are orthorhombic, and *n* is the atom carbon number of the pure C_n chain.

This linear variation expression of the crystallographic *c* parameter in the function of the carbon atom *n* number has been determined by optimization from the structural literature data on pure C_n whose unit cells are orthorhombic ($12 < n < 61$) (Fig. 4).

The crystallographic *c* long parameter of each multi-C_n mixture is associated with a chain length of a hypothetical orthorhombic pure C_n whose equivalent carbon atom $\bar{n}_c$

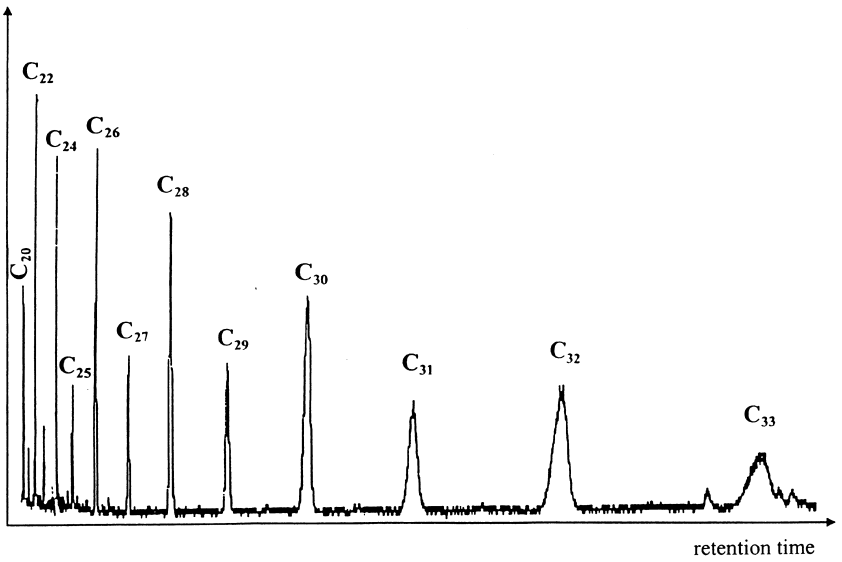

Fig. 2. Dental modelling wax 6: the gas chromatography analysis shows that the even-numbered C_{2p} concentrations are higher than those of odd-numbered C_{2p+1}.

number is calculated from this linear variation equation:

$$\text{For Sample i}: \quad \bar{n}_{ci} = \frac{c_i(\text{nm}) - 0.3842}{0.2545}$$

Table 2 compares the equivalent carbon atom $\bar{n}_{ci}$ number, calculated from the experimental values of c_i parameters of multi-C_n orthorhombic solid solutions, to the medium carbon atom $\bar{n}_i$ number obtained from the x_n molar fractions of C_n which are determined by gas chromatography analyses in the commercial products (Table 1, Fig. 1):

$$\bar{n}_i = \sum_{n=20}^{n_{\max}} x_n \cdot n$$

where x_n is the molar fraction of each C_n contained in Sample i ($19 < n < n_{\max}$), $n_{\max}$ is the carbon atom number of the longer C_n chain in commercial multi-C_n product i (Table 1).

4.1. Notable observations:

1. As in the binary and ternary molecular alloys of C_n [47–59], the molecule layer stacking periodicity of this multi-C_n β' solid solution is equal to the average length of C_n chains of Samples 3, 4 and 5 with an excess value of around 1.5 carbon atoms (Table 2): the experimental establishing of both the multi-C_n mixture composition (Table 1) and the crystallographic *c* parameter (Table 2) allows us to prove the literature assumptions[64]. All these experimental results and those of Clavell-Grunbaum et al. [39] do not agree with the hypothesis of Gerson and Nyburg [31] and Dorset [40] who claimed that the molecules are rigid in the unit cell of mixtures of 2 and 5 C_n respectively and suggested a model with a lamellar stacking spacing equal to the length of the longer chain. In fact, Clavell-Grunbaum et al. [39] showed by Raman and infrared spectroscopy that the longer C_n are flexible near their chain end in mixtures of 2, 3 and 4 C_n.
2. Sample No. 5, which is a 50–50 wt% mixture of commercial products 3 and 4, also forms a single orthorhombic solid solution: its stacking periodicity corresponds to a chain length of 28.6(5) carbon atoms (Table 2); it is equal to the average of the stacking periodicities of Samples 3 and 4 with an excess value of 0.15, calculated as follows:

$$[0.576 \cdot \bar{n}_{c3} + 0.424 \cdot \bar{n}_{c4} = 28.5]$$

Table 2
Comparison between the equivalent carbon atom number, calculated from the equation [(c_i(nm) − 0.3848)/0.2545], and the medium carbon atom $\bar{n}$ number, obtained from C_n concentrations of mixtures (Table 1)

Mixture *i*	c_i(nm)[a]	$\bar{n}_{ci} \pm 0.5$[a]	$\bar{n}_i$	$\Delta n = \bar{n}_c - \bar{n}$
1	6.91 8.00	25.6 30	28	Two phases
2	7.35 8.41 9.29	27.4 31.5 35	30	Three phases
3	7.14	26.5	25.5	1
4	8.33	31.2	29.4	1.8
5	7.67	28.65	27.15	1.5

[a]In view of reflection (0 0 *l*) overlaps (Fig. 3c–d), the relative uncertainty in *c* parameter and equivalent carbon number determination is evaluated at 3% for multi-phase mixtures 1 and 2

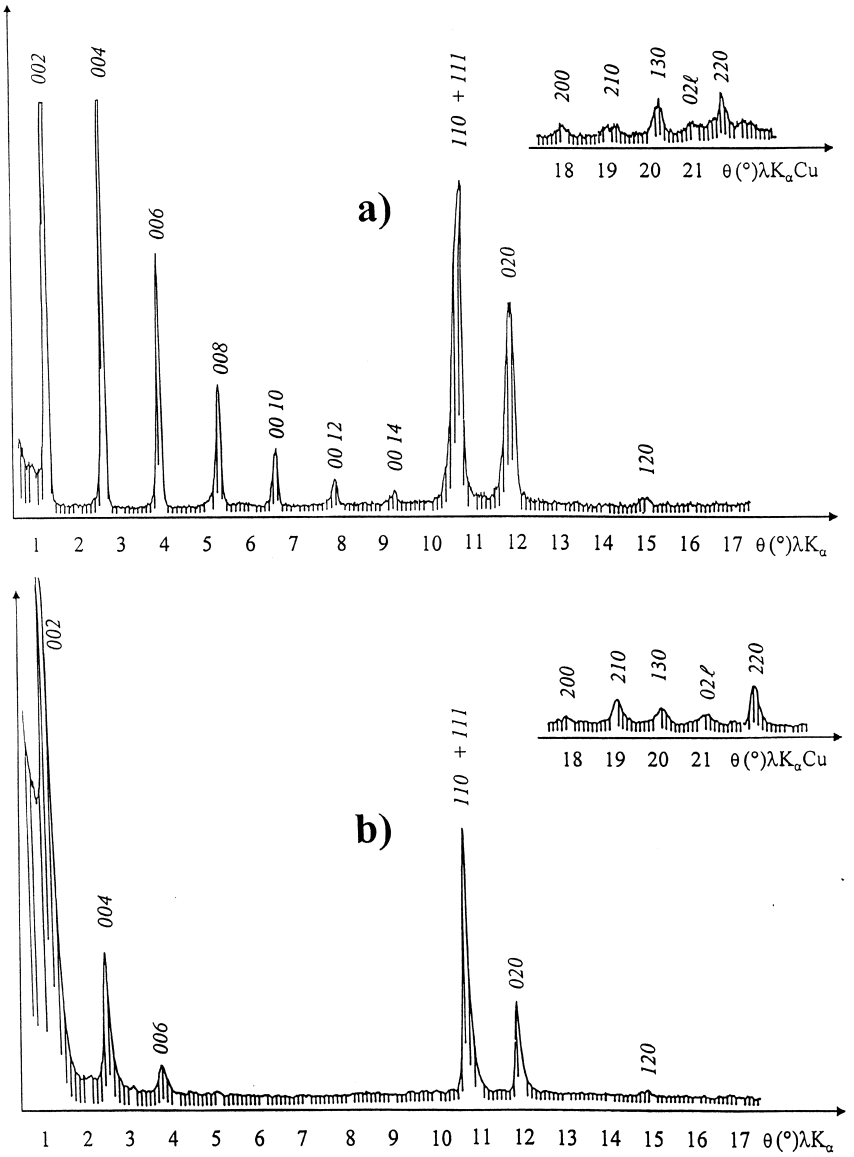

Fig. 3. X-ray diffractogramms (λCuKα) which shows: (i) the structural identity between the orthorhombic β_2' intermediate solid solution of the binary mixture (C_{23}: 85 mol% C_{25}) (a), and the orthorhombic solid solution, observed for multi-C_n mixture 3 (b); (ii) two and three families of diffraction lines (0 0 *l*), for quaternary equimolar mixtures 1 (c) and 2 (d) respectively; (iii) a single series of peaks (0 0 *l*), for multi-C_n samples 3 (e), 4 (f) and 5 (g); (iv) the presence of an orthorhombic phase and of an amorphous solid in dental modelling wax 6 (h).

NB: 0.576 and 0.424 are the molar fractions of Samples 3 and 4 in mixture 5 respectively (Table 1).

These excess values are certainly due to the conformational disorder of chain stacking in the multi-C_n orthorhombic solid solutions as described by Clavell-Grunbaum et al. [39]: the equivalent carbon atom $\bar{n}_c$ number of the multi-C_n phase, which is determined from the crystallographic *c* parameter, defines the space between the molecule stacking crystalline planes; the C_n chains whose carbon atom *n* numbers are greater than $\bar{n}_c$ must bend to insert themselves between these crystalline planes (Fig. 5): these bends of longer molecules probably generate disturbances in the interface regions of chain stacking layers.

4.2. Influence of the distribution, the composition and the chain length differences of C_n

When the distribution of consecutive C_n is discontinuous in multi-C_n products, as in Sample 6, or when the mixtures consist of non-consecutive C_n with too-major chain length differences (four carbon atoms in Samples 1 and 2, for instance), the crystalline unit cell cannot adapt to all these gaps; in this case it is difficult to obtain a single solid solution:

1. For Sample 6, the even-numbered C_{2p}, in excess in relation to the distribution of the odd-numbered C_{2p+1}

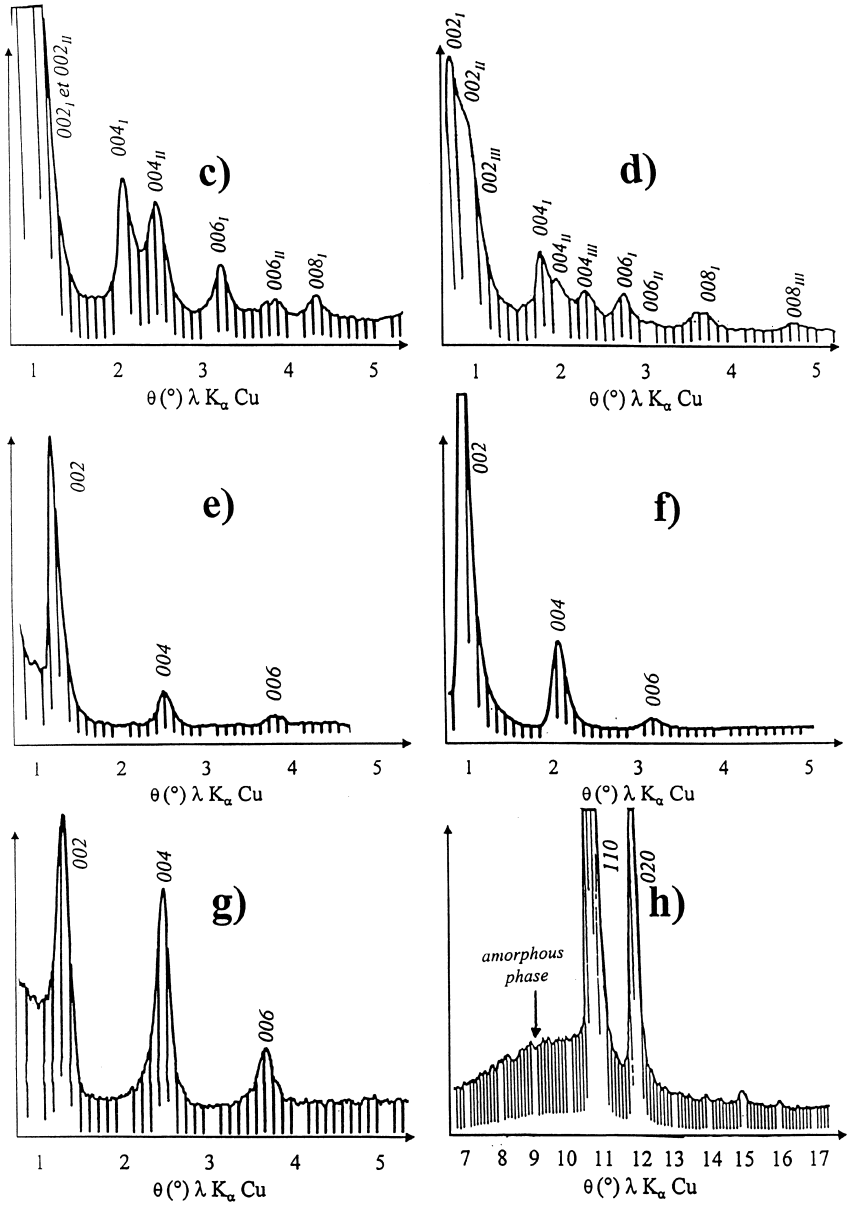

Fig. 3. *continued*.

(Fig. 2), are not present in the orthorhombic solid solution and their distribution is not a continuous sequence of consecutive C_n with a difference of 1 carbon atom: this excess amount of C_{2p} forms the amorphous solid.

2. For Samples 1 and 2, with chain length differences of four carbon atoms, the system respectively generates two and three orthorhombic solid solutions, as observed in binary or ternary mixtures [20,39,47–59], according to Gibbs' thermodynamic law about phase equilibria. These two quaternary mixtures have two or three different molecule stacking identity *c* periods which adapt to these major chain length differences.

For quaternary equimolar mixture 1, Table 2 shows the *c* parameter lengths of the two orthorhombic phases, called Phase I and II, and their corresponding equivalent carbon atom $\bar{n}_{cI}$ and $\bar{n}_{cII}$ numbers (Table 2). The molar ratio of these two phases can be evaluated from these respective $\bar{n}_c$ values, which represent the average composition of each phase, and from the medium carbon atom $\bar{n}$ number of the mixture which corresponds to the overall composition of Sample 1, using the thermodynamic rule of the barycentre:

$$x_{\mathrm{I}} = \frac{\bar{n}_{c\mathrm{II}} - \bar{n}}{\bar{n}_{c\mathrm{II}} - \bar{n}_{c\mathrm{I}}} = \frac{30 - 28}{30 - 25.6} \cong 0.45$$

This x_{I} value is only a rough estimate because the $\bar{n}$ value corresponds to the average carbon atom number of Sample 1 and the $\bar{n}_{cI}$, $\bar{n}_{cII}$ values to the equivalent carbon atom number of Phases I and II with an excess value that should be determined to obtain a correct value of x_{I}. But to a first approximation, the majority phase in mixture 1 is Phase II

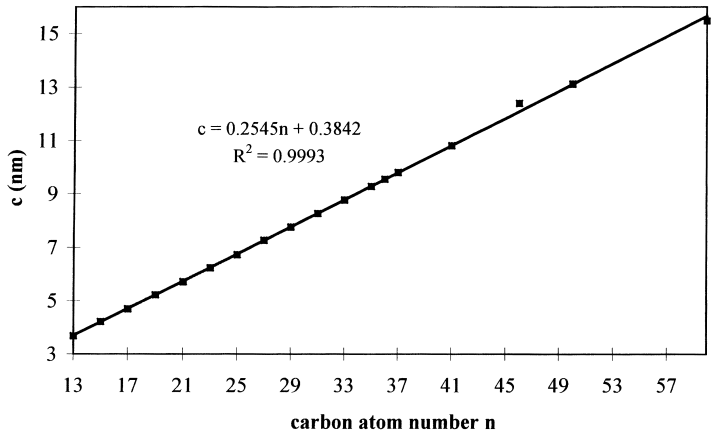

Fig. 4. Plot of the variations of crystallographic *c* parameters *versus* carbon atom *n* number of pure C_n chains which have an orthorhombic unit cell [1–6].

whose molecule layer stacking periodicity is higher than that of Phase I.

5. Conclusion

The X-ray diffraction analyses lead to the following notable observations.

1. The numerous *n*-alkanes—respectively 23 and 33 C_n with chain lengths between C_{20} and C_{52}—form a single orthorhombic solid solution in two commercial products 3 and 4 and their 50–50 wt% mixture 5 where the distributions are continuous and regular (Fig. 1a, b and c): its structure is identical to the β' orthorhombic intermediate phase of binary and ternary molecular alloys of consecutive C_n [13,20,31,39,47–59].
2. Like the pure orthorhombic odd-numbered C_{2p+1}, this multi-C_n solid solution presents a single lamellar structure of molecule layer stacking. The establishing of both the average molar composition and the values of the crystallographic long *c* parameter allows us to demonstrate that the stacking identity *c* period of this lamellar structure corresponds to a chain length of a hypothetical orthorhombic C_n whose carbon atom number is equal to the average carbon atom number of the multi-C_n mixture with an excess value of around 1.5 carbon atoms. MacCrorie [64] only assumed that this relation existed between the long *c* parameter and the average composition of dental modelling waxes, because he did not know the formulae of components nor their accurate concentration.
3. This periodicity does not correspond to the length of the longer chain as suggested by Gerson and Nyburg [31] and Dorset [40] for mixtures of 2 or 5 C_n, but to the average length of chains, and thus the longer chains must bend to insert themselves between molecule layer stacking crystalline planes and must find a smaller partner in order to maintain a coherent molecule layer (Fig. 5) and form a single solid solution.

However, if the distribution of C_n chain lengths is discontinuous with considerable length differences, as observed in the two quaternary mixtures of non-consecutive

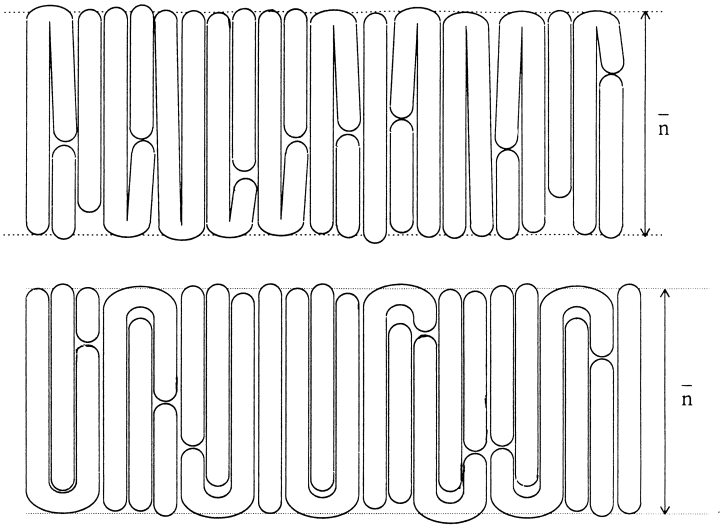

Fig. 5. Probable configurations of C_n molecules in packing layers of the multi *n*-alkane solid solution: more accurate techniques must be used to confirm them.

C_n, or with fluctuations of concentrations, as between the even-numbered and odd-numbered C_n amounts in commercial multi-C_n product 6, certain molecules do not find partners and the system adapts creating either two or three orthorhombic solid solutions in the first two cases or an amorphous solid in the last example where there are too many 'unmarried' molecules with multi-length chains.

The X-ray diffraction allows the observation of the very complicated mixtures of C_n without any modifications of their natural state and leads to statistical and overall structural information on the whole sample; it also demonstrates its interesting applications in the analytical determination of the average concentration of mixtures and of the proportion of solid phases. However, the molecule configurations (Fig. 5) and the atomic occupancies will have to be confirmed from natural samples by more accurate diffraction and spectroscopy techniques, as described in the literature [20,28,29,31,39,40].

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