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# Structural behaviour of molecular alloys: *n*-pentacontane ($n$-$C_{50}H_{102}$)–*n*-pentacosane ($n$-$C_{25}H_{52}$); *n*-pentacontane ($n$-$C_{50}H_{102}$)–*n*-tricosane ($n$-$C_{23}H_{48}$) at room temperature

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**Abstract**

This paper displays a study of binary mixtures of *n*-alkanes whose ratio of chain length is around two. The systems composed of *n*-tricosane ($n$-$C_{23}H_{48}$)–*n*-pentacontane ($n$-$C_{50}H_{102}$) and *n*-pentacosane ($n$-$C_{25}H_{52}$)–*n*-pentacontane ($n$-$C_{50}H_{102}$) have been studied by means of X-ray analyses. These latter, performed at room temperature, showed in both cases, the existence of a large domain where the phases characteristic of each pure component coexist. These mixtures obey Kravchenko's rule relative to the solubility of the *n*-alkanes according to the chain length of each component. The mixtures studied do not form an intermediate solid solution. In other words, there is no particular arrangement of the shorter molecules inside the crystallographic unit of the longer. © 2001 Elsevier Science Ltd. All rights reserved.

*Keywords*: *n*-Alkanes; Molecular alloys; X-ray analyses

## 1. Introduction

In the exploitation and transportation of paraffinic crude oils, accumulation of waxy deposits is a commonly occurring problem. In order to limit the undesirable effects, addition of chemical agents, scrapping or heat tracing of flowlines are commonly used. Nevertheless, these actions increase production costs. In these conditions, studies of behaviour of *n*-alkanes (hereafter noted $C_n$) and their mixtures in the solid state [1–14] and in solvents [15–19] are necessary in order to elaborate thermodynamic models.

Müller and Saville [1] carried out the first structural study on normal alkanes. Since then, their crystalline structures have been the subject of several publications in the literature in particular Turner [2], Heyding et al. [3], Gerson et al. [4], Craig et al. [5] and Srivastava et al. [20] which present exhaustive monographs and results.

Concerning normal alkane mixtures, there is in the literature a rule that states precisely the nature of the mixture: continuous solid solution, eutectic type or no miscible solids, according to the molecular length difference of the components. It is Kravchenko's rule [21]. Precisely, this rule indicates that the mixture of two *n*-alkanes lead to a continuous solid solution when the difference in molecular length ($[n' - n]/n'$, $n$ and $n'$ symbolise the carbon atom number of each *n*-alkane) is inferior to 5–6%; to an eutectic type system when this difference is higher than 15%. Between these two extremes, the author recommends further experimental precisions. Obviously, this rule supposes that the crystallographic systems are identical, in agreement with Palatnik and Landau's [22] law.

The case of the binary systems for which the difference in molecular chain length of the *n*-alkanes is in the range of 6–15%, is largely reported in the literature [6–9]. The aim of these articles is to establish the binary [23–29] or ternary [30,31] phase diagrams. These works show at room temperature, the existence of several intermediate solid solutions which are isostructural to phases generally called $\beta'_n$ or $\beta''_n$ (with index $n$ identifying the isostructural phases of different stoichiometries in the same binary system).

It is clear that Kravchenko's [21] rule is linked to a dimensional factor. Nevertheless, the situation in which two *n*-alkanes present the orthorhombic structure but a molecular length ratio of about two, has never been studied.

The purpose of this paper is to present the experimental results of a structural study relative to two systems associating $C_{50}$ with $C_{25}$ or $C_{23}$. The aim is to determine the stacking

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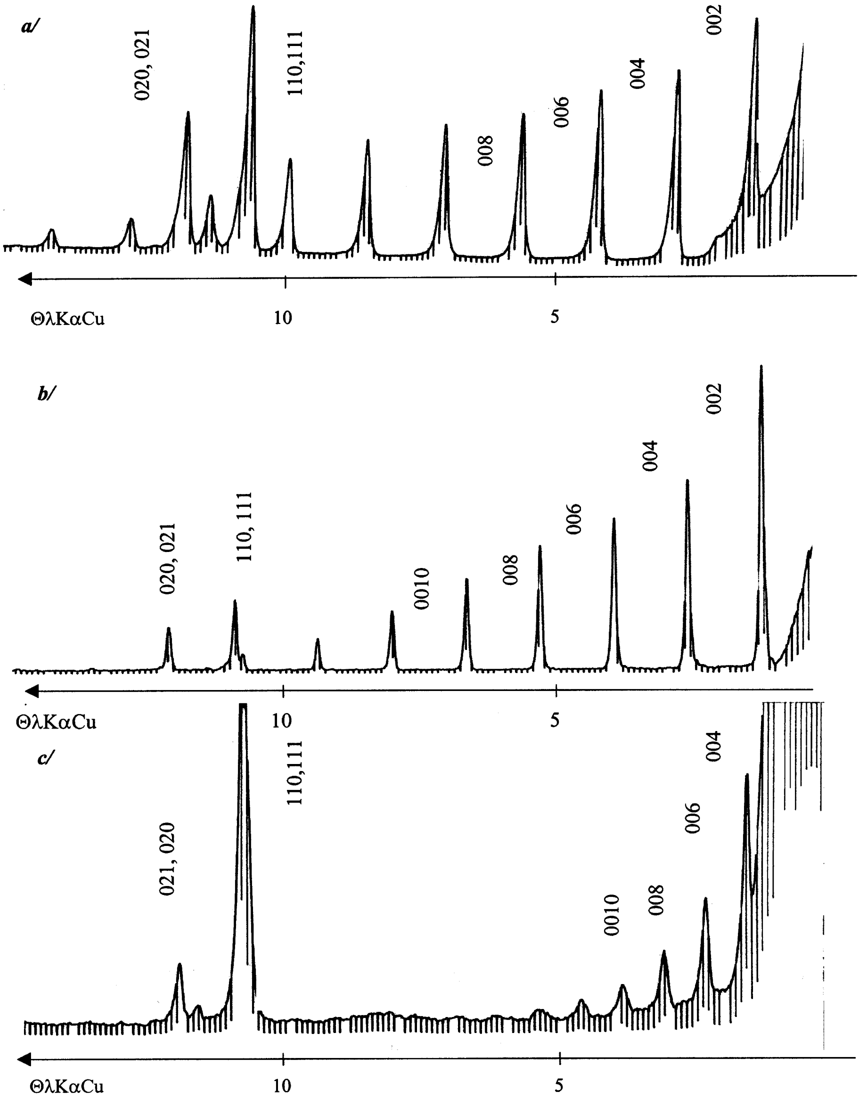

Fig. 1. (a) Diffractogram of pure *n*-tricosane ($C_{23}$), (b) *n*-pentacosane ($C_{25}$) and (c) *n*-pentacontane ($C_{50}$) prepared by fusion and low cooled upon a water surface and examined according to a reflection method, at room temperature.

arrangement of the shortest molecules into the crystallographic unit of the longest.

## 2. Experimental method

All pure components come from the Aldrich Chemical Company. Their purity grades are given as over 99%. These values were confirmed by gas chromatography and mass spectrometry analyses. The *n*-alkane mixtures were obtained by quenching, in nitrogen liquid of molten mixtures previously obtained by weighing each component in the appropriate proportions. Such rapid cooling ensured a uniform steric concentration of components in the mixture and homogeneity of the final molecular alloy.

The systems were studied by means of X-ray diffraction, at room temperature. Diffractograms were obtained with a counter diffractometer using $\lambda_{K\alpha}$ copper radiation. Samples were prepared by melting and cooling on a water surface in order to obtain preferential crystallographic orientations. Samples thus obtained, can be examined according to a reflection or a transmission method. This first makes it possible to determine the number of phases contained in the molecular alloy and then allows to calculate with a good accuracy the $c$ parameter of each one of them since the $00\ell$ reflections intensities are increased. Examination according to a transmission method leads to the determination of $a$, $b$ crystallographic parameters.

## 3. Results and discussion

The samples examined by means of X-ray diffraction were prepared according to the method previously detailed.

Firstly, the pure components ($C_{23}$, $C_{25}$ and $C_{50}$) were examined according to the reflection method, at room temperature (Fig. 1). Examination of the X-ray patterns shows many $00\ell$ reflections, allowing calculation of the *c* parameter with a good accuracy. The *c* parameters of these *n*-alkanes are respectively 6.220, 6.742, 11.618 nm for the $C_{23}$, $C_{25}$ and $C_{50}$. The values characteristic of the tricosane and pentacosane are in a good agreement with the data of the literature [5]. As concerns the pentacontane, the *c* parameter calculated seems to indicate that $C_{50}$ crystallises in the orthorhombic structure of space group Pbca as $C_{38}$, $C_{40}$ and $C_{44}$.

The *a* and *b* parameters have been determined from the diffractograms of the samples examined according to a transmission method. The values obtained are respectively for $C_{23}$, $C_{25}$ and $C_{50}$ of 0.495, 0.498, and 0.496 nm for the *a* parameter and of 0.747, 0.748, and 0.744 nm for *b*. These data are in good agreement with those reported in the literature [5].

Now, let us examine the results of the X-ray analyses obtained with molecular alloys composed of $C_{50}$ and $C_{25}$. The ratio of carbon atom number is equal to $n_{C_{50}}/n_{C_{25}} = 2$ and the ratio of unit cell volumes is $V(C_{50})/V(C_{25}) = 1.94$ according to Ref. [5]. So, a particular arrangement of the shorter molecules inside the unit cell of the longer can be imagined. This situation should provoke an increase of the solubility of $C_{25}$ in $C_{50}$ or a stabilisation of a long-range order phase. In order to verify these assumptions, molecular alloys whose compositions range from 0 to 100% molar in $C_{50}$ were examined by X-ray diffraction at room temperature. Table 1 reports the composition of the molecular alloys studied and Fig. 2 presents the *c* parameter evolution versus molar concentration in $C_{50}$. Examination of the graph leads to important remarks:

Table 1
Composition of the molecular alloys composed of *n*-pentacosane and *n*-pentacontane studied by means X-ray diffraction

| Composition in % molar in $C_{50}$ | Phases observed |
|---|---|
| 0 | $\beta_0(C_{25})$ |
| 2.11 | $\beta_0(C_{25})$ |
| 5.00 | $\beta_0(C_{25})$ |
| 6.27 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 7.93 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 10.73 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 14.88 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 22.6 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 25.05 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 49.03 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 75.60 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 78.92 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 81.10 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 84.60 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 85.75 | $\beta_0(C_{25}) + \beta_0(C_{50})$ |
| 88.50 | $\beta_0(C_{50})$ |
| 93.00 | $\beta_0(C_{50})$ |
| 100 | $\beta_0(C_{50})$ |

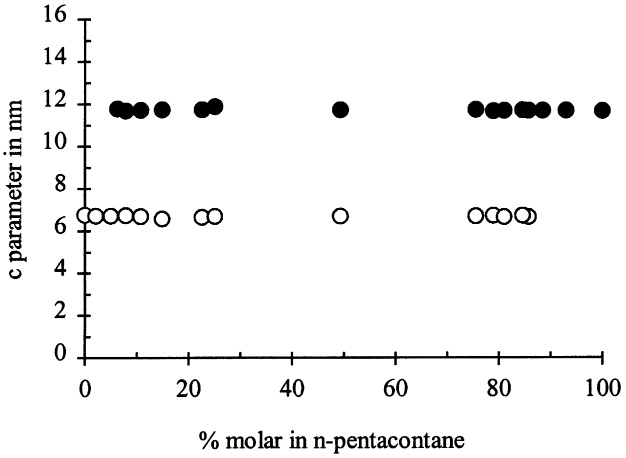

Fig. 2. Evolution of the *c* parameter versus composition of binary mixtures composed of *n*-pentacosane ($C_{25}$)–*n*-pentacontane ($C_{50}$).

1. There is a large composition domain in which two series of $00\ell$ reflections are observed. These reflections are characteristic of both pure components: $C_{25}$ and $C_{50}$. Existence of the domain where two phases coexist is in agreement with Kravchenko's [21] rule. In fact, the ratio of molecular length is largely superior to the value of 15%, value for which a eutectic type system must be observed. The phase appearance sequence at room temperature versus the $C_{50}$ concentration is then:

   $\beta_0(C_{25})/[\beta_0(C_{25}) + \beta_0(C_{50})]/\beta_0(C_{50})$

   Nota Bene: the symbol β represents an orthorhombic phase and the index 0 corresponds to the pure component.
2. The second remark concerns the solubility of these components. Examination of Table 1 shows that the terminal solid solution $\beta_0(C_{25})$ is stable between 0 and 5% in molar in $C_{50}$ and the one characteristic of *n*-pentacontane ($\beta_0(C_{50})$) is stable between 88.5 and 100% molar in $C_{50}$. These results indicate a large domain in which the two phases ($\beta_0(C_{25}) + \beta_0(C_{50})$) coexist. The solubility of the shorter molecule inside the unit crystallographic cell of the longer is then higher than the opposite. Such observations have been made previously [23–25,30,31] on the binary mixtures. These observations must be to correlate with the results of a recent study [32] in which the authors have studied long *n*-alkanes ($C_{210}$ and $C_{198}$) by means real-time LAM spectroscopy and SAXS and have shown particular reorganisations of the chains in the crystal.

In short, this study indicates that there is no particular arrangement of the molecule inside the crystallographic unit cell of $C_{50}$. In other words, *n*-alkane mixtures do not lead to a long-range order in contrast to that observed in several metal alloys.

Nevertheless, the system $C_{25}/C_{50}$ does not constitute the best example for such study. In fact, there is a shorter

Table 2
Composition of the molecular alloys composed of *n*-tricosane and *n*-pentacontane studied by means X-ray diffraction

| Composition in % molar in $C_{50}$ | Phases observed |
|---|---|
| 0 | $\beta_0(C_{23})$ |
| 5.01 | $\beta_0(C_{23})$ |
| 7.70 | $\beta_0(C_{23})$ |
| 8.07 | $\beta_0(C_{23})$ |
| 11.78 | $\beta_0(C_{23})$ |
| 13.45 | $\beta_0(C_{23})$ |
| 15.58 | $\beta_0(C_{23}) + \beta_0(C_{50})$ |
| 20.40 | $\beta_0(C_{23}) + \beta_0(C_{50})$ |
| 24.40 | $\beta_0(C_{23}) + \beta_0(C_{50})$ |
| 75.18 | $\beta_0(C_{23}) + \beta_0(C_{50})$ |
| 88.5 | $\beta_0(C_{23}) + \beta_0(C_{50})$ |
| 89.25 | $\beta_0(C_{50})$ |
| 92.32 | $\beta_0(C_{50})$ |
| 100 | $\beta_0(C_{50})$ |

*n*-alkane than $C_{25}$ crystallising in the orthorhombic system: $C_{23}$. The ratio of carbon atom number is then equal to $n_{C50}/n_{C23} = 2.17$ that corresponds to a ratio of unit cell volume [5] $V(C_{50})/V(C_{23}) = 2.10$. This value indicates that two molecules of $C_{23}$ represent roughly the length of one molecule of $C_{50}$. In these conditions, a long-range order in $C_{23}/C_{50}$ molecular alloys can be expected.

X-ray analyses were realised on molecular alloys with compositions ranging from 0 to 100% molar in $C_{50}$ (Table 2). Measurements of interplanar distances of the $00\ell$ reflections and the calculation of *c* parameters gave the results presented on Fig. 3. It appears that the terminal solid solution $\beta_0(C_{23})$ is stable in the domain ranging from 0 to 13.45% molar in $C_{50}$ and this of $\beta_0(C_{50})$ between around 89.25 and 100% molar in $C_{50}$. These results carried out a large domain in which the two terminal solid solutions $[\beta_0(C_{23}) + \beta_0(C_{50})]$ coexist. In conclusion, no particular arrangement of $C_{23}$ molecules inside the unit cell of $C_{50}$ is observed as earlier.

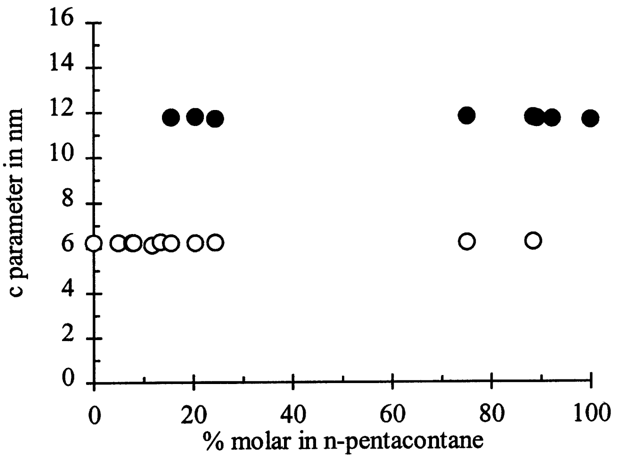

Fig. 3. Evolution of the *c* parameter versus composition of binary mixtures composed of *n*-tricosane ($C_{23}$)–*n*-pentacontane ($C_{50}$).

## 4. Conclusion

Study of the systems $C_{25}$–$C_{50}$, and $C_{23}$–$C_{50}$ have shown at room temperature, no particular organisation of the shorter molecules ($C_{23}$ or $C_{25}$) inside the unit crystallographic cell of $C_{50}$. This observation corroborates Kravchenko's results [21] which indicate that mixtures of *n*-alkanes whose difference in molecular length is higher than 15%, lead to a eutectic diagram. Moreover, it emerges that such molecular alloys do not crystallise in a superlattice, no long-range order is observed in the systems: $C_{25}/C_{50}$ and $C_{23}/C_{50}$. The binary phase diagrams correspond certainly to eutectic-type systems.

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