

## Powder XRD investigations on $n\text{-C}_{32}\text{H}_{66}$ : $n\text{-C}_{16}\text{H}_{34}$ hydrocarbon mixtures

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**Abstract.** Powder XRD of dotriacontane and hexadecane hydrocarbon mixtures was made. The patterns were analysed and phase behaviour recorded. Results were interpreted based on the concept of phase separation.

**Keywords.** Powder XRD investigations;  $n\text{-C}_{32}\text{H}_{66}$  :  $n\text{-C}_{16}\text{H}_{34}$  hydrocarbon mixtures.

### 1. Introduction

Vera Daniel (1953) reviewed the structure, bonding and disorder in long chain molecular crystals. Turner (1971) published a detailed review on hydrocarbons and their binary mixtures. Boistelle (1980) reviewed the crystallography and crystallization related topics and Wesolowski (1981) reviewed applications of DTA, TC and dilatometry. Srivastava *et al* (1993) reviewed DSC, dilatometry, IR spectroscopic and XRD studies on  $n$ -alkanes and their binary mixtures. Among the literature that was surveyed in the present study, it appeared that investigations were basically made on binary mixtures, where the pair of hydrocarbons employed had a small chain length difference.

It was our aim to look at binary mixtures, where the components have a considerable chain length difference, such that one of the two compounds (of short chain length, yet non-volatile) plays three different roles (as its concentration in the mixture increases): (a) phase promotor, (b) component of binary mixture and (c) solvent. The final aim of the study was to look at the phase behaviour and first order phase transitions. Some results on phase behaviour are presented in the present report.

### 2. Materials and methods

Fluka made linear chain saturated hydrocarbons, dotriacontane ( $n\text{-C}_{32}\text{H}_{66}$ ) and hexadecane ( $n\text{-C}_{16}\text{H}_{34}$ ) having purity better than 98% were used in the present investigations. Dotriacontane and hexadecane shall be referred to as C32 and C16, respectively in this report. The pure as-received sample of C32 shall be referred to as pure C32.

Five different mixtures were prepared by mixing weighed quantities of C32 to weighed quantities of C16 in molar ratio. The samples were heated to a temperature of about 10°C above the melting point of C32 and slowly cooled to ambient temperature. Powder XRD patterns were recorded after some ageing, employing a computer interfaced Jeol Powder X-ray Diffractometer, using  $\text{CuK}\alpha$  radiation;  $\lambda = 1.5418 \text{ \AA}$ . Potential was 40 kV at 20 mA current. The  $d$  values were computer evaluated with the input of  $2\theta$  values of peaks, selected by the usual cursor movement procedure.

All print-outs of the XRD patterns were set to have the same values of counts ( $y$ -axis) and angle  $2\theta$  ( $x$ -axis), so that comparison of patterns could be relatively error free.

#### 2.1 XRD pattern analysis

Attention was given to the two regions in the XRD patterns. Existence of region I was noticed even in the case of pure C32 (figure 1a). Whereas, region II was noticed in the XRD patterns of C32–C16 mixtures (figure 1b). In all the patterns, area in region I was measured. The differential areas (difference between the area of region I of XRD pattern of any mixture and region I of XRD pattern of pure C32 sample) were plotted against the concentration of C32 in C16 (figure 2a); it was noticed that area of region I on an average increased with fall of concentration of C32 in C16.

We tried to find a relation between the concentration of C32 in C16 and area of region I. It was noticed that an empirical equation could be written down in the following form:

$$A = C e^{(KC^{-1/3})},$$

where  $A$  and  $C$  represented area and molar concentration

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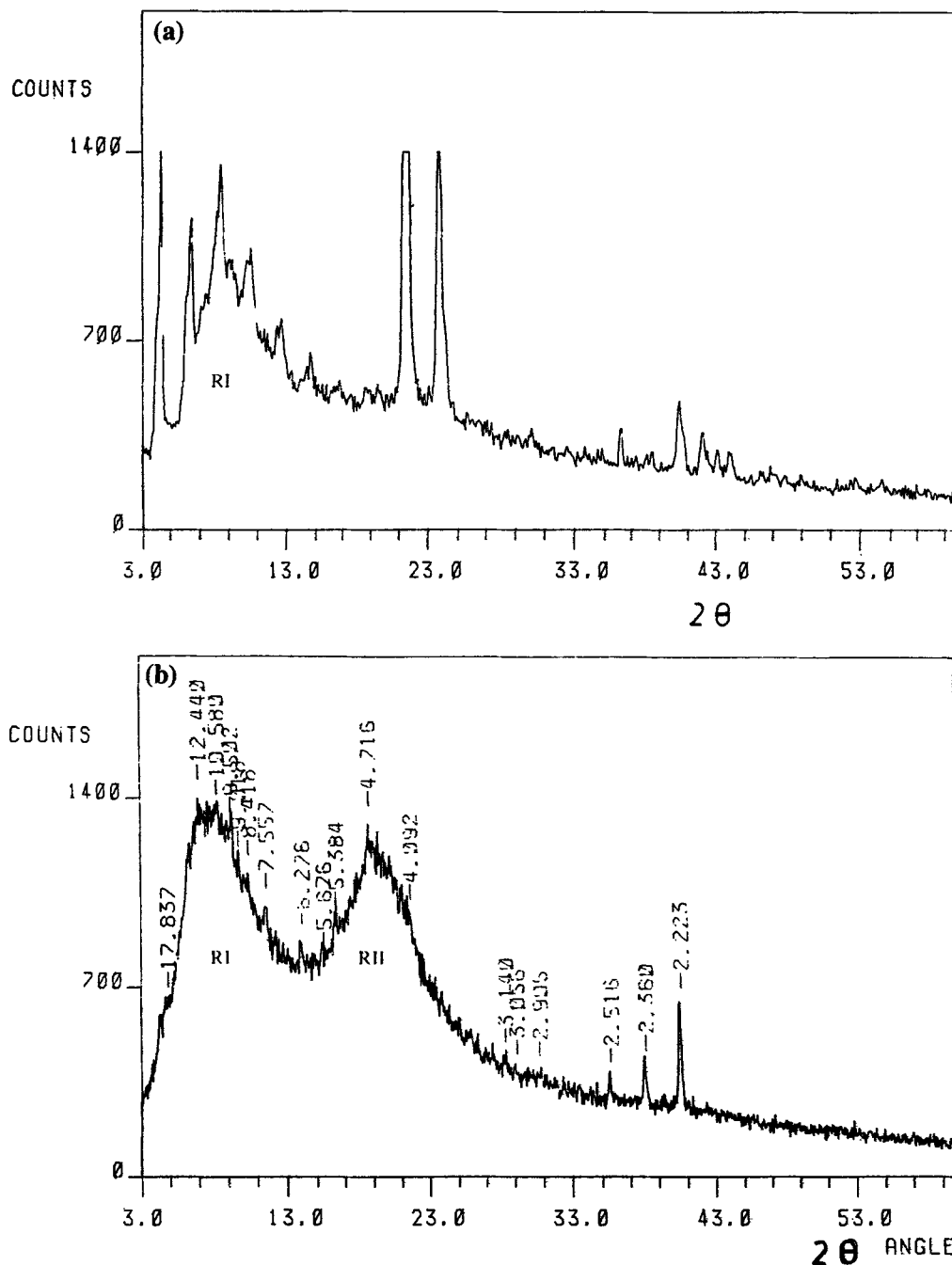
of C32 in C16, respectively;  $K$  was a constant.  $A$  and  $C$  were reasonably connected when  $K=7.200$ .

The same equation was also seen to connect the area of region II with concentration, when  $K=7.039$ . Differential areas (of region II) were also estimated; the value of  $K$  was calculated. The average value of  $K$  was found to be 6.129. The data is given in table 1.

We attempted to establish the crystal form of C32 in presence of C16, in each case and used C36 as a model

for comparison. The reasons for using C36 for such a purpose are given below.

C32 and C36 were almost neighbouring even carbon number homologues (having only one member C34 in between them). As such the polymorphic behaviour was similar (Broadhurst 1962), since the chain length difference was not much. The other odd carbon number homologues (such as C31, C33, C35) cannot be used, as their crystallographic description and polymorphic



**Figure 1.** (a) Existence of region I (indicated as RI) in the powder XRD record of pure C32 and (b) existence of regions I and II (RI, RII) in C32-C16 mixture: molar concentration = 0.047 : 1.

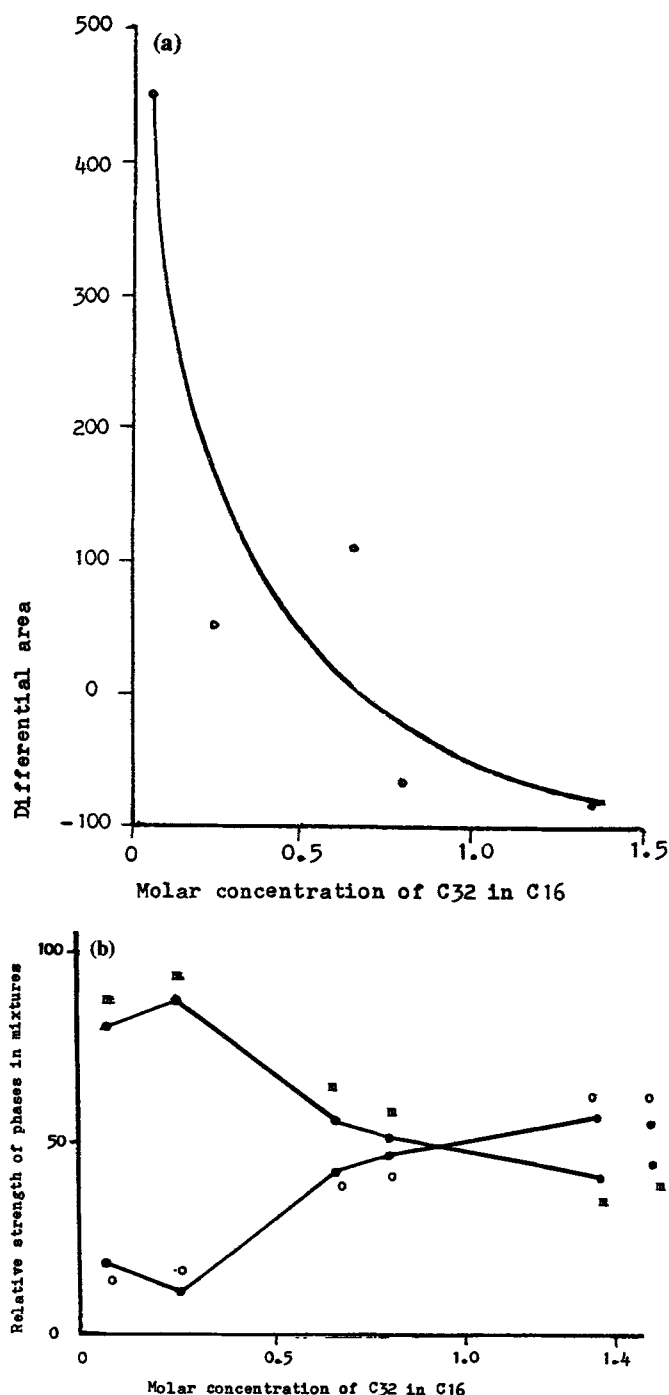
behaviour differ much from that of even carbon number *n*-alkanes (Boistelle 1980). The *d* values of peaks recorded in the present study, in case of C36 are given in table 2. It is known (Broadhurst 1962) that C36 has  $d(001) = 47.61 \text{ \AA}$  in orthorhombic form and  $d(001) = 42.25 \text{ \AA}$  in monoclinic form. An examination

of the *d* values given in table 2 and comparison with the established  $d(001)$  values (Broadhurst 1962) showed that the hydrocarbon C36 was in monoclinic form. It is important to note the fluctuations in the  $d(001)$  values shown in table 2.

As an example,  $d(001)$  values of C32 in the mixture (composition was 1:36:1) are shown in table 3. The reported  $d(001)$  values (Broadhurst 1962) of C32 were  $42.7 \text{ \AA}$  (orthorhombic and hexagonal phases) and  $37.8 \text{ \AA}$  (monoclinic phases). Similar to the case of fluctuations in the *d* values of C36, there were fluctuations in the *d* values of C32 also. It could be said that the observed fluctuations in the *d* values of C32 (in presence of C16) were not to be associated with C16.

The possibility of slight variations in the values of lattice parameters in case of ionic materials was discussed by Sirdeshmukh (1989). Due to several other reasons, such as loose lattice binding, such deviations might be a bit more in case of long chain molecular lamellar crystalline compounds. However, we do not wish to stress much on such reasons, in view of the fact that a very small error in the placement of cursor, meant to define the apex of a peak, can cause a small deviation in the  $d(001)$  values. In order to achieve higher accuracy in the  $d(001)$  values, however, higher resolution cannot be adopted due to the setback that, in such a case only a partial spectrum can be recorded; the measurement of total areas (as outlined in the previous paragraphs) shall become a difficult task. As such importance was given to the total areas rather than accurate measurement of *d* values.

Examination of the *d* values of C32 was made and probable phases were recorded. It could be seen that the sample contained both monoclinic and orthorhombic phases. All the XRD patterns were similarly examined and number of peaks corresponding to orthorhombic and monoclinic phases were recorded. The relative dominance of phases (the ratio between number of peaks corresponding to a particular phase and total number of peaks corresponding to orthorhombic and monoclinic phases) and the corresponding concentrations are shown in figure 2b. It could be noticed from figure 2b that in case of pure C32 sample and the sample with composition 1:36:1, the number of crystallites in orthorhombic phases were more than the crystallites in monoclinic phase. It is interesting to note that, with the fall of concentration of C32 in C16, more of C32 assumed monoclinic phase than orthorhombic phase.



**Figure 2.** (a) Differential area of region I in XRD records of mixtures vs molar concentrations and (b) relative dominance of orthorhombic and monoclinic phases in the mixtures at various compositional values.

### 3. Discussion

#### 3.1 Regions I and II

The nature of regions I and II suggests that it is a manifestation of line broadening, in combination with

variable peak heights. The often cited reasons for the line broadening are: (i) fine particle size, (ii) mechanical strain, (iii) lattice strain and (iv) range of composition.

In case of region I (which was also noticed in case of pure C32), the possibility of (i) and (ii) may be ruled out as reasons for the line broadening. The lattice strain and the range of composition (monoclinic and orthorhombic phases) should be responsible for the observed broadening. On the other hand, in case of region II, the excessive area is absent in pure C32 and present in case of mixture samples (in the form of a hump). The increase in the area and the applicability of empirical equation (at least to the first approximation) strongly suggests that the composition aspect played a major role; this subject shall further be discussed in the next section. It may also be stated that in the range of composition investigated, there is no evidence for a gel-like or

amorphous-state-like behaviour of mixture, in view of the fact that neither the sizes nor the shapes of the humps are comparable to the humps reported by Srivastava *et al* (1996).

### 3.2 Phase behaviour

As indicated in the earlier discussion, the pure C32 contained a mixture of orthorhombic and monoclinic phases. It is interesting to note that the predominance of orthorhombic phase prevailed even in case of mixture with 1.36 : 1 composition and there was a reversal of dominance in the subsequent compositions. It is true that among the monoclinic and orthorhombic phases, monoclinic phase is energetically low phase. However, there are other factors which may deserve consideration.

**Table 1.** Information on areas of regions I and II at different compositions and the corresponding *K* values.

Sl. no.	Concentration (molar ratio) C32 : C16	Total area	Area of region I	Value of <i>K</i>	Area of region II	Value of <i>K</i>	Differential area (Region II)	Value of <i>K</i>
1.	1 : 0	3452	1359	—	—	—	—	—
2.	1.36 : 1	3665	1278	7.102	899	6.737	201	5.178
3.	0.819 : 1	3363	1291	7.153	941	6.861	243	5.540
4.	0.671 : 1	4115	1472	7.307	1366	7.235	688	6.555
5.	0.245 : 1	3755	1407	7.249	1282	7.165	584	6.506
6.	0.047 : 1	4904	1807	7.1898	1830	7.198	1132	6.870
Average values of constants				7.200		7.039		6.129

**Table 2.** The *C* values of pure C36: presence of orthorhombic and monoclinic phases is indicated.

Sl. no.	<i>d</i> value	Reflection	<i>C</i> value (Å)	Monoclinic phase
1.	20.532	(002)	41.064	m
2.	14.018	(003)	42.054	m
3.	10.517	(004)	42.068	m
4.	8.499	(005)	42.495	m
5.	7.075	(006)	42.450	m
6.	6.104	(007)	42.728	m
7.	5.273	(008)	42.184	m
8.	4.716	(009)	42.444	m
9.	2.820	(0015)	42.300	m
10.	2.650	(0016)	42.400	m
11.	2.493	(0017)	42.881	m
12.	2.348	(0018)	42.264	m
13.	2.225	(0019)	42.275	m
14.	2.130	(0020)	42.600	m
15.	2.079	(0021)	43.659	m
16.	1.984	(0022)	43.648	m
17.	1.754	(0024)	42.096	m
18.	1.691	(0025)	42.275	m
19.	1.574	(0027)	42.498	m

**Table 3.** The *C* values of C32 in the mixture (composition 1.36 : 1).

Sl. no.	<i>d</i> value	Reflection	<i>C</i> value (Å)	Orthorhombic (o)/ monoclinic (m) phases
1.	20.066	(002)	40.132	m
2.	13.799	(003)	41.397	o
3.	12.100	(003)	36.300	m
4.	10.517	(004)	42.068	o
5.	8.581	(005)	42.905	o
6.	7.190	(006)	43.140	o
7.	6.146	(007)	43.000	o
8.	5.304	(008)	42.432	o
9.	4.716	(008)	37.728	m
10.	4.458	(009)	40.122	m
11.	4.092	(009)	36.828	m
12.	3.690	(0010)	36.900	m
13.	2.348	(0016)	37.560	m
14.	2.220	(0017)	37.740	m
15.	2.121	(0020)	42.420	o
16.	1.988	(0019)	37.770	m
17.	1.924	(0022)	42.320	o
18.	1.854	(0023)	42.640	o
19.	1.679	(0025)	41.975	o

It is well known (Ubbelohde 1938; Boistelle 1980) that the presence of homologous impurities can cause a hydrocarbon to assume higher symmetry (orthorhombic) in crystallization process. If an examination of the present case is made, based on the impurity effect, it seems that at least, at lower concentrations of C16 (case of 1:36:1), C16 is able to promote crystallization in orthorhombic phase, even when the chain length of C32 and C16 are in the ratio of 1:0.5. However, it appears, as the concentration of C16 in the mixture increases, it withdraws its role as phase promotor. We believe that such a trend is due to the phase separation (Dorset 1985; White *et al* 1990). Probably when the population density of C16 molecules reach a critical value (it appears from figure 2b that such a critical value is in the range 0.9:1-1:1), they form isolated packets, may be monomolecular thick layers, alternating between the layers of C32. This proposal bases on situations discussed by Dorset (1985). As the concentration of C16 increases further, there is every possibility that it could form more extended layers and that in both cases (of high and low concentrations), C16 molecules from their layers could penetrate into the C32 layers. Such process can generate defects and can cause lattice strain. The frequency of occurrence of such events may increase with the increase in the concentration of C16, as the mixture becomes more and more loosely packed one. The combined effect of such factors might be responsible for the line broadening, discussed in the earlier section. Now, once the C16 develops a tendency for phase separation, intuitively it could be predicted that C32 molecules get a freedom in alignment. If the non-impurity-like behaviour of C16 (beyond the critical composition value) is coupled with

it, it emerges out that C32, prefers to assume energetically low monoclinic phase.

There is a possibility that the first order phase transitions might take place with relative ease, as a result of freedom-offering environment. We are looking at this aspect.

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