Powder XRD studies on $n\text{-C}_{28}\text{H}_{58} : n\text{-C}_x\text{H}_{2x+2}$ ($x = 10, 12, 14, 16, 18$) hydrocarbon mixtures: Phase strength analysis

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Abstract. Powder XRD investigations were made on mixtures of title compounds and strength of monoclinic, orthorhombic and super-lattice phases were evaluated. Interpretations were made in terms of the influence of tunnel-like defects (TLIDs) and a linear relationship was noticed between the strength of orthorhombic phase and $\langle \ell_{\text{TLID}} \rangle$.

Keywords. Powder XRD; linear saturated hydrocarbons; binary mixtures; strength of phases; tunnel-like defects (TLIDs).

1. Introduction

Even though the linear long chain saturated hydrocarbons are often referred to as ‘compounds that are chemically inactive (paraffinic)’, they have been enjoying the status of important materials, from both experimental (Turner 1971; Strobl 1977; Boistelle 1980; Kim *et al* 1989; Shashikanth and Prasad 2001a) and theoretical (Beret and Prausnitz 1975; Kim *et al* 1986; Gasem and Robinson 1990; Magoulas and Tassios 1990; McCabe and Jackson 1999) view points. The present authors carried out (Shashikanth and Prasad 1999, 2001b, c, 2003) powder X-ray diffraction (PXRD) studies on two long chain hydrocarbons, $n\text{-C}_{36}\text{H}_{74}$ and $n\text{-C}_{32}\text{H}_{66}$; in mixed state with certain shorter chain even carbon number saturated hydrocarbons, briefly SMOLLENCS ($\text{C}_x\text{H}_{2x+2}$, where $x = 10, 12, 14, 16, 18$), the theme of the studies was to investigate the strength of phases (S_p) and the influence of tunnel-like defects; briefly TLIDs (Shashikanth and Prasad 2001c).

PXRD investigations were made on binary mixtures of linear chain hydrocarbons with certain chain length difference; one component of the binary mixture was long-chain hydrocarbon, $n\text{-C}_{28}\text{H}_{58}$, and the second component was a shorter chain hydrocarbon, $n\text{-C}_x\text{H}_{2x+2}$, where x ranged from 10–18. The PXRD data were analysed and interpretations were made in terms of the strength of (i) monoclinic (b_m), (ii) orthorhombic (b_o), and (iii) super-lattice (b_{sl}) phases. The results of the study are presented in this paper.

2. Experimental

Saturated linear chain hydrocarbons, n -octacosane ($n\text{-C}_{28}\text{H}_{58}$), n -decane ($n\text{-C}_{10}\text{H}_{22}$), n -dodecane ($n\text{-C}_{12}\text{H}_{26}$), n -tetradecane ($n\text{-C}_{14}\text{H}_{30}$), n -hexadecane ($n\text{-C}_{16}\text{H}_{34}$) and n -octadecane ($n\text{-C}_{18}\text{H}_{38}$), were employed in the present study (for convenience, the compounds are abbreviated as C28, C10, C12, C14, C16 and C18, respectively). The compounds were Fluka (Switzerland) made, with a purity >99%.

The following binary mixtures of hydrocarbons were prepared: (i) C28:C10, (ii) C28:C12, (iii) C28:C14, (iv) C28:C16, and (v) C28:C18. In case of each type of binary mixture, there were five samples with different molar ratio (MR) values (table 1). Preparation of mixtures was identical to the earlier method (Shashikanth and Prasad 2001c).

The mixtures were subjected to PXRD, by employing a Philips X-ray diffractometer, type PW1710. The operating conditions were: 25 mA current at 40 kV potential; $\text{Co-K}\alpha$ -2 radiation ($1.79285 \text{ \AA}$). PXRD patterns shown in figure 1 are representative of the diffraction patterns recorded in case of different binary mixtures.

Strength of b_m , b_o and b_{sl} phases was evaluated from the PXRD data, employing the same procedure adopted earlier (Shashikanth and Prasad 2001c). It may be mentioned that the quality of PXRD data that was used in the present investigations has considerable importance, since the interpretations made are relative to the PXRD. As an indicator of this aspect, PXRD data recorded in case of C28:C14 at MR = 2.0350 is given in table 2. The possible d -values of C28 alkane in b_m and b_o phases were computer generated through an appropriate program and compared with the observed values, while keeping in view the intensity condition for long spacings, $I[d_{00(n)}] > I[d_{00(n+1)}]$,

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Figure 1. PXRD patterns of C28:C14 binary mixture with MR = 2.0350. Inset: Compressed PXRD patterns of five binary mixtures with MR values: (a) 2.0350, (b) 1.5870, (c) 0.9859, (d) 0.4872 and (e) 0.2410.

Table 1. Molar ratios (MR) of different binary mixtures.

Binary mixture	MR values				
C28:C10	0.2746	0.6254	0.9962	1.5876	1.9067
C28:C12	0.1991	0.5997	1.0054	1.4005	1.9247
C28:C14	0.2410	0.4872	0.9859	1.5870	2.035
C28:C16	0.2382	0.5152	1.0172	1.4729	1.9884
C28:C18	0.2467	0.4912	0.9813	1.4929	2.0040

where I is intensity of a peak with index $00(n)l$ and $n \geq 1$; such condition being characteristic of long chain molecular compounds (Markley 1947; Vainshtein 1966). This led to identification of phase, to which a given peak belonged. The areas enveloped by peaks were estimated from high resolution computer printouts of PXRD patterns. The strength of phases was evaluated by integrating such areas.

It is well established that (i) the diffraction patterns function as finger prints in identification of phases of a given material (Vand 1960), (ii) solid-solutions, crystal size and strain effects can alter the relative intensities (Taylor 1960), and (iii) the strong forces connecting the carbon atoms within the chain and the weak Van der Waals lateral binding between neighbouring molecules results in a very pronounced anisotropy of compressibility (Evans 1966). The vast difference in the shape of molecules (highly elongated in the direction of chain axis) leads to pronounced orientational preferences, thus promoting (i) lamellar formations and (ii) enhanced and restricted diffusion of molecules, in the directions parallel and normal to the chain axis, respectively (Padilla and Toxvaerd 1991). Due

to these reasons, the solid-solutions (formed by binary mixtures of long linear chain alkanes) still retain the lamellar character and promote super-lattices (Boistelle 1980; Shashikanth and Prasad 2001, 2003, 2005; Prasad *et al* 2004, 2005). The intensities (of such super-structures) may differ (Taylor 1960) from standard values of the pure alkane. However, based on the information of lamellar thickness (d_{001}), such super-lattices can be broken down into its components, in order to find the phase state of molecules (i.e. whether it belongs to b_m or b_o phase). For example, in case of C28:C18 binary mixture (Prasad *et al* 2004), let both molecules be in vertical mode (b_o phase), forming super-lattices. Then the expected $d_{001}^{SL} = 1.27 \times 27 + 1.27 \times 17 + 2 \times 3.5 = 62.88 \text{ \AA}$. Here $1.27 \text{ \AA}$ is C-C distance along chain axis; there are 27 and 17 bonds in C28 and C18, respectively. $3.5 \text{ \AA}$ is inter-lamellar spacing. A peak in the diffraction pattern has d -value = 4.1895 . This value with index (0015) gives 62.8425 . It may be inferred that C28 molecule in this super-lattice configuration is with b_o phase. A similar reasoning holds for b_m phase. This approach illustrates how the information on phase state can be retrieved even from super-lattices. However, in the present study, we did not brake down the super-lattices (as indicated above), in order to avoid any possible ambiguity, and left it in the form of strength of super-lattice phase (b_{sl}).

3. Observations

The variations in the strength of b_m , b_o and b_{sl} phases, with MR values, are shown in figures 2–4, respectively.

Table 2. PXRD data on C28 : C14 binary mixture with MR = 2.0350.

d -spacings (Å)	Relative intensity (%)	Angle (°2 theta)	Peak height (counts/s)	Background (counts/s)	Tip width (°2 theta)	Significance
10.58274	53.14	8.34809	664.89	121.15	0.08000	3.25
10.26366	16.78	8.60811	209.99	118.97	0.08000	0.63
8.02931	29.87	11.01011	373.77	102.89	0.10000	3.70
7.73147	6.76	11.43564	84.60	101.06	0.08000	0.86
6.47849	16.53	13.65702	206.79	104.42	0.10000	1.93
5.41515	11.78	16.35558	147.34	144.35	0.06000	2.19
4.66306	10.68	19.01629	133.67	223.87	0.06000	1.16
4.01884	100.00	22.10020	1251.28	251.57	0.10000	6.59
3.97509	53.59	22.34655	670.50	247.88	0.10000	2.50
3.94050	47.34	22.54529	592.34	244.90	0.06000	2.49
3.89991	62.85	22.78303	786.43	241.34	0.08000	2.42
3.85659	23.23	23.04242	290.64	237.64	0.06000	1.48
3.80328	11.92	23.36996	149.14	232.55	0.06000	1.24
3.64065	16.44	24.42966	205.70	216.67	0.04000	1.02
3.59297	15.64	24.75892	195.70	211.74	0.10000	1.86
3.44180	1.34	25.86484	16.80	195.17	0.40000	0.72
3.26179	2.04	27.31915	25.52	177.00	0.64000	1.76
2.97233	2.44	30.03926	30.52	156.84	0.40000	1.26
2.88451	4.42	30.97643	55.30	151.27	0.24000	1.68
2.74071	2.67	32.64590	33.39	141.33	0.48000	2.43
2.53006	2.98	35.45028	37.23	134.25	0.40000	1.40
2.45641	5.22	36.55021	65.36	133.15	0.12000	0.81
2.40485	31.57	37.36247	395.06	132.34	0.08000	2.05
2.39827	27.48	37.46884	343.81	132.23	0.06000	1.15
2.37608	10.03	37.83194	125.49	131.87	0.06000	1.67
2.35349	9.23	38.20901	115.51	131.50	0.12000	1.95
2.33693	8.01	38.49044	100.23	131.21	0.16000	0.66
2.26995	5.46	39.67299	68.35	130.03	0.04000	0.64
2.22780	6.20	40.45623	77.61	129.25	0.16000	0.72
2.20117	14.23	40.96751	178.08	128.74	0.06000	0.94
2.18033	22.49	41.37684	281.36	128.33	0.04000	3.87
2.08429	13.59	43.37765	170.05	126.33	0.06000	0.65
2.05800	6.10	43.96025	76.28	125.75	0.20000	1.05
2.01379	6.01	44.97755	72.21	124.73	0.12000	0.91
1.96656	3.33	46.11929	41.64	123.59	0.32000	1.34
1.87613	6.45	48.48121	80.66	121.23	0.16000	0.72
1.82593	0.75	49.90379	9.37	119.81	0.28000	1.12
1.71980	6.42	53.21682	80.33	131.51	0.24000	1.87
1.69177	3.73	54.16967	46.67	132.58	0.10000	0.61
1.68091	4.13	54.54883	51.68	133.01	0.16000	0.68
1.63504	2.85	56.21242	35.67	134.88	0.12000	0.65

Figure 2. Strength of b_m phase of C28, in mixed state with different SMOLLENCs; C10 has least influence.

Figure 3. Strength of b_o phase of C28, in mixed state with different SMOLLENCs.

Figure 4. Strength of super-lattice phase, when C28 was crystallized in presence of different hydrocarbons.

The maximum S_p values of b_m , b_o and b_{sl} phases formed by C28, in mixed state with each SMOLLENC is shown in figure 5. A few details noted are as follows.

3.1 Case of C28 : C10

Apart from the initial small differences, C10 promoted maximum b_m phase (figure 2) in the entire range. It promoted lowest b_o phase (figure 3), when concentration of C10 was more than that of C28 and lowest b_{sl} phase (figure 4), when concentration of C10 was equal to or less than that of C28.

3.2 Case of C28 : C12

The C12 promoted lowest b_m phase (figure 2) around the mid concentration region (MR = 1.0). The curve representing

the strength of b_o phase (figure 3) almost lies in between the rest of the curves (except at MR = 1.4), indicating that the role of C12 in promoting b_o phase was neither low nor high. The strength of b_{sl} phase (figure 4) is almost constant at two MR values (1 and 1.4), which suggests the stability of super-lattice structures over a range of MR values.

3.3 Case of C28 : C14

It is evident that strength of b_m phase (figure 2) decreased from high to low value with decrease in the molar ratios from 2.0-0.2. In case of b_o phase (figure 3), the S_p value was lowest (MR = 1.5-2.0). The overall variation in the S_p value was about 12% in the entire MR range. Interestingly, the b_{sl} phase (figure 4) was maximum at MR = 2 and gradually fell to a low value at MR = 1 and increased to a high value in the low concentration (of C28) region, where MR = 0.2.

3.4 Case of C28 : C16 and C28 : C18

The S_p curves of b_m phase (figure 2) of C28 in presence of C16 and C18 were almost similar, in the MR range 1–2, and differed on the lower concentration side (MR = 1–0.2). In case of b_o phase (figure 3), the S_p value was high for C16 (except at MR = 1.48) and the value gradually decreased with decreasing value of MR, except at the last point (MR = 0.2). The S_p curves of b_{sl} phase (figure 4) due to C16 show strong fluctuations, whereas the S_p curves

due to C18 are relatively smooth and are almost free from fluctuations in MR range, 2–0.5. These observations indicate that at high concentrations of C28 (MR ≥ 1), the features are determined by the incorporation of SMOLLENCs, in the C28 matrix. At lower concentrations (MR < 1), the features are determined by individual phases (due to phase separation). The features at MR = 1 are a mid way between the state of incorporation and phase separation. The studies on C32 : C16 system also led to similar conclusions (Shashikanth and Prasad 1999).

4. Results and discussion

It can be noticed that the strength of b_o and b_{sl} phases increase, as the length of SMOLLENCs increases (figures 5a, e), whereas the strength of b_m phase decreases with increase in the chain length of SMOLLENCs (figure 5c). The average strength of b_o and b_m phases was estimated, while considering the S_p , recorded in case of all the five samples in case of each combination of hydrocarbons. The curves due to average strength of phases (figures 5b, d) are almost identical to the curves due to maximum S_p (figures 5a, c). The curves due to b_{sl} phase slightly differ from each other (figures 5e, f); however, importance is not given to such variation, as they are limited only to a part of the curves (corresponding to the value due to C16). The agreement between the two sets of curves (figure 5) strongly indicates that the strength of b_o phase of C28 certainly increases with the chain length of the SMOLLENCs and that the curves resulting from the consideration of maximum strength of phases (figures 5a, c, e) are not chance curves.

The influence of chain length of SMOLLENCs on the S_p of b_o phase is interpreted (Shashikanth and Prasad 2001c) in terms of TLIDs. We suggested (Shashikanth and Prasad 2001c) that TLIDs cause a decrease in the energy of b_o phase, leading to its stability. It appears that lowering the energy of a phase also makes it a preferred phase, thus leading to increase in the S_p of that phase. The length of tunnel-like defects (ℓ_{TLID}), arising due to the incorporation of SMOLLENCs molecules into the C28 matrix, both in monomeric and dimeric modes, are shown in table 3.

Figure 5. Maximum S_p promoted by different SMOLLENCs: (a) b_o ; (c) b_m ; (e) b_{sl} . Average S_p (of five samples in each case): (b) $\langle b_o \rangle$; (d) $\langle b_m \rangle$; (f) $\langle b_{sl} \rangle$.

Figure 6. Linear dependence of S_p of b_o on $\langle \ell_{\text{TLID}} \rangle$.

Table 3. TLIDs generated by different SMOLLENCs (C_x).

C_x	ℓ_{TLID} (Å)			$\langle \ell_{\text{TLID}} \rangle$ (Å)		Probably operative $\langle \ell_{\text{TLID}} \rangle$ (Å) (f)
	M (a)	D (b)	T (c)	$D/2$ (d)	$(M + D/2)/2$ (e)	
C10	22.86	7.93	(-)7.0	3.96	13.41	3.96
C12	20.32	2.85	—	—	10.87	10.87
C14	17.78	(-)2.23	—	?	?	0
C16	15.24	(-)7.31 (*)	—	—	—	15.24
C18	12.7	(-)12.39 (*)	—	—	—	12.7

(*) Not considered.

In case of monomeric incorporation of C10 and C18, the ℓ_{TLID} values are expected to be maximum and minimum, respectively and are expected to promote highest and lowest S_p of $\mathbf{b}_o$ phase, respectively. However, the curve of $\mathbf{b}_o$ phase (figure 5a) does not support this point of view. Moreover, the S_p of $\mathbf{b}_o$ is lowest in case of C14 (figure 5a), which is not expected in case of monomeric incorporation.

The resulting ℓ_{TLID} , when dimeric incorporation is considered are shown in column b (table 3). The ℓ_{TLID} is negative in case of dimeric incorporation of C16 and C18, and therefore such incorporation is not taken into consideration, as its contribution does not promote $\mathbf{b}_o$ phase. (But they can cause serious disturbance in the order of lamellae). Among the SMOLLENCs, C10, C12 and C14, C10 offers longer ℓ_{TLID} (in monomeric state) and consequently should be able to promote a high S_p of $\mathbf{b}_o$. But such conclusion is not supported by figure 5(a, b). In order to overcome such conflict, it is assumed that both monomeric and dimeric incorporations occur, resulting in an average value of ℓ_{TLID} . The adopted scheme is: (i) C10 and C14 are incorporated as dimers only (monomeric incorporation is totally absent) and (ii) C12 is incorporated both in monomeric and dimeric modes.

The resulting ℓ_{TLID} are shown in columns d and e (table 3). In estimating the value of ℓ_{TLID} in dimeric mode of incorporation, (i) a minimum spacing of about 3–3.5 Å is left between two SMOLLENCs (present in the same tunnel) and (ii) the same scheme of probabilities (Shashikanth and Prasad 2001b) were followed. The resulting, probably operative, ℓ_{TLID} values, are shown in column f (table 3). These considerations yield average magnitudes of length of tunnel-like defects $\langle \ell_{\text{TLID}} \rangle$ in the order of C16 > C18 > C12 > C10 > C14. The relation between $\langle \ell_{\text{TLID}} \rangle$ and S_p of $\mathbf{b}_o$ is shown in figure 6. It is impressive to note from figure 6 that there appears to exist an almost linear relation between S_p and $\langle \ell_{\text{TLID}} \rangle$.

Interestingly, in case of C28 : C14 mixture, the S_p of $\mathbf{b}_o$ is minimum (figure 5a). When C14 is incorporated in dimeric mode, the resulting configuration is almost identical to a normal C28 matrix (with some distortions); it may be the reason for the occurrence of minimum S_p of $\mathbf{b}_o$.

In view of the above discussion, the following conclusions may be made, in case of the maximum S_p of $\mathbf{b}_m$ phase (figure 5c).

Case of C10: The freedom offering environment (relatively less steric hindrance to inclined structure) favours the formation of $\mathbf{b}_m$ phase. Since C10 was not very effective in promoting the $\mathbf{b}_o$ phase, then the $\mathbf{b}_m$ phase (the lower energy phase) was promoted, such that its S_p was high.

Case of C14: Since a dimer of C14 almost fills the entire tunnel, the C28 matrix almost remains invariant. As such little influence was observed and the lower energy phase ($\mathbf{b}_m$) was preferred.

Case of C18 and C16: It is expected that $\ell_{\text{TLID}}^{\text{C16}} > \ell_{\text{TLID}}^{\text{C18}}$. Consequently and interestingly, the S_p of $\mathbf{b}_m$ due to C16 was less than that due to C18 (figure 3). This result is important because, incorporation of both C16 and C18 are monomeric and probably indicates that S_p of $\mathbf{b}_o$ and $\mathbf{b}_m$ (also $\mathbf{b}_{sl}$) phases are distributed in a definite way in a given sample, obeying certain criteria of partitioning of total energy over the two or three phases (this matter shall be discussed (Shashikanth and Prasad 2005) separately while reviewing the findings on C36, C32 and C28. However, recent considerations (Prasad *et al* 2004) based on the first law of thermodynamics showed the influence of TLIDs on phase transitions).

Case of C12: Even though the S_p of $\mathbf{b}_o$ is in agreement with the sequence of $\langle \ell_{\text{TLID}} \rangle$, viz. C16 > C18 > C12, the S_p of $\mathbf{b}_m$ is not in agreement with the expected sequence ($\mathbf{b}_m^{\text{C12}} > \mathbf{b}_m^{\text{C18}} > \mathbf{b}_m^{\text{C16}}$). Since C12 is active in promoting $\mathbf{b}_{sl}$ (figures 5e, f), probably some of its $\mathbf{b}_m$ phase, in pure form, may be missing.

5. Conclusions

Evidently, there is almost a linear relationship between strength of $\mathbf{b}_o$ phase of C28 hydrocarbon (attained in the presence of SMOLLENCs) and the $\langle \ell_{\text{TLID}} \rangle$. A similar relationship was noticed in case of other system (Shashikanth and Prasad 2003). As such, the strength of a particular phase ($\mathbf{b}_o$), being modified by the defect structure (TLIDs) is established.

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