Linear $C_{32}H_{66}$ hydrocarbon in the mixed state with $C_{10}H_{22}$, $C_{12}H_{26}$, $C_{14}H_{30}$, $C_{16}H_{34}$ and $C_{18}H_{38}$: Comparison of strength of phases and role of tunnel-like defects

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Abstract. Strengths of b_m, b_o and U_p phases of linear dotriacontane hydrocarbon in mixed state with certain shorter chain length homologues (SMOLLENCs), estimated from powder XRD analysis, are compared. The results suggest strong evidence in favour of tunnel-like defects (TLIDs).

Keywords. Linear chain hydrocarbons; strength of phases; tunnel-like defects; super lattices.

1. Introduction

Phase promotion (monoclinic $b_m \rightarrow$ orthorhombic b_o) in certain linear long-chain hydrocarbons in the presence of neighbouring homologues has been a fascinating topic and was studied earlier by Smith.[1] The present authors carried out powder XRD investigations to study the influence of shorter chain length homologues ($C_{10}H_{22}$ to $C_{18}H_{38}$), briefly SMOLLENCs, on the phase state of three linear-chain saturated hydrocarbons, $C_{36}H_{74}$, $C_{32}H_{66}$ and $C_{28}H_{58}$ (briefly C36, C32 and C28 respectively). The chain length differences between the long-chain hydrocarbons (C36, C32, C28) and the SMOLLENCs are rather large and, obviously, the two groups cannot be classified as neighbouring homologues to each other. Therefore the scope of the study undertaken by the present authors is wider than the earlier one.[1]

Results of powder XRD studies on C32–C16,[2] C32–C10 and C32–C10-ol,[3] and C36–C10 to C36–C18[4] were reported earlier. Powder XRD investigations were also carried out on C32–C12, C32–C14, C32–C18 and C28–C10 to C28–C18[5] systems. The purpose of the present reports is to compare the results obtained in case of five systems of C32, i.e., C32–C10, C32–C12, C32–C14, C32–C16 and C32–C18 and to further examine the validity of the model of tunnel-like defects[3] (briefly TLIDs).

2. Methods

Five hydrocarbons of even carbon numbers, C10, C12, C14, C16 and C18 (SMOLLENCs) were employed to form binary mixtures with C32. For each SMOLLENC–C32

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combination, five mixtures were prepared with different molar ratios and the mixtures were analysed by powder XRD. (Related details are given elsewhere.[2,3]) The PXRD patterns of four systems, C32–C10, C32–C12, C32–C14 and C32–C18 are illustrated in figures 1 to 4 (in the figures, the peak heights were chopped off at 1500 cps). The powder XRD patterns of C32-C16 were presented earlier.[2] In earlier studies,[2-4] the phase strength was evaluated by employing the line number density approach.[6-8] In the present study, the total peak intensity approach was employed for the evaluation of strength of the orthorhombic (b_o), monoclinic (b_m) and unidentified phase (U_p) phases. Each binary system gives five sets of b_o, b_m and U_p values. The maximum and minimum values of phase strengths recorded in the case of each system are shown in figure 5.

The average strength of the b_o phase of C32, when crystallized in presence of SMOLLENCs (C10 to C18), was estimated (figure 6, curve A). The length (L_{tlid}) of the TLIDs in case of all combinations, i.e. C32–C10, C32–C12, C32–C14, C32–C16 and C32–C18, were estimated (table 1), while assuming that if two shorter chain length molecules occupy the site of one C32 molecule (in the matrix of C32 molecules), then the gap between the two methyl end groups has to be equal to the usual interplanar spacing,[9] about 3 to 3·5 Å. The values of estimated total length of TLIDs, formed due to combination of C32 with SMOLLENCs of different chain lengths, is shown in figure 6 (curve B).
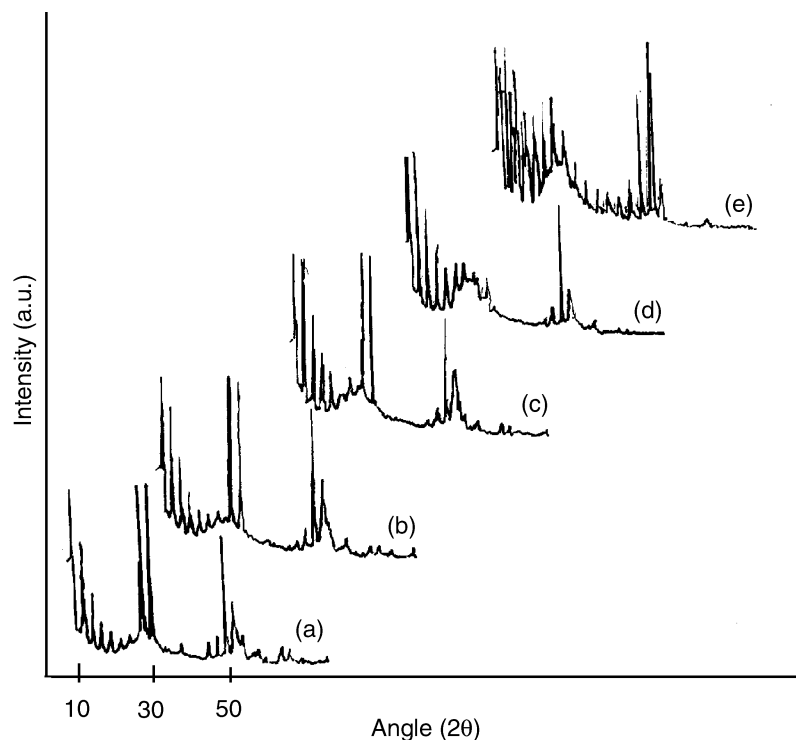

Figure 1. Powder XRD of C32 : C10 mixtures. MR (molar ratio) values: (**a**) 1·955, (**b**) 1·3167, (**c**) 1·2009, (**d**) 0·6274 and (**e**) 0·2946.
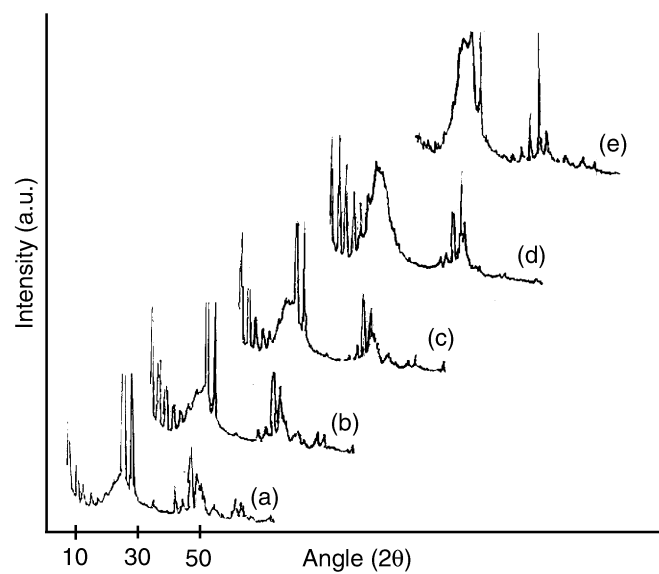
Figure 2. Powder XRD of C32 : C12 mixtures. MR values: (**a**) 1·8041, (**b**) 1·3958, (**c**) 0·9976, (**d**) 0·4910 and (**e**) 0·1976.
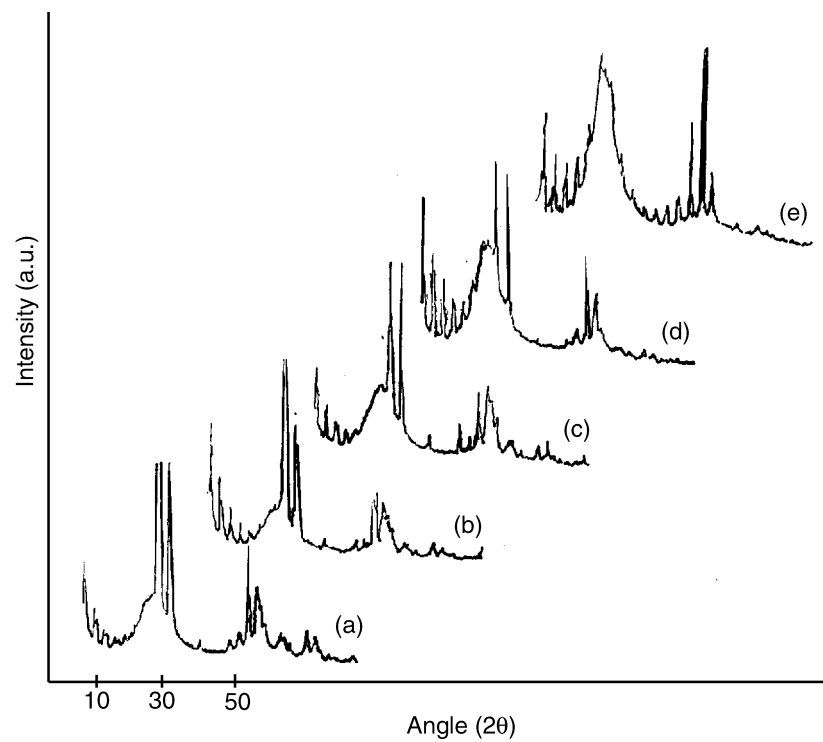
Figure 3. Powder XRD of C32 : C14 mixtures. MR values: (**a**) 1·92, (**b**) 1·510, (**c**) 1·00, (**d**) 0·517 and (**e**) 0·2019.
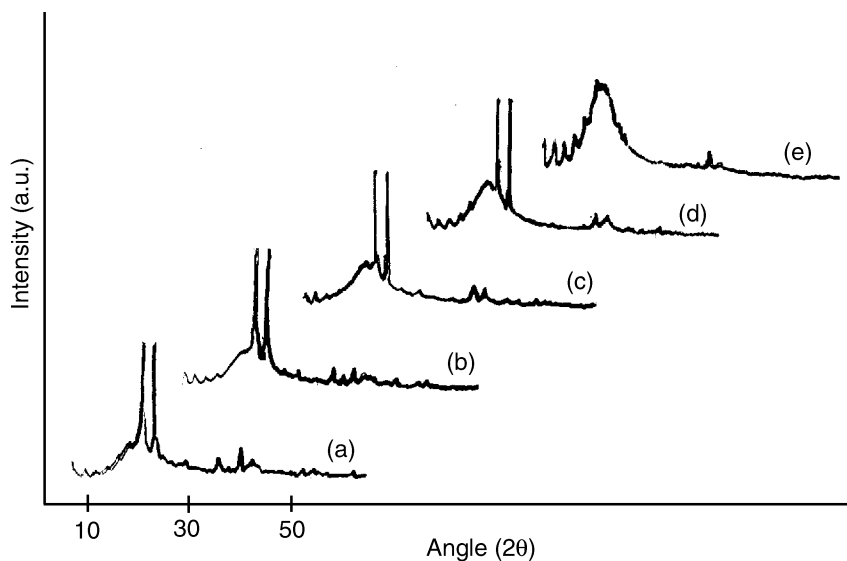
Figure 4. Powder XRD of C32 : C18 mixtures. MR values: (**a**) 1·8451, (**b**) 1·5097, (**c**) 0·9406, (**d**) 0·6027 and (**e**) 0·2702.
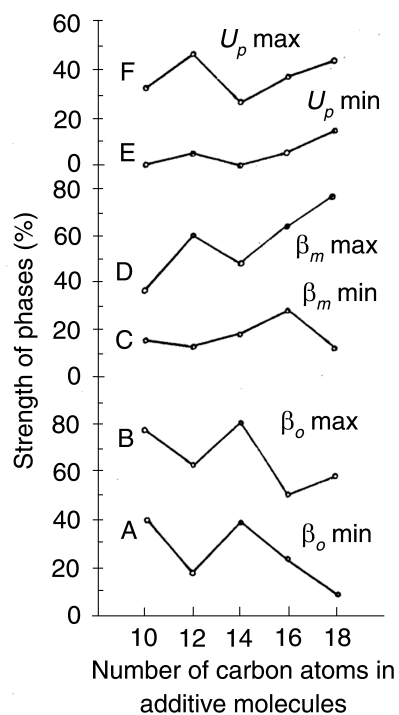

Figure 5. Maximum and minimum strength of phases of $C_{32}H_{66}$ hydrocarbon in presence of SMOLLENCs.
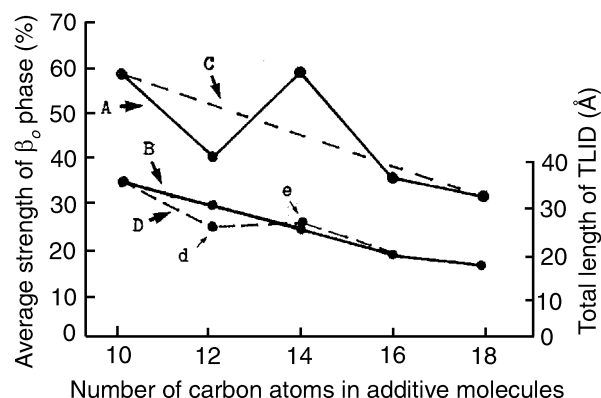
Figure 6. Average strength of b_o phase of $C_{32}H_{66}$ hydrocarbon (for details see text).

Table 1. Variation in L_{tlid} with the length of SMOLLENC molecules.

C32–SMOLLENC	Number of SMOLLENC molecules participating	L_{tlid} (Å)	Total effective L_{tlid} (Å)
C32–C10	1	27·94	
	2	13·51	34·695
	3	– 0·92*	
C32–C12	1	25·4	29·615
	2	8·43	
C32–C14	1	22·86	24·535
	2	3·35	
C32–C16	1	20·32	2032
	2	– 1·73*	
C32–C18	1	17·78	17·78
	2	– 6·81*	

*These values are not considered, as no TLID is formed in such combinations

3. Discussion

Fall in the average strength of b_o phase (figure 5, curves A, B) with increasing chain length of SMOLLENC molecules (and thus decreasing total L_{tlid}) in the binary mixture, can be seen as direct proof of the model of interaction and the role of TLIDs as proposed earlier.[3] It is also noticed that the strength of unidentified phase U_p (figure 5, curves E, F) increases with chain length of SMOLLENC component of the binary mixtures (U_p was recognized as due to superlattices[3]); this aspect can be explained as follows.

With increase in the chain length of SMOLLENC molecules, viscosity of the compound also increases.[10] It can therefore be envisaged that the higher the viscosity the higher the possibility formation of ordered layers (between stable molecular layers, such as formed by C32), due to the reduced possibility of the disruption of such layers. (It may be noted that disruption of layers can be caused even by restricted diffusion.) In case of long-chain molecular compounds, it can also be envisaged that increasing the viscosity
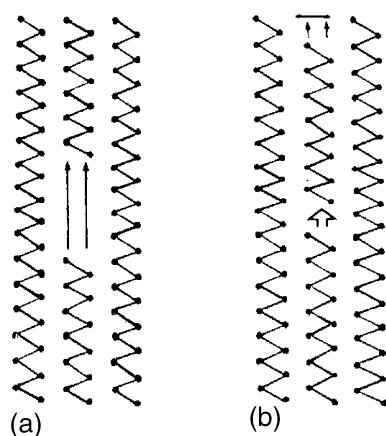
Figure 7. (**a**) Case of $C_{32}H_{66}$–$C_{12}H_{26}$. TLID (parallel arrows) formed between $C_{12}H_{66}$, molecules; ineffective TLID. (**b**) Case of $C_{32}H_{66}$–$C_{14}H_{30}$. The $C_{14}H_{30}$ molecules separated by the usual interplanar distance (hollow arrow). TLID (parallel arrows) formed at one end; active TLID.

should lower the diffusion. It is also known that the longer the chain length of the molecule, lesser the diffusion.[11] Therefore, superlattices formed by the interaction of C32 and SMOLLENCs of increasing chain length tend to acquire better stability. This could be the possible reason for the increased strength of the U_p phase with increased chain length of SMOLLENCs (figure 6, curves E, F).

It is interesting to note that curve B (figure 6), representing the relation between length of TLID and chain lengths of SMOLLENCs, almost defines the curve C (figure 6); curve C seems to represent a value, which is the average of curve A (figure 6). An intriguing observation here is that curve B defines only the average of curve A (in the form of curve C) and not curve A itself. In order to find a plausible reason, we re-estimated the values of L_{tlid}, while assuming that (i) in the case of the C32–C12 combination, if two C12 molecules occupy the site of one C32 molecule in the C32 molecular matrix, then the two C12 molecules may prefer the extreme positions (figure 7a). Consequently, the TLID left between the two C12 molecules remain inactive in the phase promotion.[3,4] The total value of TLID in the C32–C12 combinations is thus reduced (point d, figure 6). (ii) In case of the C32–C14 combination, a small increase in the value of L_{tlid} can be realized (point e, figure 6), if it is assumed that two C14 molecules are always separated by a minimum gap[9] of 3 to 3·5 Å (figure 7b) and larger gaps are not allowed. However, the reason for such nonlinearities (if not triggered by unknown impurities) is yet to be understood.

4. Conclusions

The reasonable correspondence that is seen to exist between (i) experimentally derived average b_o phase strength values, and (ii) the length of TLIDs, estimated from a combination of shorter and longer chain length molecules (figure 6, curves B, C), strongly indicate that length (or volume) of TLID plays a key role in the phase promotion as suggested earlier.[3] Further work is in progress.

Acknowledgement

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