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Powder XRD investigations on dotriacontane in mixtures: Phase strength and super lattices

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Abstract. Powder XRD investigations on dotriacontane-decane and dotriacontane-decanol mixtures are made. Phase strength, phase separation and formation of superlattices are discussed. The role of tunnel-like defects is considered.

Keywords. Hydrocarbons; mixtures; phase strength; tunnel-like defects; super lattices.

1. Introduction

In the world of organic chemistry, the linear chain saturated hydrocarbons (or paraffins), are the simplest system in the class of long chain molecules. Smith[1] and Mnyukh[2] contributed the basic ideas on the role of chain length differences on the phase state in these materials. The present authors made investigations on certain hydrocarbons in the areas of heat induced first order phase transitions[3–6] and additive promoted phase transitions and phase state in binary mixtures[7,8]. In order to gain further understanding of the behaviour of binary mixtures of high purity hydrocarbons and on the role of tunnel-like defects in phase promotion, the phase state of normal dotriacontane hydrocarbon was studied in mixed form with certain chain length alkanes, employing powder XRD technique. The results of the study are presented in this report.

2. Materials and methods

Linear chain saturated hydrocarbons *n*-dotriacontane (*n*-$C_{32}H_{66}$), *n*-decane (*n*-$C_{10}H_{22}$) and *n*-decanol (*n*-$C_{10}H_{21}OH$) from Fluka (Switzerland) were used (purity > 99%); the materials shall be referred to in brief as C32, C10 and C10-ol respectively.

Binary mixtures of C32 were prepared with C10 and C10-ol in molar ratios (MR). Five mixtures of different ratios were made in each case. The mixtures were heated to 10ºC above the melting point of C32, with vibrational shaking for thorough mixing of the components. After cooling, all the samples were weighed in order to correct any weight losses due to evaporation; and final molar ratios were calculated.

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Powder X-ray diffraction analysis of all the samples was carried out with a Philips powder X-ray diffractometer, type PW1710. Operating conditions were: 25 mA current at 40 kV potential; Co-Kα-2 radiation (1·79285 Å).

Scanning parameters and the method of analysis of powder diffractograms were similar to those used in previous studies [5–9].

3. Observations

In the case of the C32-C10-ol system, the phase strength curve (figure 1) shows peculiar behaviour; at various molar ratios, the orthorhombic and monoclinic phases increase and

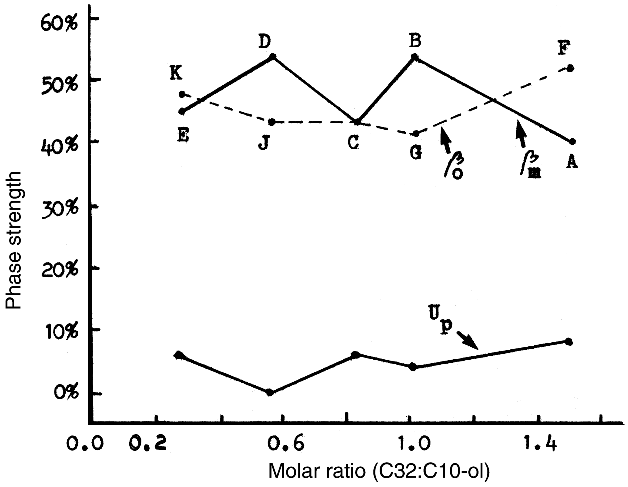

Figure 1. Observed strengths of orthorhombic, monoclinic and unidentified phases in $C_{32}H_{68}$ in presence of C10-ol at different molar concentrations; b_o: orthorhombic; b_m: monoclinic; and U_p: unidentified phase.

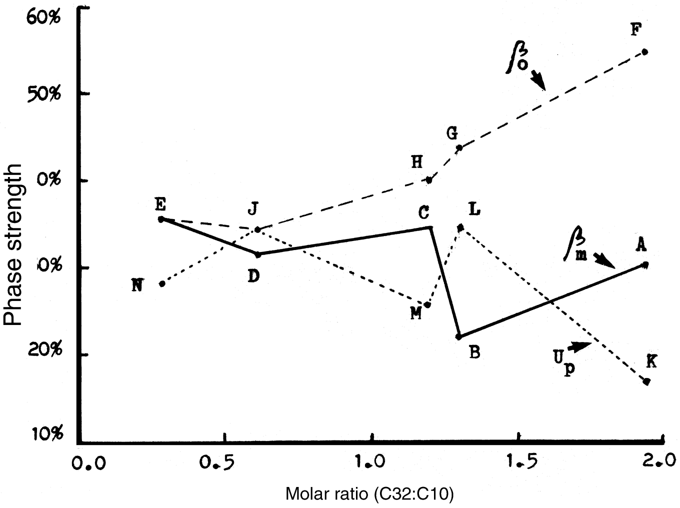

Figure 2. Observed strengths of orthorhombic, monoclinic and unidentified phases in $C_{32}H_{68}$ at different molar concentrations.

then decrease alternatively. The phase strength curves of C32-C10 (figure 2) show that at lower concentrations of C10, the orthorhombic phase predominates and an increase in the concentration of C10 leads to an increase in the phase strength of monoclinic phase. Both the orthorhombic and monoclinic phase strengths coincide at the lowest ratio presently studied.

The maximum peak height value was 5900 cps for the C32-C10-ol system and 5700 cps for the C32-C10 system. With increase in the molar ratio values, the values of (i) peak height (figure 3), and (ii) peak width (figure 4) also increased. The maximum peak width values for C32-C10-ol and C32-C10 were 4·6 and 2·1 units respectively; it may be noted that the value in case of C32-C10 is half that in the case of C32-C10-ol. The curves

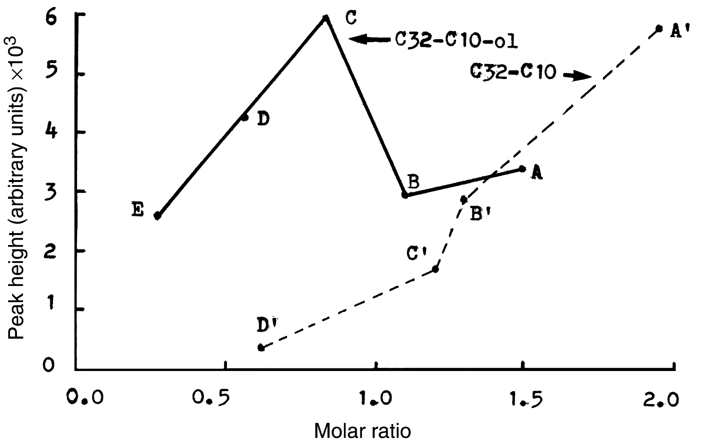

Figure 3. Maximum peak height (at $2q \approx 26°$) recorded in the powder diffraction patterns at different molar ratios.

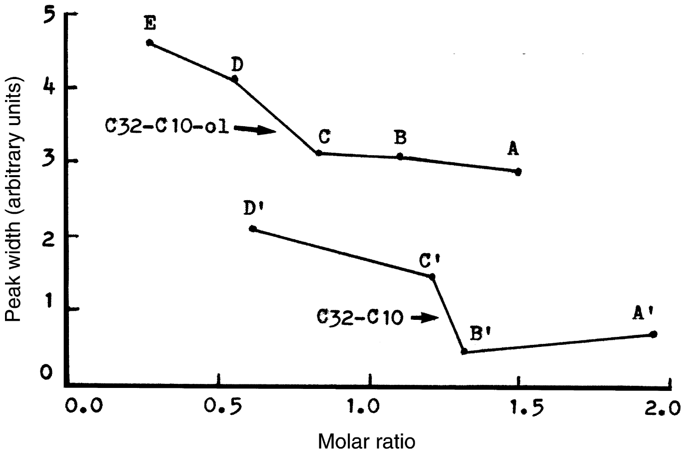

Figure 4. Maximum peak widths (at $2q \approx 26°$) recorded in the powder diffraction patterns at different molar ratios.

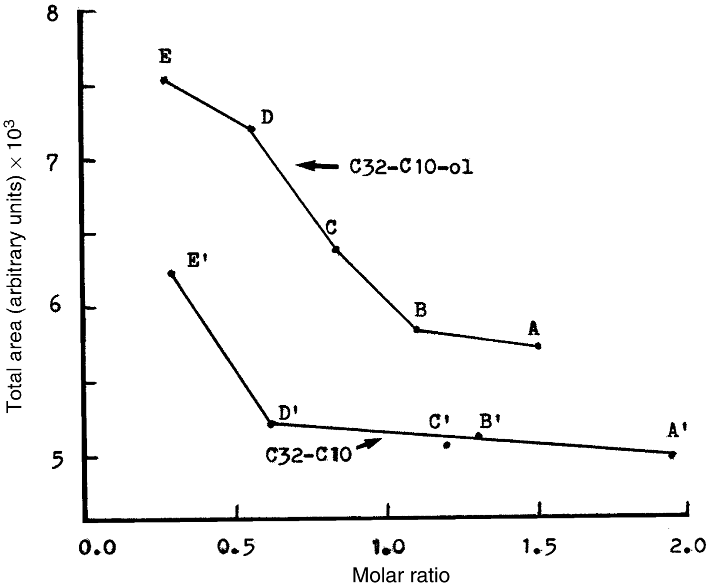

Figure 5. Total areas (diffuse scattering) enclosed by powder diffraction patterns.

(figure 5) related to the total diffuse (background) areas and the molar ratios show that there are distinct differences in the defect substructure of the two systems, C32-C10-ol and C32-C10.

During the evaluation of (00l) values it is seen that certain peaks cannot be indexed either as monoclinic or orthorhombic, in view of the non-matching of the resulting X-ray long spacing values with that of the C-value of the b_m or b_o state. This type of situation is observed in lesser degree in the case of the C32-C10-ol system, in comparison with C32-C10 system. Some of the details are shown in table 1. The unidentified peaks are assumed to represent certain unidentified phases (U_p) and were also shown in figures 1 and 2 in the form of separate curves.

4. Discussion

4.1 *Case of C32-C10-ol*

At MR = 1·5, the C10-ol molecules, because of low population density, can be incorporated as monomers, generating long tunnel-like defects (TLIDs) and these defects contribute to the generation of more b_o phase (point F: figure 1) than b_m phase (point A: figure 1). At MR = 1·1, reversal of phase strength should be due to incorporation of C10-ol as dimers (when C10-ol molecules are incorporated into the matrix as dimers, the length of the TLID is smaller as compared to when C10-ol is incorporated into the matrix as monomer); this situation is shown by points B (b_m) and G (b_o) in figure 1. At point C (MR = 0·83), both b_o and b_m phases have equal phase strength; limited incorporation of C10-ol as monomer and dimers and also simultaneous enhanced phase separation[10,11] could be the factors responsible. From the phase equilibrium point of view, it can be stated that the probability of phase separation increases with increase in the concentration of shorter chain molecules in a mixture of short and long chain molecular compounds,

Table 1. Molar ratios, number of unidentified peaks (N_{up}) and corresponding *d*-values.

C32-C10-ol			C32-C10				
MR	N_{up}	$2q$	MR	N_{up}	$2q$	(00*l*)	*d*(Å)
1·5009:1	1	55·535	1·955:1	3	10·080	(005)	51·0195
					42·700	(0020)	49·246
					64·535	(0033)	53·7312
1·1092:1	0	–	1·3167:1	7	7·930	(004)	51·856
0·8303:1	0	–			25·605	(0012)	48·5448
0·5656:1	0	–			28·090	(0013)	48·0194
					28·555	(0015)	54·5235
					42·830	(0020)	49·102
					55·900	(0026)	49·7276
0·2724:1	0	–			62·295	(0031)	53·7261
			1·2009:1	7	7·840	(004)	52·4504
					10·230	(005)	50·2736
					12·625	(006)	48·9174
					15·040	(008)	54·7968
					25·400	(0012)	48·93
					50·215	(0023)	48·5898
					55·910	(0026)	49·7198
			0·6274:1	7	7·800	(004)	52·7192
					10·195	(004)?	50·4455
					12·585	(006)	49·0722
					15·000	(008)	54·9424
					17·400	(009)	53·3376
					19·815	(0010)	52·1000
					25·050	(0012)	49·6032
			0·2946:1	6	8·290	(004)	49·608
					8·740	(004)?	47·0584
					10·180	(005)	50·5195
					12·580	(006)	49·092
					41·710	(0019)	47·842
					48·080	(0025)	55·0125

leading to the formation of isolated packets of short chain molecules (the system still is much below the solubility limit, so that the short chain molecules do not behave as solvent molecules). Therefore enhanced phase separation and lesser incorporation of C10-ol (which is however still higher than the value at point B) is responsible for the formation of relatively lesser b_o phase and more b_m phase at MR = 0·56 (points D and J: figure 1). The concentration of C10-ol is quite high at MR = 0·2. Such a situation can favour the formation of several extended packets of C10-ol molecules. In view of the increased strength of the b_o phase (point K in figure 1), as compared to its value at point J (figure 1), it can also be stated that C10-ol is present in the C32 matrix in considerable numbers as dimer and probably the number of such incorporated molecules may be lesser than at MR = 1·5.

4.1a *Diffuse scattering and peak heights:* The (i) low increase in the diffuse scattering (total area: T_a) in figure 5, corresponding to the region between point A and B, and

(ii) high increase in T_a between points B and D, low increase in T_a between D and E should be due to continuous increase in defect concentration and eventual formation of isolated layers of C10-ol. In matters related to the peak heights, it may be stated that the region between points B and C (figure 3: MR = 1·1 to 0·8), favours the formation of large number of lamellae with near-identical orientation, thus contributing to high values of peak height. The region C–E (figure 3: MR = 0·8 to 0·26) indicates continuous fall in regularity in the orientations of lamellae. Continuous reduction in size of diffracting crystal domains is indicated[12,13] by continuous decrease in the values of peak width curves shown in figure 4. It can be stated that both peak height and peak width (figures 3 and 4) curves support the prediction made about phase behaviour.

4.2 *Case of C32-C10 system*

It was indicated in §3 that there were several unidentified peaks (corresponding to some unidentified phase U_p). It was interesting to note that even at the higher value (MR = 1·95), there was considerable strength of U_p. Clearly the unidentified phase was formed due to incorporation of C10 molecules. It may also be stated (on comparison of figures 1 and 2) that the influence of C10 on the phase state of C32 was much more than C10-ol, in view of the fact that the strength of U_p was larger in the case of the C10-C32 system. It may also be noted that the strength of b_o phase is almost 20% greater than the b_m phase at MR = 1·95. The following simple explanation may be offered to explain this observation. Unlike the case of C10-ol, no end-on (partial) ionic forces are active in case of C10. As such, no dimers can be formed by C10 molecules. Therefore, under low concentration conditions (such as MR = 1·95), only monomer C10 molecules can be incorporated into the matrix. As such, the length of every TLID that is formed shall invariably be larger than the TLIDs that are formed by C10-ol. Consequently C10 has to be more effective in promoting the b_o phase. At MR = 1·31, increased concentration of C10 has definitely contributed to the formation of more TLIDs and thus generated more b_o phase and lesser b_m phase (point B in figure 2). Interestingly, the b_o phase, instead of experiencing enhancement in phase strength, has in fact undergone reduction (point G: figure 2). At the same time it may be noted that the strength of U_p has shot up from a low level (point K) to a high level (point L: figure 2). It can therefore be stated that the U_p phase grows at the expense of the b_o phase.

The fall of phase strength of b_o from point F (MR = 1·95) to almost the last point E (MR = 0·29) indicates that the pure b_o phase is progressively less preferred, and formation of U_p more favoured, with modifications imposed by the phase separation. For example, between the points G and H, there is steep fall in peak heights (figure 3), steep rise in peak width (figure 4) and continuous increase in T_a (figure 5); in addition, the b_m value also increases. This situation could arise due to the phase separation, explained in §4 earlier. There is a certain fall in the value of b_m (as compared to its value at point C), coupled with increase in the phase strength value of U_p. Obviously more of b_m phase is converted into the U_p phase. At point E (MR = 0·29), both b_o and b_m phases have equal priorities and the strength of U_p is almost 1/3 of the total strength of the b_o and b_m phases. The small increase in the phase strength of b_m from point D (MR = 0·62) to E (MR = 0·29) results from the clear preference of the system for the low energy state under the changed environment.

4.2a *Diffuse scattering and peak heights:* The total disappearance of peak height (figure 3) and the consequent absence of peak width (figure 4) at point E, and the steep increase in the T_a value (figure 5) and the nature of the phase strength curve (figure 2), indicate that C10 has stronger influence (than C10-ol) on the arrangement of C32 molecules.

4.3 *Unidentified peaks and super lattices*

If a lamella consists of a monomolecular layer of C32 and one monomolecular layer of C10 in a sequence and forms a super lattice, then its thickness is about 51·13Å (C32 in b_m phase) and 56·13Å (C32 in b_o phase); the length of C10 molecules[14] is taken as 11·43Å.

A fascinating aspect is that the values of unidentified peaks fall well in the above range of lamellar thickness (table 1). It may be stated that there is a strong case in favour of existence of superlattices in case of the C32–C10 system, particularly in mixtures with low molar ratios. The melting temperature of additives (C10 and C10-ol) used in the present study are below the ambient temperature. The extent of conformational stability that these molecules possess (in the fully extended form), though linear alkanes as such have sufficient order in the liquid state[15], is the most important parameter that contributes to the formation of super lattices. It can be envisaged that there may be reduced liquid-like behaviour in C10 molecules if they form monomolecular thick assemblies, with not very extensive basal areas. Liquid alkane molecules have strong steric hinderences for mobility, in directions that are not parallel to their long axis[16]. Therefore the interior molecules in a monomolecular alkane liquid layer can be thought of as in a bonded state, akin to molecules in soft solids. If the possibility of diffusion of molecules in directions parallel to their long axis is restricted, further stability of the monomolecular thick layers of C10 can be expected. In the present case, the C32 layer can play the role of 'basal surface stabilizer'. Under these circumstances, a sequence of layer structures, such as 'C32-C10-C32-C10-C32-C10', can lead to the formation of super lattices.

4.4 *Role of tunnel-like-defects (TLIDs) in phase promotion – A model*

We propose the following basic model to explain the mechanism involved in phase promotion by shorter chain additives. Different modes of incorporation of molecules of C10-ol and C10 in the crystalline matrix of long chain molecules is shown in figure 6a. It can be seen that, owing to the presence of TLID, a part of each molecule (surrounding the TLID) bends back (due to the imbalance in the forces responsible for side-on bonding) leading to small expansion in the neighbouring lattices (figure 6b). If a_1 is the area of 2D lattice in the (*hko*) plane and if the 2D lattice expends to a value a_2, then increase in the area of the 2D lattice is $\boldsymbol{d} = a_2 - a_1$. If the length of a TLID is l, then the increase in the volume (of the tunnel-like void) is $l\boldsymbol{d}$. If w is the work done (by the system) per unit volume increase, then the energy spent per tunnel (of length l), to the first approximation is $E = kw\ (l – c)\boldsymbol{d}$, where k is the constant of proportionality and c is a correction factor. Further, if (i) v_1 and (ii) v_2 are the potential energies of the immediate neighbouring molecules (with respect to the next immediate molecules), when (i) the central site is occupied by a molecule, and (ii) when it is empty (TLID) respectively, then $(v_1 – v_2)$ is the fall in the potential energy and thus

$$v_2 = v_1 – kw(l–c)\boldsymbol{d}.$$

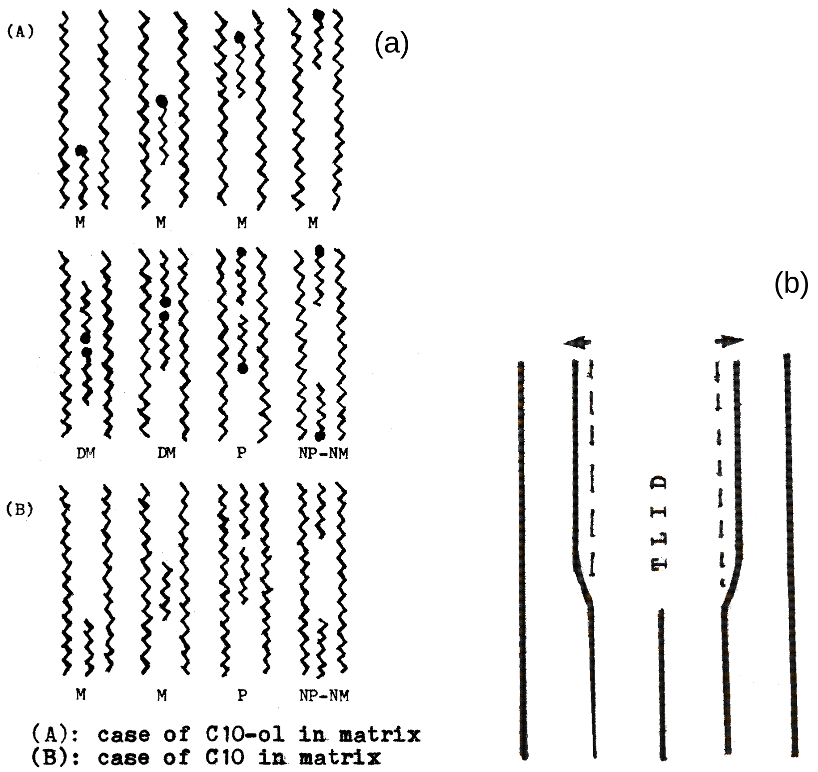

Figure 6. (a) Various modes of incorporation of shorter chain molecules; (b) Backward bends in the molecules in the neighbourhood of a TLID, leading to the formation of a smooth-bottomed tunnel.

If the number of neighbouring molecules taken into consideration is n, then the total potential energy difference becomes

$$v_1 - v_n = (l - c)\{k_1 w_1 d_1 + k_2 w_2 d_2 + \ldots.\ k_n w_n d_n\},$$

and gives

$$v_n = v_i - (l - c)\left\{\sum_{i=1}^{i=n} k_i w_i d_i\right\},$$

and

$$v_o = v_n / n,$$

where v_o is the potential energy per molecule. Let E_{bo} and E_{bm} be the energies per molecule in the b_o and b_m phases respectively, and let $E_{bo} - E_{bm} = E$. If $v_o = E$, then it can be stated that the TLIDs stabilize the b_o phase, even at room temperature, where only the low temperature phase (b_m) is expected to exist.

Investigations that are currently being carried out on *n*-octacosane, *n*-hexatriacontane and further investigations on *n*-dotriacontane hydrocarbons will lead to probable refinement of the model and estimation of parameters that appear in the present model.

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