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Self decoration: Case of *n*-octacosane hydrocarbon crystals

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Abstract. Some observations related to the decoration of *n*-octacosane hydrocarbon crystal surfaces, by the same material, when crystallized from a solution containing a non-solvent in trace quantity (which is completely miscible with solvent) as impurity, are discussed.

Keywords. Hydrocarbon; crystal face; steps; decoration; secondary nucleation.

1. Introduction

Tolansky (1968) defined decoration as any event, whether accidental or deliberate, which enhances the details of a crystal face. Chernov (1994) described the process of decoration in terms of build up of supersaturation at certain preferred points. Normally a material other than solute is used to decorate a crystal face, such as decoration of NaCl crystals with gold (Basset 1958) and SiC crystal faces by precipitation of NH_4Cl crystallites from vapour (Lemmlein and Gliki 1954). In case of high purity hydrocarbon crystals, we noticed occurrence of decoration by the same hydrocarbon. The details and process are presented in this report.

2. Materials, methods and observations

Fluka made 99% pure *n*-octacosane (n-$C_{28}H_{58}$) hydrocarbon, AR grade hexane, acetone, acetone + 5% water were used as materials. Crystals of hydrocarbon were grown by slow solvent evaporation technique at room temperature. Polarization and optical microscopy were employed for observing the crystals.

It is well known in case of hydrocarbon crystals that the values of acute angles are characteristic of the crystal symmetry (Smith 1953; Teare 1959; Caterina *et al* 1979). Therefore, values of acute angles (ϕ) of the hydrocarbon crystals were measured from photomicrographs which were found to vary between 70 and 75°, giving an average value of 72·72°. The established values are: (i) $\phi = 74°$ (elongated crystals) for triclinic symmetry; (ii) $\phi = 74°$ (lozenges) for monoclinic symmetry and (iii) $\phi = 68 \pm 2°$ (lozenges) for orthorhombic symmetry (Smith 1953; Teare 1959; Caterina *et al* 1979). On comparison of ϕ values, the symmetry of present rhombic (lozenges) crystals was found to be monoclinic.

Optical microscopic observations of the rhombic crystals grown from acetone solutions revealed the presence of dot-like features (DLF) on the (001) and (110) faces of some of the crystals. The DLFs were distributed in such a way that occasionally they were defining a spiral (figure 1a) or simply curved lines (figure 1b). Occasionally the DLFs were present along the edges of the (001) face (figure 1c). A set of less well formed DLFs were noticed in case of relatively thin, incompletely formed crystals. At this stage of observation, a question arose about the position of DLFs as to if they were present on the surface of crystal or inside the crystal (in the form of inclusions etc). In order to probe this aspect, oblique incidence technique was employed and a series of photomicrographs obtained (figure 2). An examination and comparison of the shadows formed by DLFs and crystal edges revealed that DLFs were present on the crystal surfaces.

Observations of the crystals of hydrocarbon, grown from acetone + 5% water solutions showed the presence of thick population of DLFs on the crystal faces (figure 3a,b). However, DLFs were not observed in case of crystals grown from hexane solutions.

The crystal surfaces were reexamined eight months after the initial observations and photomicrography. The continued existence of DLFs was noticed.

3. Discussion

It appears that DLFs grow after the growth of the host crystals and thus leading to decoration of the low step height spirals. It is probable that acetone solution covers the crystal face in the form of a thin layer, as the solvent nears complete evaporation. With further evapo-

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ration of solvent from such thin layer, the layer could become rich in water (which was present in the solvent as impurity, to an extent of 0·2%).

Since hydrocarbons are hydrophobic, the adhesion of acetone solution layer to the crystal surface should effectively be lowered with progressive evaporation of acetone, making the solution rich with water. This situation may lead to the formation of droplets (Bickerman 1957) of water-rich acetone; such droplets may possibly cover several spiral steps. As the evaporation of the solvent (water–acetone mixture) continues, secondary nucleation sets in and the hydrocarbon present in the droplets deposits preferentially along the step edges, spiral steps and at the points on the surface, where

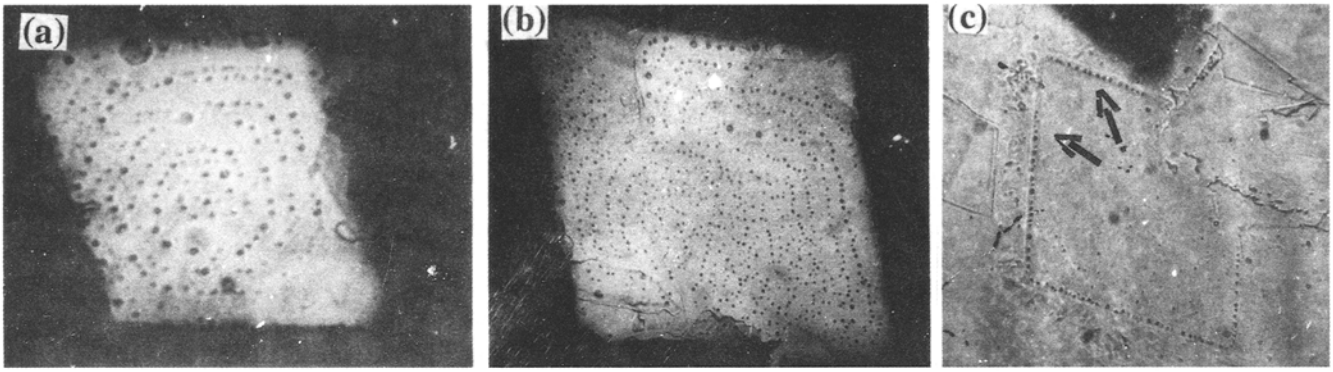

Figure 1. **a**. DLFs present on a hydrocarbon crystal, defining a spiral. Crossed polarized light (CPL) (× 100), **b**. DLFs on a hydrocarbon crystal defining many curved lines; the lines possibly indicate edges of incomplete layers (CPL) (× 100) and **c**. DLFs present along the edges of (001) face of a hydrocarbon crystal (× 100).

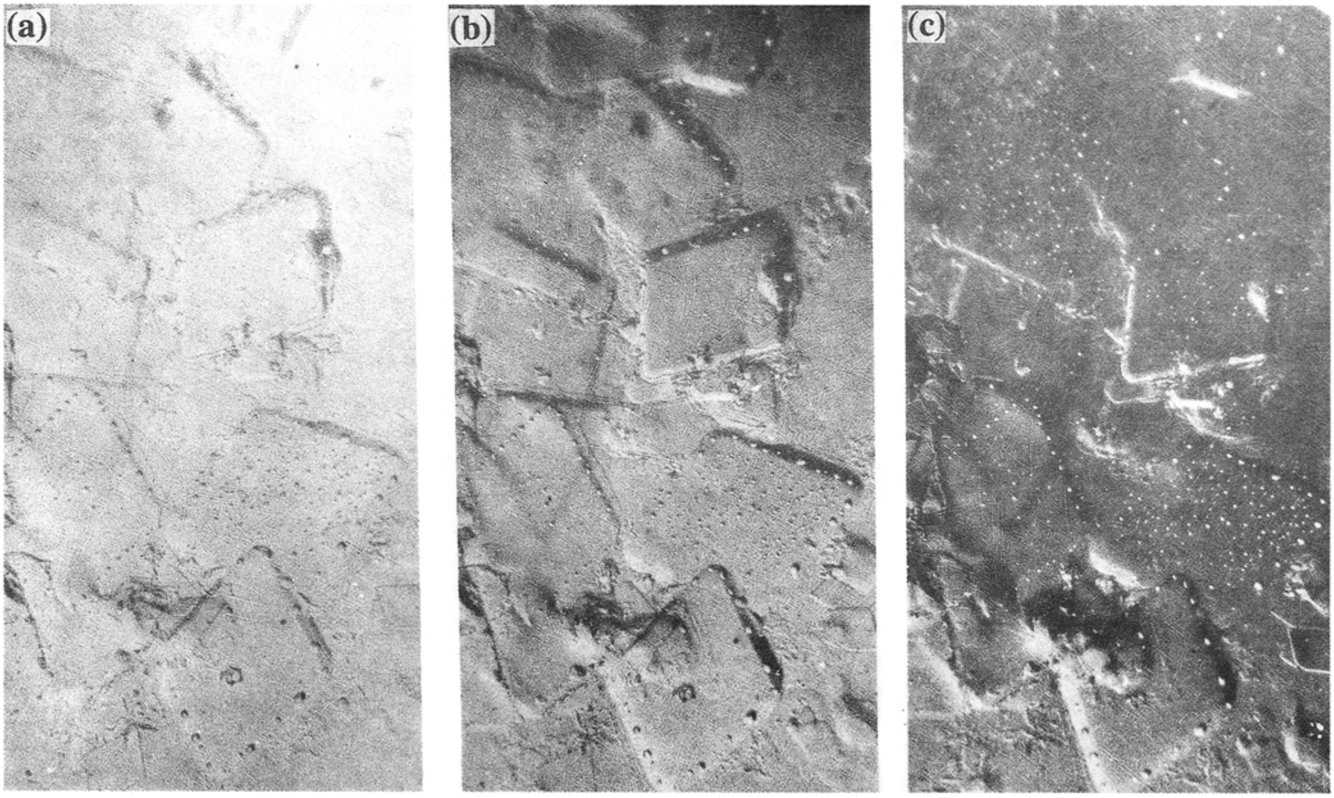

Figure 2. **a**. Some hydrocarbon crystals containing DLFs. Unpolarized light (× 100), **b**. same crystals; DLFs can be seen to be present on (001) faces. Oblique incidence illumination, (× 100) and **c**. same crystal as in **a** and **b**, with increased oblicity in incidence of illuminating light beam. The DLFs clearly show up as present on (001) face of hydrocarbon crystals.

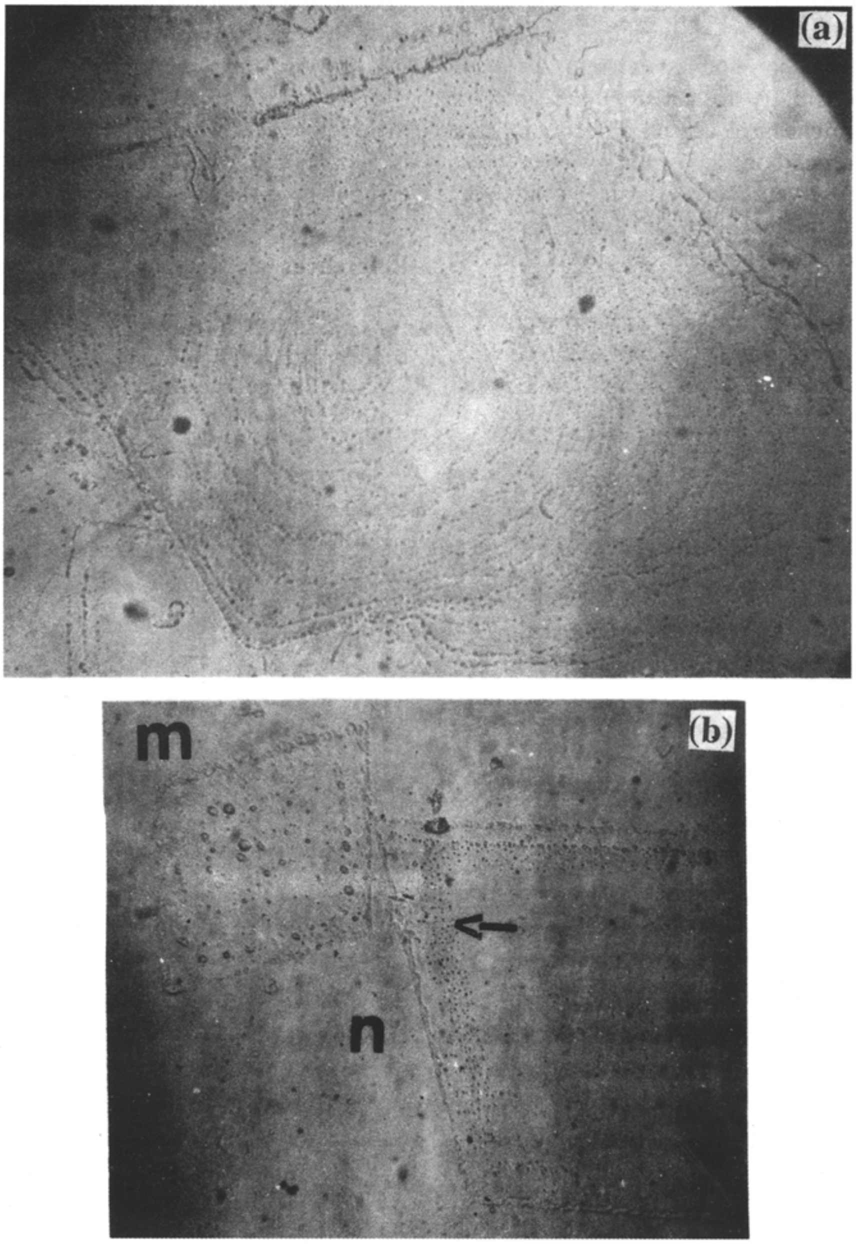

Figure 3. **a**. Decorated (001) face of a hydrocarbon crystal, showing up a closed loop pattern. Unpolarized light (× 100) and **b**. crystal '*m*' contains relatively large drops of solution. The alignment of drops may be noticed. Crystal '*n*' shows up fully decorated (001) face; thick decoration band may be noticed along the crystal edge (arrow mark). Unpolarized light (× 100).

dislocations or other defects are present. This view is based on the findings reported by Dai *et al* (1997). Incompletely formed edges of the topmost layers of (001) face can also offer nucleation sites for secondary nucleation, which was witnessed in figure 1c.

Such a deposition leads to the decoration of steps in particular and crystal faces in general. This is obviously a local deposition. The morphology of the deposits can be different, unlike the crystals growing on the identical crystalline substrates isoepitaxially (Prasad and Bhagavan Raju 1983). Such a change in the morphology can be caused by the presence of water as impurity in the solvent. For example, morphology of stearic acid crystals greatly differ, when crystallized from 2% water containing acetone (Swamy *et al* 1985) and pure acetone (Prasad 1985). It thus explains the different morphologies (hemispherical) of the deposits (DLF) noticed. The question as to whether the DLFs are fully crystalline or do they contain hydrocarbon in amorphous state, remains open.

There may be a possibility for an argument that the water droplets alone might have caused a decoration and no other process (hydrocarbon deposition) was involved in it. We recall the observation reported in the last para of § 2. Undoubtedly, microscopic size water droplets present in unprotected environment can never survive for eight long months, in a temperature range 15–40°C. Therefore, such a possibility can safely be discarded.

Since it is the solute material that causes the decoration of its own crystal face, the process is termed self decoration.

4. Conclusions

Hydrocarbons form soft and low melting point (below 100°C) crystals. These factors make the hydrocarbon crystals unsuitable for morphological studies through SEM, without going in for the replica techniques. However, the present study shows that the self decoration technique indicated in this report (achieved by adding a trace non-solvent as impurity) could be of some utility in exploring the surface morphology of (001) surfaces of alkane crystals.

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References

Basset G A 1958 *Philos. Mag.* **3** 1042

Bickerman J J 1957 *Second int. conf. surface activity* **3** 427

Caterina R, Aquilano D and Boistelle R 1979 *Acta Crystallogr.* **A35** 992

Chemov A A 1994 *Modem crystallography III* (Germany: Springer-Verlag) p. 80

Dai Q, Hu J and Salmeron M 1997 *J. Phys. Chem.* **B101** 1994

Lemmlein G G and Gliki N V 1954 *Dokl. Akad. Nauka SSSR* **94** 473

Prasad P B V 1985 *J. Cryst. Growth* **72** 663

Prasad P B V and Bhagavan Raju I V K 1983 *Cryst. Res. Technol.* **18** 445

Smith A E 1953 *J. Chem. Phys.* **21** 2229

Swamy R S N, Prasad P B V and Bhagavan Raju I V K 1985 *Cryst. Res. Technol.* **20** 803

Teare P W 1959 *Acta Crystallogr.* **12** 294

Tolansky S 1968 *Microstructure of surfaces using interferometry* (London: Edward Arnold)