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The crystal morphology and growth rates of triclinic N-docosane crystallising from N-dodecane solutions

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ABSTRACT

A detailed analysis of the crystal morphology of triclinic n-docosane ($C_{22}H_{46}$) is presented together with a preliminary assessment of the supersaturation-dependence of the growth rates for the predicted (*hkl*) faces. A methodology to index the experimentally observed crystal faces, based on a combined BFDH and zone axis methodology is defined. Analysis using this methodology yields the morphological indexation of n-docosane to be (001), (112), (102), (010), and (1 − 33) or (130) based on the expected triclinic crystal structure. Crystals of n-docosane growing from supersaturated n-dodecane ($C_{12}H_{26}$) solutions, as studied using in-situ optical microscopy, at three different supersaturation (σ) levels 0.01, 0.02 and 0.05, reveal that the crystal morphology changes with increasing in supersaturation, evolving from a habit consistent with a triclinic crystal system to a habit that is perhaps more representative of an orthorhombic structure. Growth rates determined for the (112) and (102) faces as well as for those less dominant faces range between 0.51 and 9.85 μm/s, in good agreement with previously reported data for other organic molecules including n-alkanes.

1. Introduction

The crystallisation behaviour of n-alkanes (C_nH_{2n+2}) has been the subject of numerous studies due to its importance in practical applications, especially in terms of understanding their role with respect to the cold flow behaviour of fuels. Previous work using single crystal and powder X-ray diffraction have characterised the solid-state properties for some of these compounds, suggesting they follow an overall scheme, in terms of the expected crystal structures as a function of the parity (n) of the number of carbon atoms within the molecule to be as follows: – triclinic, for n-alkanes with even carbon number $6 \leq n \leq 26$; – monoclinic, for $26 \leq n \leq 36$; and – orthorhombic for $n \geq 36$, and also for n odd $11 \leq n \leq 39$ [1].

In this respect, n-docosane crystallises in a triclinic structure, $Z=1$, $P\overline{1}$, with unit cell parameters $a=4.289$, $b=4.823$, $c=29.544$, $\alpha=86.237$, $\beta=70.661$ and $\gamma=72.097$ [2] in good agreement with the predictions of Nyburg and Potworowski [3].

Most single long-chain n-alkanes with carbon chain lengths >26, generally grow from solutions as rhombic-shaped thin platelets with large and well-developed (001) faces together with much smaller (110) side faces. Polygonized growth spirals [4,5] have been observed on the (001) faces when grown from n-alkane solutions (hexane and heptane) [6]. This is consistent with n-alkane solvent molecules incorporating as impurities. Growth from more complex solvents (cyclohexane) was found to result in no observable growth defects (spirals) [7]. Although, these particular crystals are typically bounded by (110) faces some additional small faces can occur for orthorhombic and for monoclinic phases for growth near equilibrium and this often results in a crystal morphology with a more “hexagonal” habit [7].

Although the bulk crystallisation of n-alkanes has been studied extensively [2,8–14], the dynamics of this process and the complex nature of their crystal morphology have not so far allowed an extensive investigation to be made into their growth kinetics. Single long-chain n-alkane solutions systems crystallise comparatively easily and are characterised by small metastable zone widths (MSZW). This is associated with very fast lateral growth in which fully faceted crystals can be difficult to observe. Additionally, both the small thickness of the crystals together with the

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Abbreviations: Cif, Crystallographic information file; BCF, Burton–Cabrera–Frank model; BFDH, Bravais–Friedel–Donnay–Harker model; B&S, Birth and Spread model; RIG, Rough Interface Growth model; 2D, Two dimensional; 3D, Three dimensional

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List of symbols

d_{hkl}	Inter-planar distances within morphological (hkl) forms
$MSZW$	Metastable zone width
R	Single face growth rate ($\mu m\ s^{-1}$)
T	Solution temperature (K)
T_d	Equilibrium dissolution temperature (K)
T_c	Crystallisation temperature (K)
x	Mole fraction of solute in solution
σ	Relative supersaturation
ΔH_d	Molal enthalpy of dissolution $\left(\mathrm{J\ mol^{-1}}\right)$
ΔS_d	Molal entropy of dissolution $\left(\mathrm{J\ mol^{-1}\ K^{-1}}\right)$

– very low birefringence in the direction normal to the dominant morphological form add to the difficulty of their observation using polarised light microscopy.

In spite of this, some studies have been carried out to measure the growth rates of individual faces. For instance, in the case of n-octacosane ($C_{28}H_{38}$) and n-hexatriacontane ($C_{36}H_{74}$), the observed crystals displayed a thin-lozenge plate-like morphology with well-developed (001) faces together with smaller (110) faces. Analysis of the growth rate kinetics measurements of the (110) faces was consistent with a dislocations-mediated [15] or two dimensional nucleation [16] growth mechanism for n-octacosane and n-hexatriacontane crystals, respectively. The observed crystal growth rates for these systems were found to be below 14 μm/s for supersaturations σ in the range of 0.007–0.15. The dominant (001) faces in the case of n-hexatriacontane crystals was found to develop by the slow incorporation of growth units by surface diffusion at the surface steps defined by the growth spirals [17,18].

In the case of the lower chain length n-alkane crystals, whose morphology is determined by crystallisation into the triclinic structure, such studies are scarcer due, in part, to the greater complexity in terms of preparing single crystals, controlling their growth and determining their corresponding crystal morphology. Some observations on the morphology of n-tetracosane ($C_{24}H_{50}$) crystallising from both n-hexane and n-octane solutions have been presented in Liu X-Y and Bennema P [19], together with the prediction of their morphologies using different models. However, the determination of the face-specific growth kinetics of these crystals has not as of yet been reported. Previous studies have been limited to only the development of instrumentation for collection of experimental data, e.g. associated with attempts to study the kinetics of n-eicosane ($C_{20}H_{42}$) crystallising from n-dodecane solutions [20].

This paper builds on this previous body of work and addresses both the assessment of the crystal morphology and the measurement of the growth rates of the individual faces, for the lower chain length n-alkane crystals. For this purpose n-docosane crystals growing from n-dodecane were studied as a function of solution supersaturation.

2. Materials and methods

2.1. Materials

Both n-docosane $C_{22}H_{46}$, the solute, and n-dodecane $C_{12}H_{26}$, the solvent, were purchased from Sigma-Aldrich. The purity of both materials was higher than 99% and no further purification was carried out.

2.2. Experimental apparatus for crystal growth measurements

In-situ crystal growth studies were carried out using an experimental set-up described earlier [21]. This comprised an inverted optical polarising microscope (Olympus Optical IMT-2), operated in bright field transmission mode, which was integrated with a Lumenera Infinity 3.3 megapixel CCD camera which captured crystal images as a function of time. The images were then analysed using the INFINITY ANALYSE software (http://www.lumenera.com/support/downloads/microscopy-downloads.php). The associated growth cell comprised a simple temperature-controlled annular tank (diameter 11 cm, depth 3.5 cm) sealed with two removable circular glass plates. The solution was secured within a 0.5 ml sealed UV glass cuvette with a path length of 1 mm which was placed within the cell as close to the objective lens of the microscope as feasible. The temperature within the cell was measured using a PT100 temperature probe and controlled using a Haake F3 circulating water bath that circulates water through the growth cell. The overall system is shown in Fig. 1.

2.3. Experimental procedure

The solubility and MSZW for n-docosane in n-dodecane solutions was measured using turbidimetric methods [22]. The solubility was modelled according to the van't Hoff equation:

$$\ln x = -\frac{\Delta H_d}{RT} + \frac{\Delta S_d}{R} \tag{1}$$

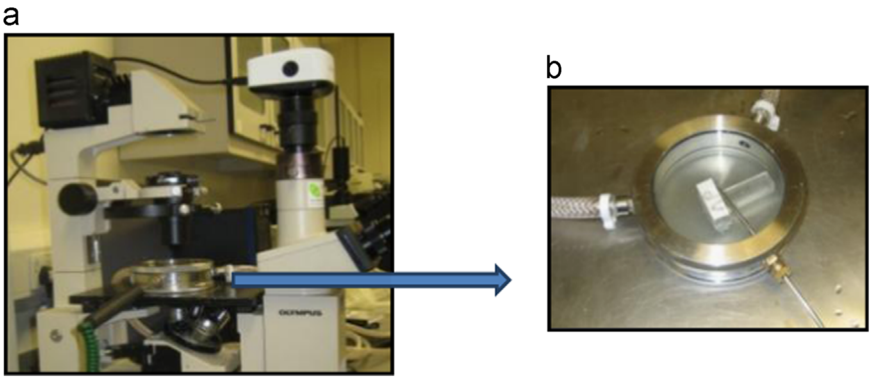

Fig. 1. Experimental set up for crystal growth rates measurements, after [21]. (a) Olympus IMT-2 inverted optical polarising microscope integrated with Lumenera Infinity 3.3 megapixel CCD camera. (b) Enlarged picture of the crystal growth cell.