THE INVESTIGATIONS OF THE GROWTH MORPHOLOGY OF NAPHTHALENE CRYSTALS

B. Marciniak, E. Różycka - Sokołowska
Institute of Chemistry, Pedagogical University
42200 Częstochowa, al. Armii Krajowej 13/15

ABSTRACT

The influence of organic solvents on the habit of naphthalene crystals was examined experimentally. It was found that the activity coefficient of naphthalene in solution may be used as a measure of the solute-solvent interactions which are important for growth morphology of crystal. A good agreement between real and theoretical morphology was obtained when the Hartman-Perdok and Donnay-Harker models were used to calculate this morphology.

INTRODUCTION

It is well known that the habit of crystal is determined by the relative growth rates of the various crystal faces bonding the crystal. The habit is therefore dependent on several factors that can be classified as internal ones (such as, for example, structure, symmetry, intermolecular forces and dislocations) and as external ones imposed by the crystallization conditions (temperature, pressure, super-saturation, type of solvent).It is often difficult to separate these factors by mere observation.

It is possible to define a theoretical habitwith growth determined in a certain way by the properties of the ideal crystal structure on the basis of PBC theory developed by Hartman and Perdok [1].

It is now possible to predict and calculate the influence of such external factors on crystal morphology in the area of additive and solvent effects on crystal growth for molecular crystals.

We have presented in this work the results of theoretical and experimental investigations of the growth and especially the morphology of naphthalene crystal, for growth by plate sublimation and from three organic halogen derivative solvents such as 1,2-dichloroethane (1,2-dCHLE), tetrachloromethane (CCl_4) and chloroform (CHL). To characterise the solute-solvent interactions and to check their influence on crystal morphology, the values of activity coefficient of solute in particular solutions calculated from solubility data were linked to growth and theoretical morphologies defined from PBC theory.

EXPERIMENTAL

Preparation of materials

In order to avoid the effect of impurity, the materials were purified to high standard. Naphthalene of analytic grade (POCh, Poland) was purified further by two-fold recrystallization from distilled benzene and then from ethyl alcohol. After recrystallization the material was dried *in vacuo* and then vacuum sublimation and two stage zone refining were used.

At the first stage of zone purification, 100 passages with the rate of zone passes 10 mm/h in atmosphere of spectrally pure nitrogen was used. The upper portions of the ingots were then mixed with similar materials and further zone was refined for another 100 passes with the rate of zone 2.3 mm/h.

In the final samples no impurities were detected, using a Hewlett Packard 5890 gas chromatograph with flame-ionisation detector.

The solvents were all dehydrated with anhydrous sodium sulphate and then distilled in a packed column, at large reflux ratios just before each experiment.

Procedures of the growth of crystals and growth results

The growth of naphthalene crystals was carried out by two methods, *i.e.* the plate sublimation similar to that described in Karl`s work [2], and from solutions, using the procedure worked out by us especially for easily evaporating organic solutions, described in our previous work [3].

In order to orientate of the crystals faces, the X-ray method was applied, using DRON-3 diffractometer. To determine Miller`s indices of particular faces, the values of angle between them were also measured by means of the optical reflection goniometer ZRG-3.

The solubility of naphthalene was measured using well known dynamic method.

EXPERIMENTAL RESULTS AND DISCUSSION

A typical naphthalene crystal obtained by vacuum sublimation (2.5×10^{-3}Tr, T = 295K) is shown in Fig.1, and its idealised growth form is presented in Fig. 3.

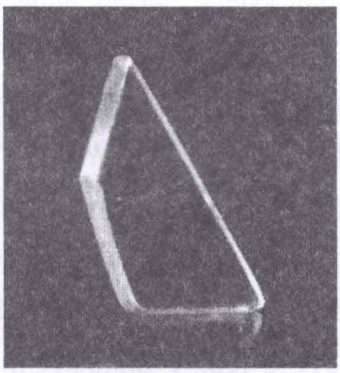

Figure 1. Naphthalene crystal grown by sublimation

These crystals ($10 \times 5 \times 2 mm^3$) exhibited tabular habit with well developed ten faces. Two major parallel faces were oriented in (001) plane; eight remaining side faces were: (110), $(1\bar{1}0)$, $(\bar{2}01)$, $(20\bar{1})$, $(11\bar{1})$, $(1\bar{1}\bar{1})$, $(30\bar{2})$

and $(\bar{3}02)$. In the case of growth under atmospheric pressure, usually non-regular plate-like crystals oriented in [001] direction were grown.
Successful growth from solution took place only in the case of 1,2-dCHLE solution. The obtained crystal (15x7x4mm^3) exhibited columnar habit with two parallel major faces oriented in (001) plane and the following seven side faces: $\{110\}$, $\{20\bar{1}\}$ and $(30\bar{2})$.
As it can be seen from a comparison of growth morphology of crystals obtained from solution and by sublimation, the main differences concern: $(11\bar{1})$, $(1\bar{1}\bar{1})$ and $(\bar{3}02)$ faces present in the sublimation crystals but not appearing in crystals from solution; and the faces $(\bar{1}10)$ and $(\bar{1}\bar{1}0)$ present in the last crystals but not exhibited by previous crystals.
In the case of other investigated solvents only plate-like naphthalene crystals oriented in the same direction [001] were obtained.
We supposed that the observed differences in morphology of crystals had been caused by solvent effect. In order to check these presumption we have considered solute-solvent interactions, which could occur in the solutions.
It is well known that in the case of regular solutions, as the ones investigated here, an activity coefficient of solute may be treated as a measure of solute-solvent interaction. Therefore, using the classical Weimer-Prausnitz relation [4], the values of this quantity have been established, basing on determined solubility data of naphthalene.

Table 1. Thermodynamical characteristics of solutions and growth conditions of naphthalene crystals

Solvent	γ_s^{exp}	γ_s^{SHE}	$\lvert\Delta\rvert$ [%]	$\overline{\Delta T_{max}}$ [K]	T_G [K]	σ [%]
	(1)	(2)	(3)	(4)	(5)	(6)
chloroform	1.0129	1.0139	0.10	4.9	308.0	8.0
tetrachloromethane	1.1830	1.1783	0.52	4.4	308.0	8.6
1,2-dichloroethane	1.0121	1.0134	0.12	5.0	308.0	3.0

It was found that for all the solutions the experimental activity coefficient γ_s^{exp} (Table 1, column 1) is greater than one, and that the solubility data well correlate with extended Scatchard-Hildebrand regular solution model [4], (column 2 and 3), what confirms a regular behaviour of all these solutions. The average deviations of experimental values of the activity coefficient from predicted values $\left(\Delta = 100\left|\left(\gamma_s^{exp} - \gamma_s^{SHE}\right)/\gamma_s^{exp}\right|\right)$ are smaller than 0.6% (column 3) for all data points, what shows that the accuracy of prediction is high.

However, the values of the activity coefficient of naphthalene (γ_s^{exp} and γ_s^{SHE}) in CHL and 1,2-dCHLE turned out close themselves; nevertheless, the activity coefficients for 1,2-dCHLE are somewhat smaller, what means that this solution is closer to the ideal solubility (without solvent). As one can see from columns 1 and 2 (Table 1), the activity coefficients of naphthalene in CCl_4 are substantially greater. It may at least partially explain the observed differences in morphology of crystals grown from 1,2-dCHLE and CHL, and moreover, to a larger extent, the differences between their morphologies and morphology of crystal obtained from CCl_4. Observed differences of morphology between solution and sublimation growth crystals may be explained by the influence of solvent.

Taking into account the super-saturation σ (column 6), at which the crystals were grown, it may be assumed that the observed morphology differences between crystals from 1,2-dCHLE and from CHL could be caused by substantial difference in solutions super-saturation. Possibility of such comparison is followed by the fact that these solutions are characterised by comparable values of temperature solubility coefficient *i.e.* $0.0225K^{-1}$ and $0.0228K^{-1}$ for 1,2-dCHLE and CHL, respectively, and they have practically the same values of estimated metastable zone width $\overline{\Delta T_{max}}$, column 4 (Table 1).

COMPARISON OF REAL AND THEORETICAL MORPHOLOGIES

In order to perform more detailed analysis of the influence of solute-solvent interactions on crystal morphology, the growth morphology of naphthalene crystals has been compared with the one calculated from PBC theory.

One of the most useful concepts that emerged from PBC theory was slice (E_{slice}) and attachment (E_{att}) energies, which are defined as the energy released on the formation of a stoichiometric growth slice and as the fraction of the total lattice energy (E_{cr}), released on the attachment of the slice to a growing crystal surface ($E_{cr} = E_{slice} + E_{att}$), respectively. The thickness, d_{hkl}, of such a growth slice is defined by the usual symmetry rules evolved by Bravais [5], Friedel [6], and Donnay and Harker [7]. Using a representative intermolecular potential one can calculate the strength of the intermolecular bonds in the solid state involved in the surface attachment process.

In order to calculate the slice and attachment energies, the computer programmes such as MORANG [8] and HABIT [9] may be used for the known bulk crystal structure. The programme MORANG, based on Donnay-Harker geometrical model, enables to identify major faces likely to dominate the crystal morphology, according to their slice thickness.

Naphthalene crystallises in the monoclinic system; space group $P2_1/a$; a = 8.213, b = 5.973, c = 8.675, β = 123.4; Z = 2 [10]. Its molecule lies in the crystallographic centre of symmetry, but it has higher symmetry (point group D_{2h}.), than it arises from the presence of crystallographic symmetry elements. Packing of the molecules in the unit cell is shown schematically in Fig.2.

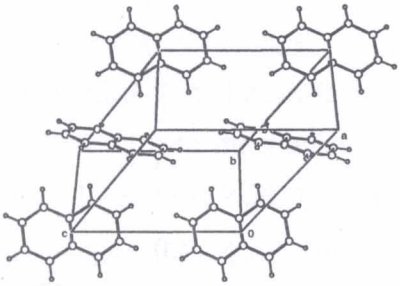

Figure 2. Packing of the molecules in naphthalene structure

In order to chose an appropriate intermolecular potential, several empirical relations proposed by Momany *et al.* [11], Govers [12], Scheraga *et al.* [13] and Wiliams [14] have been tested in this work. From a comparison of the calculated lattice energies with the sublimation enthalpy of naphthalene [15] it was found that the Govers`es potential gives the best agreement (Table 2).

Table 2. Comparison of the calculated energies with the sublimation enthalpy

Potential	$\lvert E_{cr} \rvert$ [kcal/mol]	$\lvert E_{subl} \rvert$ [kcal/mol]
Momany et al [11]	15.53	
Govers [12]	16.52	17.30 [15]
Sheraga et al [113]	19.49	
Williams [14]	19.06	

The calculated and idealised growth morphologies are presented in Fig.3.

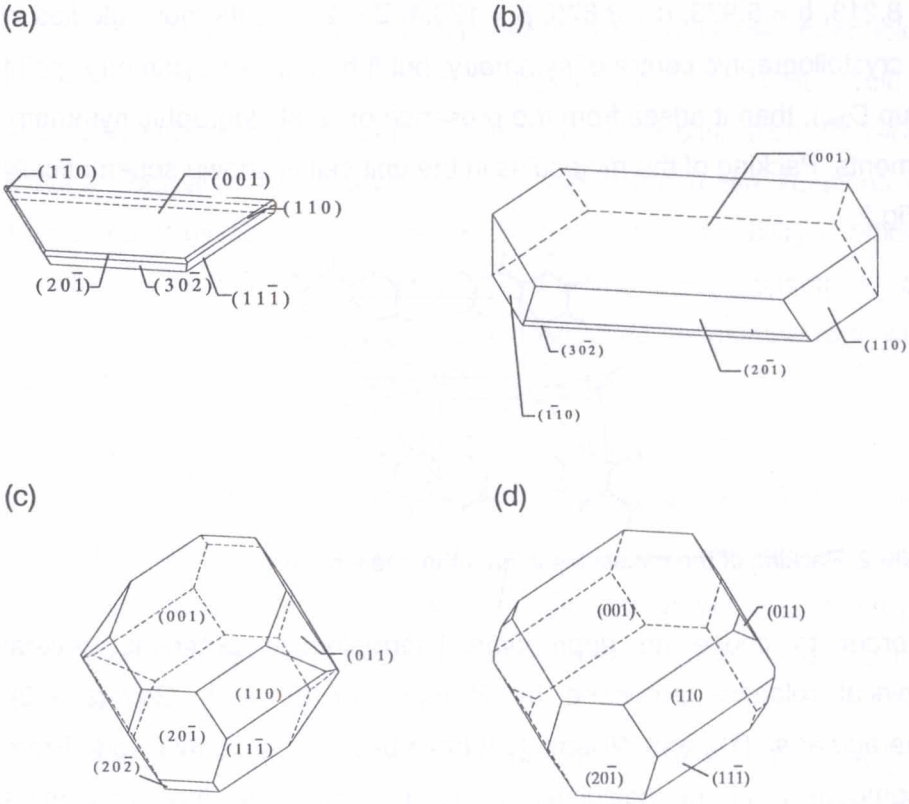

Figure 3. Projection of idealised naphthalene crystals grown from the vapour in vacuum (a), from solution in 1,2-dCHLE (b) and theoretical morphologies calculated by MORANG (c) and HABIT (d)

As it can be seen in Fig.3, the attachment energy model predicts the growth morphology with a better accuracy than the geometrical model, because it identifies the importance of the {001} faces. In the case of sublimation grown crystal main difference concerns (30$\bar{2}$) and ($\bar{3}$02) faces, which are not predicted by either theoretical model.

Basing on the comparison of theoretical and real morphologies one can assume that no present (predicted by HABIT) {011} and $\{11\bar{1}\}$ faces in crystal grown from solutions are caused by interactions of solvent, especially the faces $(11\bar{1})$ and $(1\bar{1}\bar{1})$ [form $\{11\bar{1}\}$ is present (?) in sublimation grown crystal (without solvent), Fig.3a]. It can also be found that the theoretical models underestimate the importance of the {001} faces, which dominate in growth morphology.

Moreover, on the basis of calculated entropy factor (α_{hkl}), the growth rates of particular faces and their growth mechanism have been established. The entropy factors were: 4.78, 2.97, 2.58, 1.89 and 1.80 for {001}, {110}, $\{20\bar{1}\}$, $\{30\bar{2}\}$ and $(11\bar{1})$, respectively. Since relative growth rates of these faces increase in the following row: $R_{\{001\}} < R_{\{110\}} < R_{\{20\bar{1}\}} < R_{\{30\bar{2}\}} < R_{\{11\bar{1}\}}$, one can conclude that major flat face (001) grows by dislocation mechanism (BCF) and other faces – by continuous growth mechanism.

CONCLUSIONS

Both Donnay-Harker and Hartman-Perdok models identify almost all the faces (apart from $\{30\bar{2}\}$ faces) in the observed growth forms, although Hartman-Perdok model estimates better the importance of major faces {001}. The calculated values of α_{hkl} indicate that these faces grow by dislocation mechanism; the other side faces shows continuous growth.

The observed differences in growth morphology are probably caused by the solvent effect, what is well proved by activity coefficients of solute . Solute-solvent interactions can also explain the differences between morphology of crystals grown from solution and by sublimation.

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