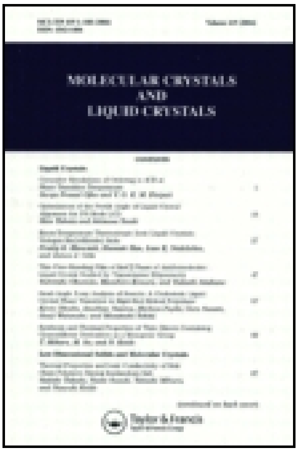

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# An Improved Procedure for the Investigation of Growth and Nucleation Processes from Organic Solutions

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# AN IMPROVED PROCEDURE FOR THE INVESTIGATION OF GROWTH AND NUCLEATION PROCESSES FROM ORGANIC SOLUTIONS

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Abstract An improved,simple procedure for the determination of reproducible relations between growth conditions, i. e. supersaturation $-\sigma$, temperature -T, type of solvent and habit of crystals, and the effects of this conditions on induction period $-\tau$ and metastable zone width ($\Delta T_{MET}$) for easy evaporate organic solutions are reported. Naphthalene and acenaphthene solutions in certain organic solvents were chosen to characterize of this procedure.

## INTRODUCTION

Polynuclear aromatic hydrocarbons (PAHs) may be treated as a model substances for the investigation of nucleation and growth processes. For example, recent interest in naphthalene is mainly due to the study for kinetic of roughening.[1,2]

These investigations demand of high stability of growth conditions i.e. supersaturation and temperature. For growth processes the most important is an experimental relation between them and morphology of crystal while for nucleation most important are relations between growth conditions and induction periods and metastable zone widths. Unfortunately most of organic solutions, especially PAHs solutions, have a high vapour pressure even at low temperatures. In order to observe these mentioned above relations we worked out an improved, simple procedure which used layer of water covering of investigated solutions. Density of the solutions must be greater then density of water and there should be no interactions or mixing. In result of the investigations, reproducible relations between growth conditions and habit of naphthalene and acenaphthene crystals from certain organic solvents were found. Moreover the effects of the growth conditions ($\sigma$, T and type of solvent) on induction period and metastable zone width for these solutions were determined.

## THE PROCEDURE

Principle of the procedure we worked out for the investigation of growth and nucleation processes in low evaporate organic solutions is schematically shown in Figure 1.

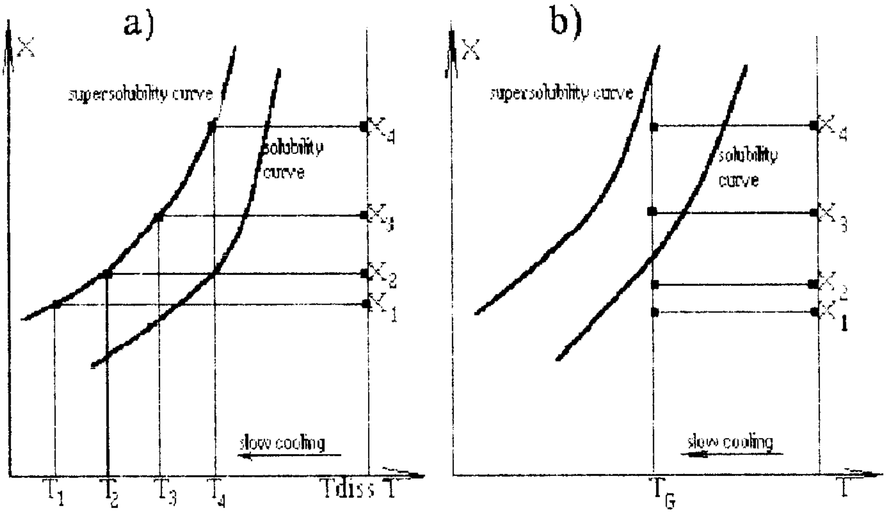

FIGURE 1 The principle of the procedure:
(a) determination of metastable zone width
(b) determination of relations between growth conditions ($\sigma$, Ta, type of solvent) and habit of crystals as well as induction periods

In Figure 2 a schematic diagram of the apparatus which was used for visual observations of growth and nucleation crystals is presented.

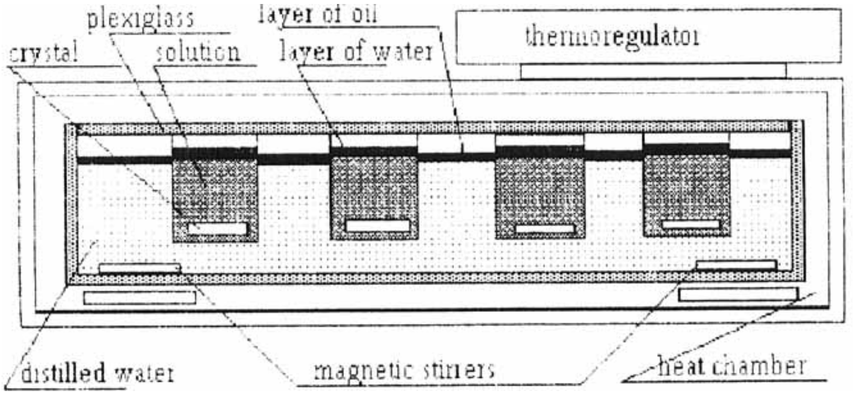

FIGURE 2 Construction of apparatus.

## EXPERIMENTAL DETAILES

### 1. Substances

Experiments were performed with the following PAHs:
(1) naphthalene (p., POCH, Poland) was vacuum sublimed,
(2) acenaphthene (p., IEL, England) was recrystallized from carbon tetrachloride ($CCl_4$) and ethyl alcohol (EtOH). After then vacuum sublimation was used.

The following solvents were used:
(1) 1,1-dichloroethane (p. a., POCH, Poland) (1,1-dCHLE)
(2) 1,2-dichloroethane (p. a., POCH, Poland) (1,2-dCHLE)
(3) chloroform (p. a., POCH, Poland) (CHL)
(4) carbon tetrachloride (p. a., POCH, Poland) ($CCl_4$)
(5) chlorobenzene (p. a., POCH, Poland) (CHLB)

All the above solvents were purified by column distillation.

### 2. Course of experiments

Solubility curves of naphthalene and acenaphthene in above mentioned solvents were determined by observation of the temperature at which the last crystal disappears. This temperature is regarded as the saturation temperature of the solution. The temperature was increased with the rate of 0.1 K/h.

Growth and nucleation experiments were carried out in apparatus shown in Figure 2. Particular samples of solutions (about 70 ml) covered of layer of water were placed in glass vessels. Set of the vessels were diped in water bath covered thin layer of oil. The temperature was kept constant within 0.02 °C and for slow cooling it was decreasing about 0.5 K/h. In order to determine of supersolubility curves the temperature at which spontaneus crystallization took place, was noticed. Induction periods were established as the difference of time of possesing of the growth temperature ($T_G$) and the time of growth process start. Experiments was performed at selected levels of supersaturation and temperature, under controlled conditions until reproducible results were obtained.

## RESULTS AND DISCUSSION

Solubilities of naphthalene and acenaphthene in considered solvents ($x_s$, $T_s$), metastable zone widths ($\Delta T_{MET}$), induction periods ($\tau$) data and calculated enthalpy of dissolution ($\Delta H_{diss}$) values are summarized in Table I. Enthalpy values were obtained from the well known, classical thermodynamic equation for regular solutions.[2] From the comparison of PAHs solubility plots ($\ln x_s = f(1/T_s)$) with the ideal solutions (without solvents) ones for them it was found that all the investigated solutions were regular and that the plot of acenaphthene in CHL is in almost full accordance with ideal line for this PAH.

TABLE I Experimental results of solubility ($x_s$, $T_s$), $\Delta T_{MET}$, $\tau$ and calculations values of $\Delta H_{diss}$.

| | solvent | $x_s$ [molf] | $T_s$ [K] | $\Delta T_{MET}$ [K] | $T_a$ [K] | $\tau$ [h] | $\Delta H_{diss}$ [$J \cdot mol^{-1}$] |
|---|---|---|---|---|---|---|---|
| | | | NAPHTHALENE | | | | |
| 1. | CHL | 0.359 | 308 | 9 | | | 18937 |
| 2. | | 0.375 | 310 | | | | 18891 |
| 3. | | 0.393 | 312.2 | | 303 | 183 | 18884 |
| 4. | | 0.412 | 313 | 6.6 | 306.4 | | 18832 |
| 5. | | 0.433 | 316 | 9.3 | 306.7 | | 18825 |
| 6. | | 0.463 | 319 | 11.8 | 307.2 | | 18799 |
| 1. | 1,2 dCHLE | 0.366 | 307 | | | | 18796 |
| 2. | | 0.382 | 308.5 | 9.5 | 307.9 | 400 | 18765 |
| 3. | | 0.397 | 310 | 8.4 | 308.2 | 391.5 | 18764 |
| 4. | | 0.402 | 311 | | 308.2 | 296.5 | 18763 |
| 5. | | 0.426 | 313 | 8.5 | 308.2 | 34.5 | 18715 |
| 6. | | 0.425 | 315 | 8.5 | 308.5 | 2.5 | 18661 |
| 1. | $CCl_4$ | 0.345 | 312 | 7 | 308 | 264 | 19211 |
| 2. | | 0.36 | 314 | | 308 | 125 | 19205 |
| 3. | | 0.375 | 314.5 | 7 | 308 | 26.5 | 19125 |
| 4. | | 0.417 | 317 | | 313 | 105 | 18974 |
| 5. | | 0.435 | 318.5 | 7 | 313 | 60 | 18939 |
| 6. | | 0.453 | 319 | 7 | 313 | 23 | 18852 |
| 1. | CHLB | 0.345 | 309 | | | | 19053 |
| 2. | | 0.361 | 310 | 11.8 | | | 18989 |
| 3. | | 0.385 | 312 | 11 | 303 | 7 | 18927 |
| 4. | | 0.419 | 316 | 10 | 303 | 6 | 18911 |
| 5. | | 0.433 | 317 | | 303 | 2 | 18876 |
| | | | ACENAPHTHENE | | | | |
| 1. | CHL | 0.238 | 305 | 10 | 303 | 783 | 22390 |
| 2. | | 0.26 | 309.5 | 11.5 | 305 | 496 | 22375 |
| 3. | | 0.28 | 312 | 8 | 308 | 255 | 22326 |
| 4. | | 0.3 | 315 | 8 | | | 22316 |
| 5. | | 0.32 | 317 | 6 | | | 22258 |
| 1. | 1,2 dCHLE | 0.2 | 306.4 | 7.6 | | | 22865 |
| 2. | | 0.22 | 309.5 | 8.5 | | | 22805 |
| 3. | | 0.24 | 312.8 | 9.2 | 310.4 | 506 | 22772 |
| 4. | | 0.26 | 316 | 8.5 | 311.4 | 288 | 22747 |
| 5. | | 0.28 | 319.2 | 11.4 | | | 22733 |
| 6. | | 0.3 | 322.5 | 12.5 | | | 22726 |
| 1. | $CCl_4$ | 0.204 | 308.8 | 9.6 | | | 22964 |
| 2. | | 0.222 | 311.6 | 7.5 | 308.5 | 332 | 22911 |
| 3. | | 0.24 | 314.2 | 5.2 | 310.1 | 243 | 22859 |
| 4. | | 0.258 | 316.6 | 4.9 | | | 22819 |
| 5. | | 0.282 | 319.6 | 4.5 | | | 22743 |
| 1. | 1,1 dCHLE | 0.159 | 305.4 | 11.2 | | | 23383 |
| 2. | | 0.172 | 307.6 | 11 | 296.8 | 1080 | 23327 |
| 3. | | 0.182 | 309.6 | 11.4 | 297.5 | 1056 | 23304 |
| 4. | | 0.193 | 311.6 | 11.4 | 300.7 | 835 | 23274 |
| 5. | | 0.204 | 313.6 | 11.4 | 302.9 | 4 | 23249 |

Also the plots of naphthalene in 1,2-dCHLE and naphthalene in CHL as well as acenaphthene in 1,2-dCHLE are placed very near of ideal lines of these PAHs. The values of $\Delta H_{diss}$ for these solutions are lowest of all. Four more interesting results of growing crystals are underlined in Table I and photographs of crystals of naphthalene from 1,2-dCHLE and acenaphthene from CHL are shown in Figures 3 and 4.

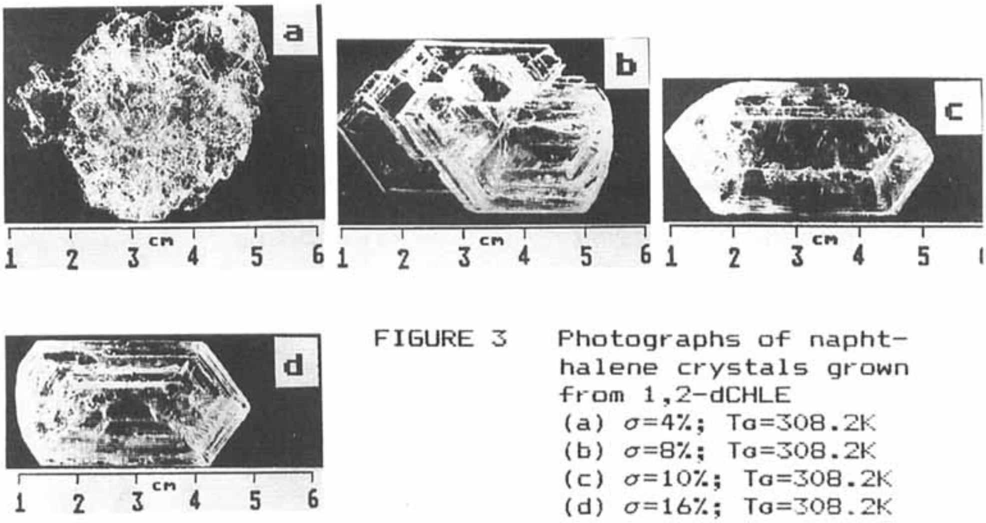

FIGURE 3 Photographs of naphthalene crystals grown from 1,2-dCHLE
(a) $\sigma=4\%$; Ta=308.2K
(b) $\sigma=8\%$; Ta=308.2K
(c) $\sigma=10\%$; Ta=308.2K
(d) $\sigma=16\%$; Ta=308.2K

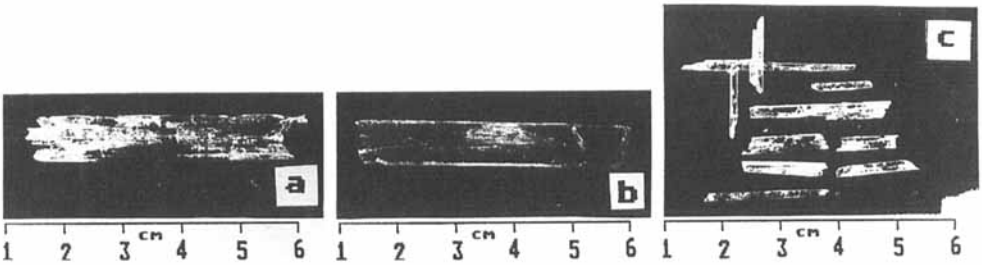

FIGURE 4 Photographs of acenaphthene crystals grown from CHL
(a) $\sigma=10\%$; Ta=308K, (b) $\sigma=9.2\%$; Ta=305K
(c) $\sigma=6.3\%$; Ta=303K

All the naphthalene crystals obtained in our experiments colud be classified, considering the shapes of crystal, in one of two types:

- two dimensional (plate - like) or
- three dimensional (prismatic).

Plate - like crystals were obtained from $CCl_4$ and CHL while the prismatic ones were got when 1,2-dCHLE was used.

In the acenaphthene case we have also two categories of crystal shapes:

- the needle - like (one dimensional) from $CCl_4$, 1,1-dCHLE and 1,2-dCHLE solutions,
- the plate - like from CHL.

These observations are in good agreement with recent results of Tanaka and Matsuoka[3]. When a solvent which has a similar dipole moment and the ideal solubility is chosen, large prismatic crystals can be expected to grow in such solution. As it could be from Table I reasonable induction periods and middle supersaturations were desirable for successful growth.

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