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# Solvent Effect on the Inclusion of 2-Acetylnaphthalene by 1,1-Di(*p*-hydroxyphenyl)cyclohexane

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**Abstract.** The effect of the solvents acetone (AT), dimethylsulfoxide (DMSO) and methylcellosolve (MCS) on the inclusion of 2-acetylnaphthalene (2-AN) in the host 1,1-di(*p*-hydroxyphenyl)cyclohexane (DHC) has been investigated. Each solvent molecule is included in DHC in a molar ratio of 1.0, when DHC is crystallized from the solvents. The evaporation rate of these solvents from the host lattice decreases in the order AT, MCS and DMSO. The order agrees well with the interaction strength between the host and solvent molecule, which was measured by DSC and IR. 2-AN cannot be included in the crystals by crystallization from MCS and DMSO solutions. However, in AT solution both AT and 2-AN are included competitively and the morphology of the crystals is different from that obtained in pure solution. The amount of 2-AN in the crystals increases continuously with its concentration in solution. This behavior indicates that AT is replaced by 2-AN and the solid solution of the molecular complex is formed. The solid solution is a metastable form and the solution-mediated transformation to the stable form (which includes only AT) was observed.

**Key words.** Crystallization, nucleation, crystal growth, polymorph, molecular complex, transformation, solvent effect.

## 1. Introduction

Molecular complexes and clathrate compounds have recently attracted special interest in their application to the production of a variety of functional materials. It has been shown that diol hosts [1] form molecular complexes with many kinds of guest compounds. In our previous paper [2] the crystallization behavior of the molecular complex of 1,1-di(*p*-hydroxyphenyl)cyclohexane (DHC) from acetone solutions containing *d*-limonene (perfume) was studied: two kinds of crystals (A, B) (polymorphs) were found to precipitate. The morphologies of these crystals are different: in the A crystals *d*-limonene is included with acetone, however, the B crystals only include the acetone molecule. Such inclusion behavior, or the selectivity for guest molecules by DHC, is expected to be intensively influenced by the solvents used in the crystallization, because the solvent can also form a molecular complex with DHC. In this paper the influence of solvents on the precipitation and inclusion behavior of the host DHC in the presence of 2-acetylnaphthalene (2-AN) has been investigated.

## 2. Experimental

Commercial grade 1,1-di(*p*-hydroxyphenyl)cyclohexane (DHC) was recrystallized from methanol twice and dried completely. The solubility of the host was measured in various solvents by adding the host crystals to the solution until saturation. Crystallization was carried out by cooling rapidly to a constant temperature (293 K) in a stirred crystallizer [2–4]. The first crystals were precipitated from solutions of acetone (AT), dimethylsulfoxide (DMSO) and methylcellosolve (MCS), including only the host. Secondly, the crystallization was carried out in the presence of 2-acetylnaphthalene (2-AN). After filtration, the change in composition of the crystals was analysed periodically in the ambient atmosphere at 293 K, using liquid chromatography for the crystals precipitated from AT and DMSO solutions, and both liquid and gas chromatography for the crystals from MCS. The precipitated solids were also subjected to X-ray powder diffraction measurements (Rigakudenki X-ray diffractometer, Rad-B with Cu$K_\alpha$ line), differential scanning calorimetry (Shimadzu DSC-50) and infrared spectroscopy (Shimadzu IR-470).

## 3. Results

### 3.1. SOLUBILITY OF THE HOST IN VARIOUS SOLVENTS

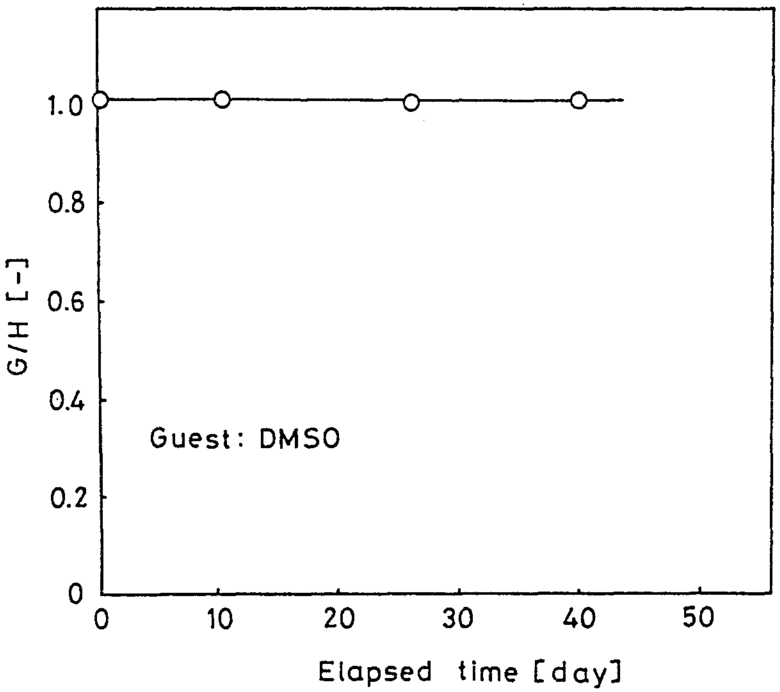
The host is highly soluble (50% or more) in tetrahydrofuran and dimethylformamide and almost insoluble in aromatic solvents such as benzene and toluene. On the other hand, some solvents have intermediate solubilities, which are adequate for crystallization, i.e. 130 g (ethylacetate), 95 g (methanol), 220 g (AT), 420 g (DMSO) and 125 g (MCS) per litre of each solvent. In this work AT, DMSO and MCS are used for the crystallization.

### 3.2. COMPOSITION CHANGE OF CRYSTALS IN THE ATMOSPHERE

Crystallization of DHC was carried out in AT, DMSO and MCS, and the compositions of the crystals were analysed. It was observed that each solvent molecule is included in the crystals and the amount decreases with elapsed time in the atmosphere. The dependences of the molar ratio of guest (solvent) to host (G/H) in the crystals on the time elapsed after the filtrations for the cases of MCS and DMSO are shown in Figure 1. It can be seen that MCS decreases slowly with a half-life of 10 days after filtration. Extrapolation of the curve in Figure 1 to time 0 indicates that the molar ratio (G/H) is 1.0 just after the filtration. The decrease of DMSO, which is also included in a molar ratio of 1.0, could not be observed even after 40 days. On the other hand, it was shown in the previous paper [2] that the G/H value of AT is also 1.0 and AT evaporates very quickly in the atmosphere, disappearing within about 3–4 hours.

### 3.3. MORPHOLOGY AND CRYSTAL STRUCTURES

The morphologies of the crystals precipitated from each solvent are different. The crystal shapes obtained from AT [2] and MCS are plate-like, although the angular relationships between the planes are different; and the crystal obtained from DMSO is prismatic. The X-ray diffraction patterns of these crystals are shown in Figure 2.



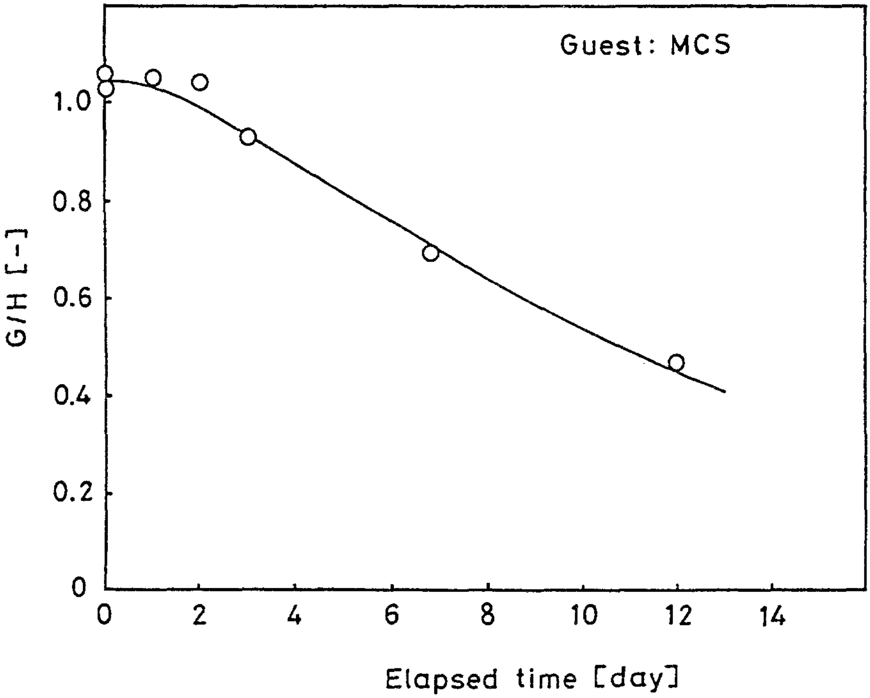


Fig. 1. Change of G/H values of MCS and DMSO in the crystals with elapsed time after filtration.

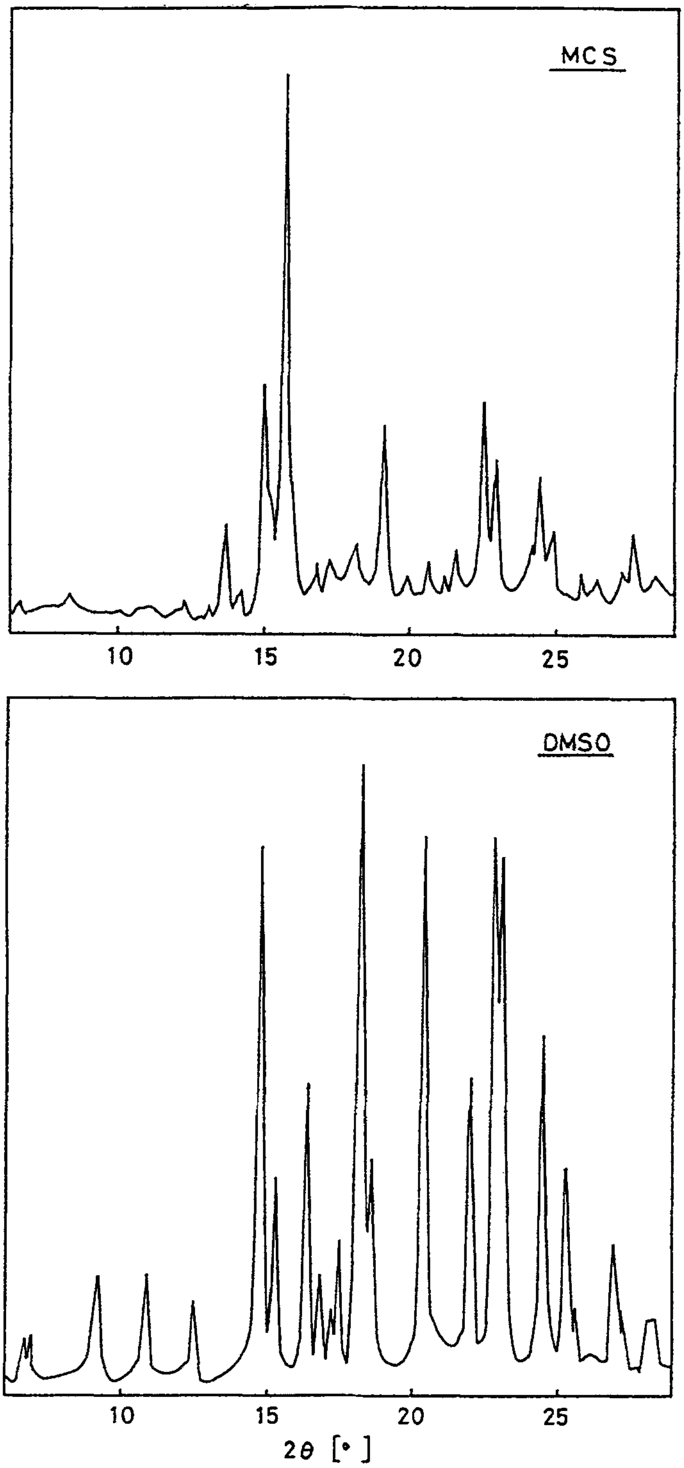


Fig. 2. X-ray diffraction patterns of crystals obtained from MCS and DMSO.

When the results are compared with the result for AT [2], it is observed that the diffraction peaks are much stronger for DMSO than for MCS and AT, and the positions of the predominant peaks are different among the patterns. These results indicate that the structures of all solvent clathrated crystals are different.

### 3.4. INTERACTION BETWEEN HOST AND SOLVENT MOLECULES

The strength of interaction between the host and solvent molecules are compared by DSC (Figure 3). It can be seen that crystals obtained from AT and MCS show two endothermal peaks. The peaks at 326 K for AT and 370 K for MCS are due to evaporation of the solvent molecules from the crystals, and the peaks at 458 K are due in both cases to melting of the host. In the case of DMSO only one peak is observed at 410 K, which is attributed to evaporation of the DMSO. The boiling point of DMSO (462 K) is higher (by 52 K) than the peak for the supposedly complexed DMSO. This means that the evaporated molecules may recondense on the host crystals and dissolve them. Actually, a solution of DMSO was observed in a pan used in the measurement at about 450 K. The temperature at which the guest

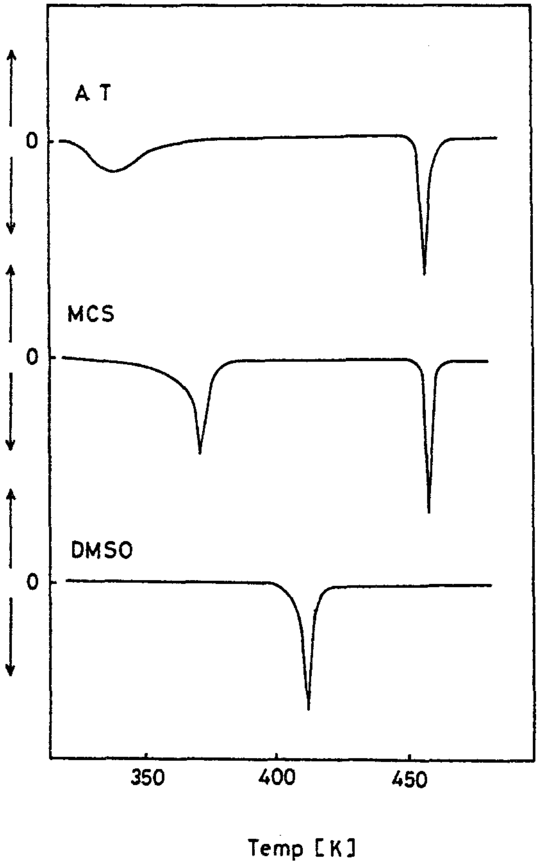


Fig. 3. DSC curves of crystals obtained from each solvent.

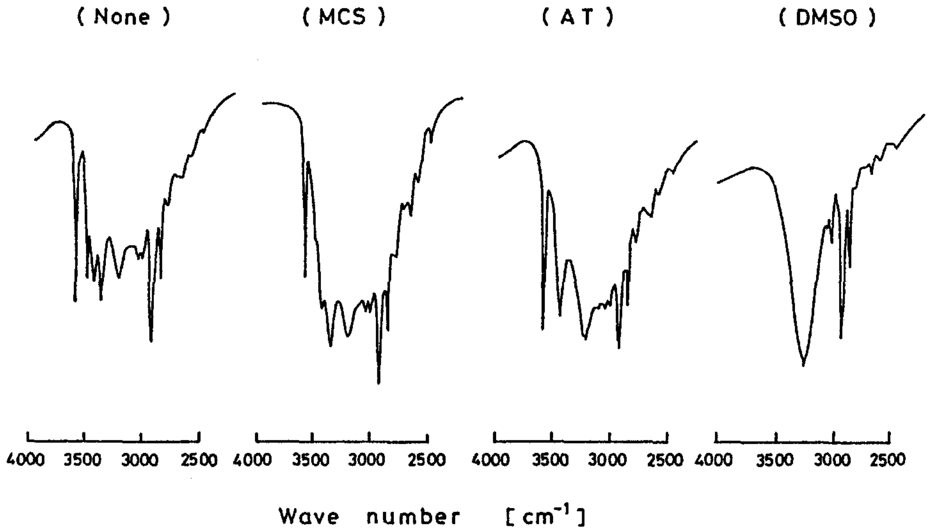


Fig. 4. Infrared spectra of crystals obtained from each solvent.

evaporates from the crystals may be related to the interaction strength between host and guest in the crystals. The results may suggest that the interaction increases in the order DMSO, MCS and AT, and the order coincides well with that of the decreasing rate of solvent molecules in the atmosphere. As the evaporation temperatures of each solvent molecule from the crystals are lower than their boiling points, the interactions in the crystals may be smaller than those between the solvent molecules.

In Figure 4 infrared spectra of the crystals from each solvent are compared with those of the empty host. It can be seen that absorptions in the 3200–3700 cm$^{-1}$ region, which are due to various O—H stretching vibrations of the host, are different among the crystals. In the spectra for AT, MCS complexes and empty host, the absorption at 3600 cm$^{-1}$ due to the isolated hydrogen bond is observed; however, in the DMSO complex it cannot be observed and only a large band appears near 3300 cm$^{-1}$. It is considered that in the case of DMSO the band attributed to the isolated hydrogen bond shifts to lower frequency by forming a hydrogen bond vibrating at 3300 cm$^{-1}$, which is stronger than the other cases. Furthermore, these results suggest that the hydrogen bond in crystals of the MCS and AT complexes is similar to that in the empty host.

The guest molecules have to diffuse to the crystal surface through the host lattice to evaporate from the complex crystals [2]. It is considered that the diffusion rate depends on the size of the guest molecule, the host–guest interaction and the crystal structure. The results in Figures 3 and 4 on the host–guest interaction seem to agree with the order of the evaporation rates of the solvent molecules from each complex crystal, indicating the importance of the host–guest interaction.

### 3.5. PRECIPITATION IN THE PRESENCE OF 2-AN

Crystallizations were carried out in solutions including both host and various concentrations of 2-AN. It was observed that a small amount of 2-AN precipitates from adhesive solutions on the crystal surface after filtration. To obtain accurate values of G/H in advance of the analysis, the crystals (300 mg) were washed quickly with *n*-hexane (5 mL) which does not form a molecular complex with the host. It appeared that in MCS and DMSO solution, even when the 2-AN concentration is increased to about 2.0 mol/L, crystals precipitated with the same morphology as that of the crystals in pure solutions, and they include a small amount of 2-AN as well as MCS or DMSO. However, 2-AN disappeared completely upon washing with *n*-hexane and only MCS and DMSO remained with a G/H value of 1.0. On the other hand, in AT solutions crystals precipitated with a different morphology from that of the crystals in pure solution (Figure 8a). The morphology is similar to that observed in the presence of *d*-limonene in the previous paper [2]. In the crystals a relatively large amount of 2-AN was detected with AT and the 2-AN remained even after washing with *n*-hexane, indicating that the host forms a molecular complex with 2-AN as well as with AT. The quantity of 2-AN included in the crystals was observed to increase with the 2-AN concentration in solution, as shown in Figure 5. It is clear that the total G/H ratios of AT and 2-AN are almost equal to 1.0 for each solid composition. This may mean that 2-AN is included with AT by forming a solid solution of the molecular complex. Little change is observed in the X-ray diffraction pattern when 2-AN was included up to a G/H ratio of about 0.3. However, a small change appeared when the G/H ratio of 2-AN increased to more than 0.4, as shown in Figure 6, i.e. a new peak appears at $2\theta = 13.3°$ and the shape of the peaks at $2\theta$ between 15° and 16.5° changes a little. These results suggest that a portion of the acetone molecules is replaced by 2-AN much more freely than by *d*-limonene and the structure of the solid solution scarcely changes, provided the amount of 2-AN in the crystals is not greater than a G/H value of 0.3; however, the lattice parameter may change by including more 2-AN. On the other

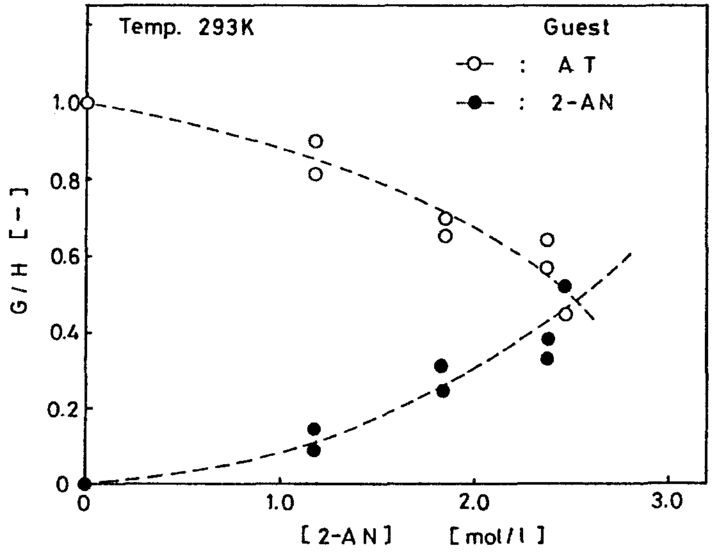


Fig. 5. Relationship between crystal composition (G/H) and 2-AN concentration in solution.

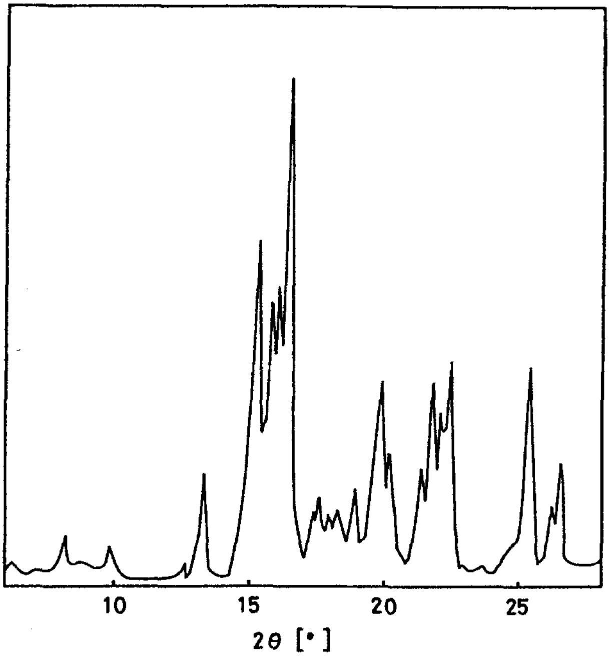


Fig. 6. X-ray diffraction pattern of the crystals including 2-AN with G/H = 0.4–0.5.

hand, the morphology change was observed even for the crystals including 2-AN at a G/H value less than 0.3. This fact is also similar to the *d*-limonene system [2].

The results shown above indicate that in MCS and DMSO solutions the solvent molecules are included more easily than 2-AN; however, both AT and 2-AN are competitively included in AT solutions. It is considered that as AT and 2-AN have a common acetyl group, the interaction with the host may be relatively weak and

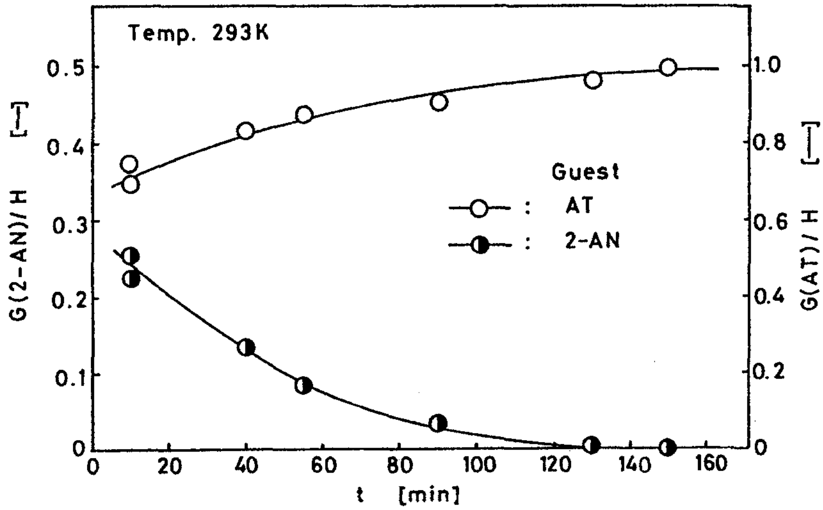


Fig. 7. Composition change of crystals in AT solutions after nucleation.

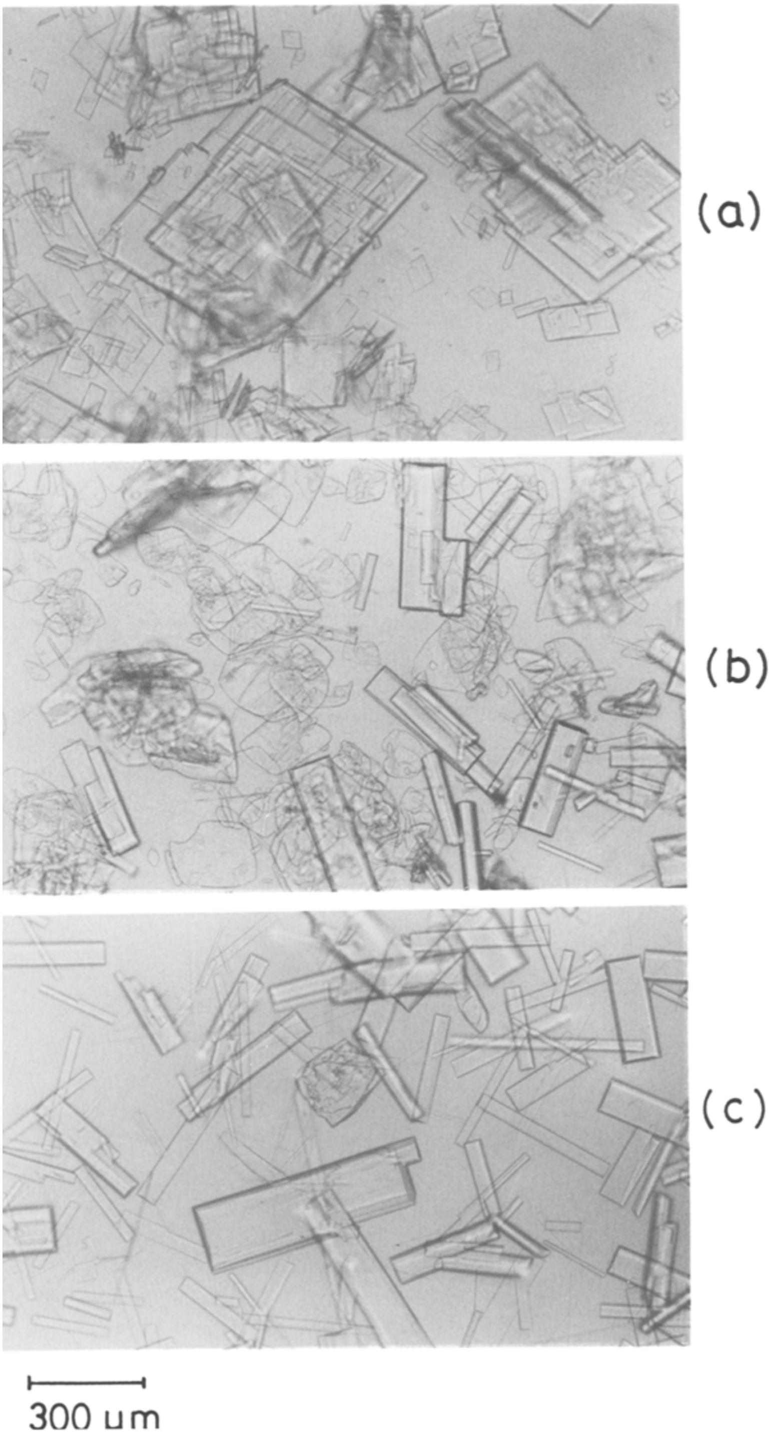


Fig. 8. Microscopic photographs of crystals in AT solutions in the course of transformation: (a) 10, (b) 40, and (c) 80 minutes after nucleation.

similar for AT and 2-AN. From Figure 5 it appears that the mole fractions of 2-AN as guest molecules in the solids are almost the same as that in solution, indicating that AT and 2-AN molecules are included in the crystals with the same ratio. Furthermore, the results suggest that the methyl and naphthyl group in AT and 2-AN cannot be discriminated by the host.

### 3.6. TRANSFORMATION IN AT SOLUTIONS

The change of solid composition was observed with elapsed time after the nucleation in AT solutions and a typical example is shown in Figure 7. The amount of AT in the solids increases and that of 2-AN decreases with elapsed time, and finally crystals are obtained containing only AT with a G/H value of 1.0. Microscopic observation after the nucleation (Figure 8) indicates that during the composition change the solid solution (A), including both 2-AN and AT, dissolves and crystals (B), including only AT, nucleate and grow. It was confirmed that the X-ray diffraction pattern of crystals (B) finally obtained coincides completely with that of crystals in pure AT. This means that the crystals of solid solution (A) are a metastable form and that crystal (B) is the stable form; and that the solution-mediated transformation [3, 4] occurs by the following route:

$$\text{Solid solution (A)} \xrightarrow{\text{dissolve}} \text{Host} + f * \text{2-AN} + (1 - f) * \text{AT}$$

$$\text{Host} + \text{AT} \xrightarrow{\text{precipitate}} \text{Crystal (B)}$$

where $f$ is the molar fraction of 2-AN in the guest molecules in crystals.

## Acknowledgement

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