

POLYMORPHISM IN ADDUCTIVE CRYSTALLIZATION OF Ni-COMPLEX IN THE PRESENCE OF 1-METHYLNAPHTHALENE

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Polymorphous clathrate crystals of β - and γ -type were observed to precipitate by crystallization in methylcellosolve (MCS) solutions containing tetra(4-methylpyridine)nickel(II)dithiocyanate (Ni-complex) and 1-methylnaphthalene (1-MN). The relative precipitation behavior of these polymorphs was divided into three Parts (I, II, III) with respect to 1-MN concentration.

By solubility measurements of Ni-complex forming the host lattice of each polymorph, it was found that there is a cross-point of the solubility curves which can be regarded as the transition point between the polymorphs concerning 1-MN concentration.

A nucleation model was proposed, assuming a competitive nucleation process for the liquid clathrates of each polymorph. By using this model it was clarified that the relative nucleation behavior of the polymorphs depends on the ratio of their supersaturation ratios.

Transformation was observed when the metastable crystals were added to the solutions in Parts I or III, and it was suggested that the main transformation mechanism was "solution-mediated".

Introduction

In clathrate compounds, guest molecules are enclosed in three-dimensional host lattice structures. Recently, such clathrate compounds are coming into practical use for two main purposes: separation of many kinds of isomers^{10,11)} and addition of new functional properties to guest molecules.^{2,10)}

To form these clathrate compounds, crystallization from solutions containing guest molecules and a host compound are mostly used. In this method, called adductive crystallization, the lattice structure of the precipitated host is not usually rigid but is changeable with crystallization conditions.^{1,8)} The species of guest molecule clathrated in the host generally depends on the host lattice structure. Accordingly, strict control of the crystallization conditions is important to increase the separation efficiency of isomeric compounds or to obtain clathrate crystals with the desired properties. Such changes of structure can be regarded as polymorphism of the host lattice. To control the precipitation behavior of these polymorphs, the mechanisms of the precipitation process must be known. Furthermore, these mechanisms are considered to be directly concerned with the separation or clathration process of guest molecules. However, little attention has yet been paid to this point. In this work adductive crystallization was carried out in a

methylcellosolve solution containing the nickel complex of tetra(4-methylpyridine)nickel(II) dithiocyanate, $\text{Ni}(4\text{-MePy})_4(\text{SCN})_2$ as the host compound, and 1-methylnaphthalene as the guest molecule, and the precipitation mechanism of the polymorphous clathrate crystals and the correlation between the relative precipitation behavior of the polymorphs and the crystallization conditions was investigated.

1. Experimental Procedure

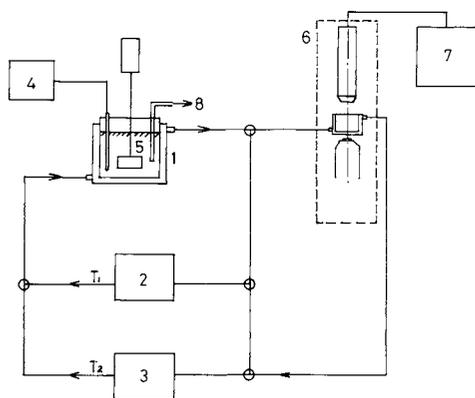
1.1 Preparation of the nickel complex (Ni-complex)

The Ni-complex $\text{Ni}(4\text{-MePy})_4(\text{SCN})_2$ was synthesized in aqueous solution by a method described elsewhere.⁴⁾ The crude Ni-complex was recrystallized twice in chloroform. As the crystals obtained include chloroform,⁵⁾ they were dried for several months in the atmosphere to remove the chloroform completely before experimental use.

1.2 Adductive crystallization

Crystallizations were done in methylcellosolve (MCS) solutions containing the host compound of Ni-complex (0.0913 mol/l) and various amounts of 1-methylnaphthalene (1-MN) as guest molecule. For the crystallization, a 200-ml jacketed cylindrical glass stirred tank was used as shown in Fig. 1. The temperature of the solution was controlled by circulating water from two thermostatted baths to the jacket of the crystallizer. Initially the temperature was kept at 333 to 343 K (T_1) to dissolve Ni-complex completely, and thereafter the solution was cooled stepwise to

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1 Crystallizer 2,3 Thermostat bath and Circulator
4 Digital thermometer and recorder 5 Impeller
6 Microscope and TV Camera 7 Monitor television
8 Sampling section

Fig. 1. Schematic diagram of experimental apparatus

the crystallization temperature of 293 K (T_2) by changing the circulating water with that from the other bath. No nucleation was observed in any run before the solution was cooled to the crystallization temperature. The solution was stirred with a glass impeller at a constant rate of 150 rpm.

1.3 Microscopic observation and analysis of crystals

After crystals appeared in the crystallizer, a small amount of slurry was periodically sampled into the glass cell and microscopic observation was done using a video camera and monitor television system. The glass cell was equipped with a jacket to keep the temperature the same as that of the crystallizer.

Furthermore, required quantities of the slurry were sampled and filtered quickly, and the composition of polymorphs in the solid was determined by X-ray diffraction measurement using a Rigakudenki X-ray diffractometer (Rad-B) with CuK_α line.

Guest molecules in the clathrate crystals were also analysed by pyrolysis gas chromatography and the molar ratios of the guest molecules to the host Ni-complex were determined. In the analysis, clathrate crystals were decomposed by a Shimadzu PYR-2A pyrolysis furnace at 673 K in a nitrogen carrier-gas stream. At this temperature Ni-complex was decomposed completely, and guest molecules and ligand molecules of 4-methylpyridine were analysed by a Shimadzu GC-7A gas chromatograph. Apiezon grease L was used as the column packing at a column temperature of 423 K.

1.4 Solubility measurements of Ni-complex in the polymorphous crystals

Solubility measurements of Ni-complex in the polymorphous crystals were carried out in MCS solutions of various 1-MN concentrations at 293 K. The MCS solutions containing 1-MN were put into a 100 ml conical flask which was dipped in thermostatically controlled water in a jacketed glass vessel.

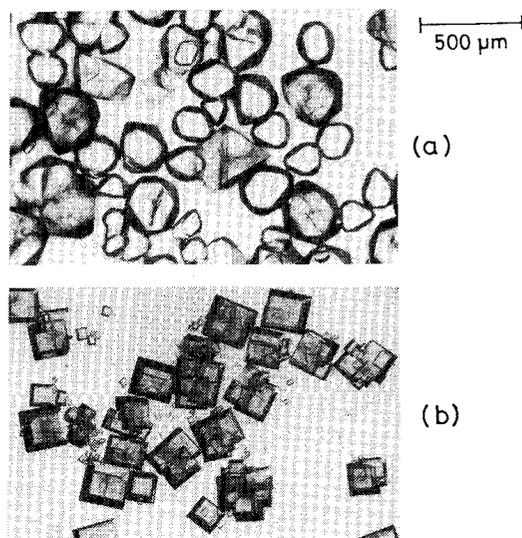


Fig. 2. Microscopic photographs of precipitated crystals with different habits of (a) (β -type) and (b) (γ -type)

Crystals of each polymorph were prepared by crystallization under the particular conditions found in the experiments. These crystals were added to the MCS solution in the flask in excess and the solution was stirred for several hours with a magnetic stirrer. The saturated solutions with each polymorph were then filtered and the concentration of Ni-complex in the filtrate was analysed by UV spectrophotometry using the absorbance of the characteristic peak of Ni-complex at 380 nm.

2. Results and Discussion

2.1 Dependence of the composition of polymorphs in the precipitated solids on the solution composition

Two kinds of crystals with different habits were observed in the crystallizations in MCS solutions. Their respective habits of octahedral and tetragonal plate-like shapes are shown in Fig. 2(a, b). Figures 3(a) and (b) are the X-ray powder diffraction patterns obtained with the crystals shown in Fig. 2(a) and (b), respectively. It was clear that the structures of crystals in Fig. 2(a, b) are different from each other. It is known that Ni-complex has three types of structures, α , β and γ . Diffraction patterns of monoclinic α -type ($P2_1/c$) and tetragonal β -type ($I4_1/a$) were shown in the previous paper.⁵⁾ From Fig. 3(a) the crystals in Fig. 2(a) were identified as β -type. On the other hand, the pattern in Fig. 3(b) is apparently different from that of either α - or β -type. The X-ray diffraction pattern of γ -type was shown by Lipkowski *et al.*⁷⁾ Although the diffraction pattern in Fig. 3(b) is a little different from their results, the crystals in Fig. 2(b) appeared to belong to the γ -type.

It was observed that the behavior of competitive precipitation of these polymorphous crystals was scarcely influenced by the initial concentration of Ni-

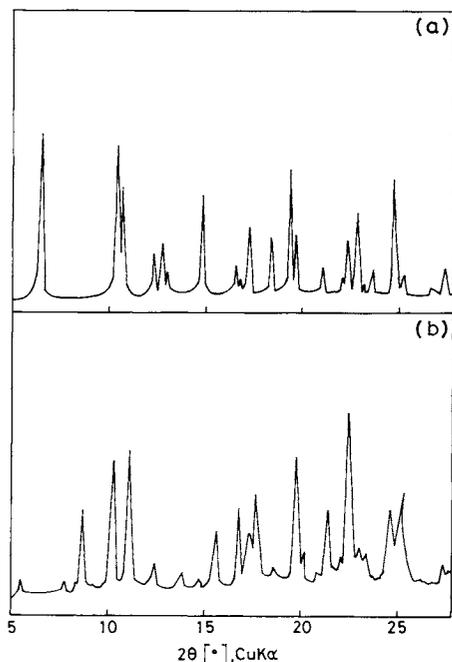


Fig. 3. X-ray powder diffraction patterns of β -type (a) and γ -type (b) crystals

complex, but was markedly influenced by the concentration of 1-MN. The dependence of weight fraction of γ -type crystals in the precipitated solids, Y_γ , on the concentration of 1-MN in solutions is shown in Fig. 4. The Y_γ values were observed to be almost independent of sampling time after the occurrence of nucleation. This means that the nucleation process in the early stage of crystallization determines the precipitation ratio of the polymorphs. The precipitation behavior can be divided into three parts with respect to the concentration of 1-MN as denoted by I, II and III in Fig. 4. At concentrations of 1-MN lower than 0.134 mol/l (Part I), only β -type crystals nucleated and grew. However, γ -type became predominant in the precipitates at 1-MN concentrations higher than 0.218 mol/l (Part III). In the narrow range, Part II, both β - and γ -types nucleated and grew competitively, and the precipitation ratio of these polymorphs changed with each run. It was certified by X-ray diffraction measurements that in no Part did transformation of the crystals occur in the solution for at least 48 hours after the crystallization.

The relationship between the molar ratio of guest molecules to Ni-complex in the precipitated solids and the 1-MN concentration are shown in Fig. 5. It was clarified that the crystals of β -type in Part I clathrate no 1-MN, but only solvent molecule of MCS with molar ratio of around 0.7 to 0.8, and that the γ -type crystals in Part III clathrate both 1-MN and MCS with the same molecular ratio of 1.0. On the other hand, the molar ratio in the crystals in Part II changed with scattering.

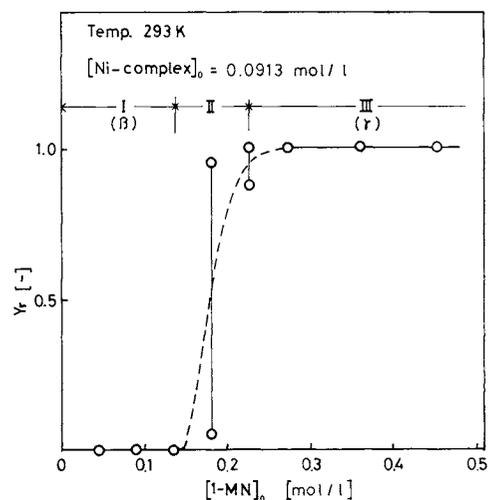


Fig. 4. Dependence of weight fraction of γ -type crystal in the precipitated solids on 1-MN concentration in the solution

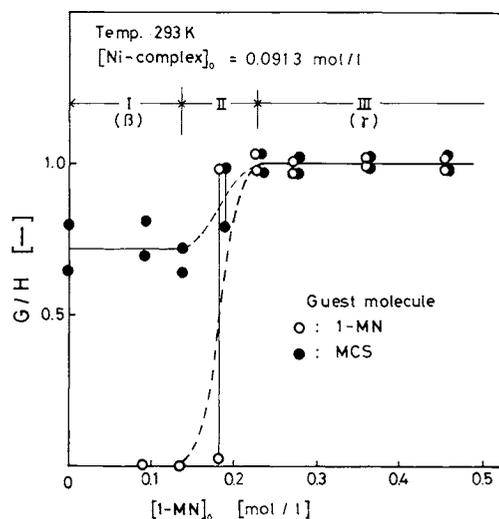
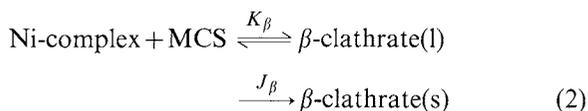
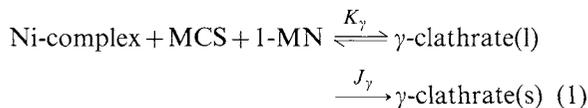


Fig. 5. Molar ratios of guest molecules to Ni-complex in the precipitated crystals

2.2 Nucleation mechanism of polymorphous clathrate crystals

As mentioned above, the polymorph composition in the precipitate is determined by the nucleation process in the early stage of crystallization and depends on the solution compositions. These facts mean that the relative interactions between Ni-complex and guest molecules of each polymorph change with solution composition. On this account, associated pairs of host and each guest molecule in the solution are assumed to be present and are called "liquid clathrate" in this work. It is considered that the formation of the cluster proceeds by aggregation of the liquid clathrates and nucleation occurs. According to the experimental results, the waiting times for nucleation were more than ten minutes for any run. Therefore, assuming that the liquid clathrates are in partial equilibrium with components consisting of clathrates

of each polymorph, the competitive nucleation processes of each polymorph can be expressed as follows.



Where l and s mean liquid and solid states, and K and J are the dissociation constant and the nucleation rate of each clathrate crystal, respectively.

The solubility of the clathrate crystal can be reduced to the equilibrium concentration of the liquid clathrate in the presence of solid clathrate. Accordingly, the supersaturation ratio, S , which is the driving force of the nucleation, can be given as the supersaturation ratio of the liquid clathrate. From Eqs. (1) and (2), the concentrations of liquid clathrates in the same supersaturated solution are given as follows.

$$[\gamma\text{-clathrate(l)}] = \frac{[\text{Ni-complex}][1\text{-MN}][\text{MCS}]}{K_\gamma} \quad (3)$$

$$[\beta\text{-clathrate(l)}] = \frac{[\text{Ni-complex}][\text{MCS}]}{K_\beta} \quad (4)$$

Thus, denoting the equilibrium condition with the subscript e , the concentrations of liquid clathrates in the saturated solutions can be written by the following equations.

$$[\gamma\text{-clathrate(l)}]_e = \frac{[\text{Ni-complex}]_{e-\gamma}[1\text{-MN}]_e[\text{MCS}]_e}{K_\gamma} \quad (5)$$

$$[\beta\text{-clathrate(l)}]_e = \frac{[\text{Ni-complex}]_{e-\beta}[\text{MCS}]_e}{K_\beta} \quad (6)$$

Using Eqs. (3)–(6), the supersaturation ratios are expressed as follows.

$$S_\gamma = \frac{[\gamma\text{-clathrate(l)}]}{[\gamma\text{-clathrate(l)}]_e} = \frac{[\text{Ni-complex}][1\text{-MN}][\text{MCS}]}{[\text{Ni-complex}]_{e-\gamma}[1\text{-MN}]_e[\text{MCS}]_e} \quad (7)$$

$$S_\beta = \frac{[\beta\text{-clathrate(l)}]}{[\beta\text{-clathrate(l)}]_e} = \frac{[\text{Ni-complex}][\text{MCS}]}{[\text{Ni-complex}]_{e-\beta}[\text{MCS}]_e} \quad (8)$$

If 1-MN concentrations in supersaturated and saturated solutions are the same, Eqs. (7) and (8) can be simplified as follows.

$$S_\gamma = \frac{[\text{Ni-complex}]}{[\text{Ni-complex}]_{e-\gamma}} \quad (9)$$

$$S_\beta = \frac{[\text{Ni-complex}]}{[\text{Ni-complex}]_{e-\beta}} \quad (10)$$

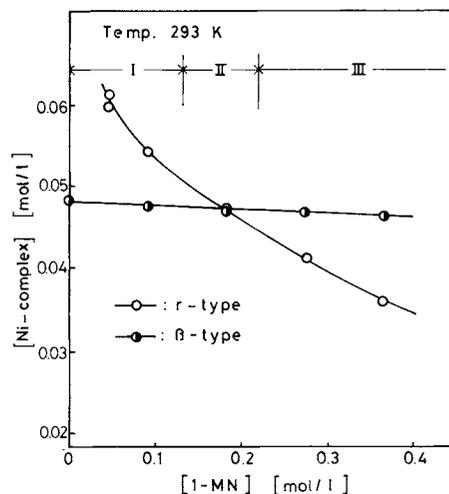


Fig. 6. Solubilities of Ni-complex forming β - and γ -type crystals

Applying these supersaturation ratios to a well-known expression,⁹⁾ the primary nucleation rates can be expressed by

$$J_\gamma = A_\gamma \exp\left[-16\pi\sigma_\gamma^3 v_\gamma^2 / \{3(kT)^3 (\ln S_\gamma)^2\}\right] \quad (11)$$

$$J_\beta = A_\beta \exp\left[-16\pi\sigma_\beta^3 v_\beta^2 / \{3(kT)^3 (\ln S_\beta)^2\}\right] \quad (12)$$

Where A is the pre-exponential term, σ is the surface energy and v is the molecular volume of the solid.

Precipitation behavior shown in Fig. 3 indicates that J_β is much larger than J_γ in Part I. However, when the concentration of 1-MN was increased the relative nucleation rates of the two polymorphs reversed in the narrow range of Part II and J_γ became much larger than J_β in Part III. In Eqs. (11) and (12), A and v are regarded as constant within the narrow concentration range of 1-MN. Accordingly, such a characteristic change of relative precipitation behavior is considered to be due to the relative change of supersaturation ratio of the two polymorphs.

2.3 Solubilities and precipitation behavior of polymorphous clathrate crystals

It is considered that free energies of the host lattices of Ni-complex are different between β - and γ -type crystals because of the difference of structures and guest molecules and are related to the solubilities of the crystals.⁶⁾ The host lattice, having lower solubility, is regarded as the stable form. Accordingly, the other one is the metastable form. Figure 6 shows the dependencies of solubilities of Ni-complex of β - and γ -type crystals on the concentration of 1-MN, indicating that the solubility of γ -type ($[\text{Ni-complex}]_{e-\gamma}$) decreases with 1-MN concentration but that of β -type ($[\text{Ni-complex}]_{e-\beta}$) is almost independent of concentration. These results seem to coincide with the prediction from Eqs. (5) and (6). Since the two solubility curves cross at about 0.183 mol/l of 1-MN con-

centration, it was found that the stable form is β -type at 1-MN concentration lower than 0.183 mol/l, but is γ -type at higher concentration. Consequently, the cross point is regarded as the transition point with respect to the concentration of 1-MN. When the concentration of 1-MN is away from the transition point, the solubility measurements of the metastable phase became very difficult because of nucleation of the stable phase. In Fig. 6, Parts I, II and III denote the same concentration regions of 1-MN as those in Fig. 3. It can be seen that only each stable form has nucleated in the crystallization in Parts I and III in Fig. 3, and that in Part II both stable and metastable forms nucleated.

The initial supersaturation ratios of β - and γ -type crystals were estimated by Eqs. (9) and (10), using the results in Fig. 6 and the initial concentration of Ni-complex (0.0913 mol/l), e.g. 1.92 and 1.81 at a 1-MN concentration of 0.134 mol/l, and 1.94 and 2.11 at a concentration of 0.218 mol/l, respectively. As mentioned above, the relative nucleation behavior of the polymorphs was scarcely influenced by the initial concentration of Ni-complex. This is also predicted from Eqs. (7) and (8) because the ratio of supersaturation ratios S_γ/S_β ($=[\text{Ni-complex}]_{e-\beta}/[\text{Ni-complex}]_{e-\gamma}$) is independent of the concentration on Ni-complex but depends on the 1-MN concentration. **Figure 7** shows the relation between the ratio S_γ/S_β and the 1-MN concentration. It can be seen from Fig. 7 that in Part I, S_γ/S_β is smaller than 0.94, corresponding to the preferential nucleation of β -type ($J_\beta > J_\gamma$), and that in Part III the ratio is larger than 1.04, and hence only γ -type nucleates ($J_\gamma > J_\beta$). In Part II where S_γ/S_β takes a value between 0.94 and 1.04, the both polymorphs could nucleate.

2.4 Mechanism of transformation between polymorphous clathrate crystals

As mentioned above, no transformation between γ - and β -type crystals was observed in Part II. However, transformation is expected to occur if the metastable phases precipitate in Parts I or III. The transformation of γ -type crystals was confirmed when γ -type crystals were added to the saturated solution of β -type in Part I, as illustrated in **Fig. 8**. As can be seen from Fig. 8, β -type crystals nucleated and grew, while γ -type crystals dissolved. This means that the transformation does not proceed through solid-state transformation, but rather by mediating the solution.⁶⁾ This transformation process including the interchange of guest molecules can be expressed as follows.

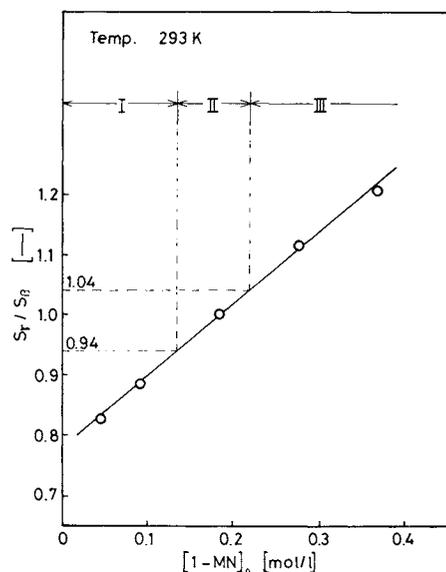
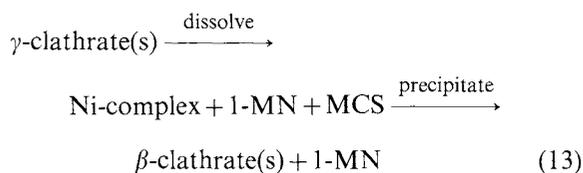


Fig. 7. Relationship between the ratio of supersaturation ratios of the polymorphs and 1-MN concentration

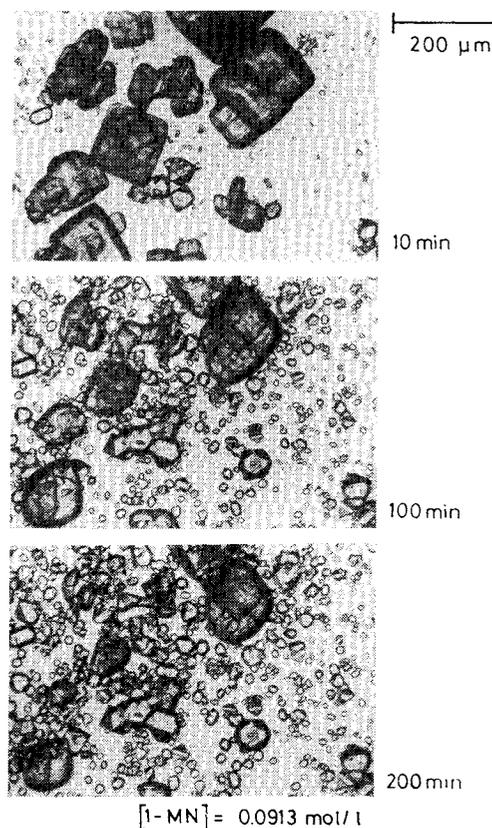


Fig. 8. Microscopic observation of transformation from γ - to β -type; 1-MN concentration of the solution is 0.0913 mol/l

On the other hand, when β -type crystals were added to the saturated solution of γ -type in Part III, two kinds of phenomena were observed in the course of the transformation of β -type crystals. Just after the addition of β -type crystals, the crystals were observed to collapse in the solution with a little bubbling as shown in **Fig. 9**. Thereafter, dissolution of β -type

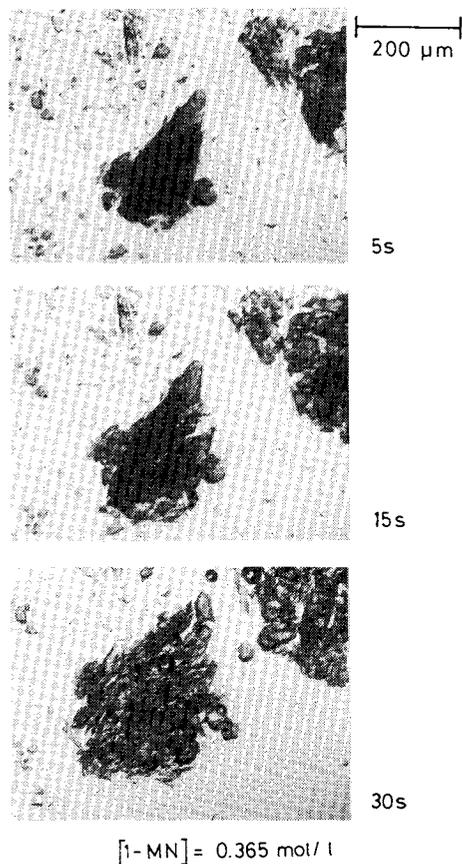


Fig. 9. Microscopic observation of collapse of β -type crystals; 1-MN concentration of the solution is 0.365 mol/l

crystals and precipitation of γ -type were observed. The latter phenomenon clearly indicates solution-mediated transformation just the opposite of Eq. (13). When the crystals were filtered from the solutions, it was observed that some part of the clathrated MCS molecules in the β -type crystals can escape into the atmosphere much more easily than the guest molecules in γ -type crystals. As the structure of the host lattice of β -type does not change, even when most guest molecules are lost, there should be some vacancies in the prepared crystals. When the β -type crystals added in the solution, 1-MN molecule may quickly penetrate into the vacancies and form γ -type clathrate in the crystals. This may induce distortion in the β -type crystals, which may then collapse in the early stage of the transformation.

Conclusion

The precipitation mechanism of polymorphous clathrate crystals was investigated in MCS solutions containing Ni-complex and 1-MN, and the following results were obtained.

1. The precipitation behavior of the polymorphs of β - and γ -type crystals hardly depends on Ni-complex concentration, but changes markedly with 1-MN concentration. The behavior was divided into

three Parts (I, II, III) concerning 1-MN concentration.

2. In β -type crystals only MCS molecule is clathrated, with a molar ratio of 0.7–0.8 to the Ni-complex, however, γ -type crystals clathrate both MCS and 1-MN molecules with the same molar ratio of 1.0.

3. It was found that there is a cross-point of the solubility curves of the polymorphs that can be regarded as the transition point between β - and γ -type crystals with respect to 1-MN concentration.

4. The respective nucleation behavior of the polymorphs could be correlated with the ratio of the supersaturation ratios of the liquid clathrates of each polymorph.

5. The transformation was observed when the metastable crystals were added to the solutions in Part I or III, and the main transformation mechanism appeared to be “solution-mediated”.

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Nomenclature

A	= pre-exponential term in Eqs. (11) and (12)	$[1/(\text{m}^3 \cdot \text{s})]$
G/H	= molar ratio of guest molecule (G) to Ni-complex (H)	$[-]$
J	= nucleation rate	$[1/(\text{m}^3 \cdot \text{s})]$
K_β	= dissociation constant of liquid clathrate of β -type	$[\text{mol}^2/\text{l}^2]$
K_γ	= dissociation constant of liquid clathrate of γ -type	$[\text{mol}/\text{l}]$
k	= Boltzmann constant	$[\text{J}/\text{K}]$
S	= supersaturation ratio	$[-]$
T	= temperature	$[\text{K}]$
v	= molecular volume of solid	$[\text{m}^3/\text{molecule}]$
Y_γ	= weight fraction of γ -type in crystals	$[-]$
2θ	= reflection angle of X-ray	$[\text{°}]$

<Subscript>

$e-\beta$	= concentration under solid-liquid equilibrium condition of β -type
$e-\gamma$	= concentration under solid-liquid equilibrium condition of γ -type
o	= initial concentration in batch crystallization
β	= β -type structure
γ	= γ -type structure

<Superscript>

l	= liquid state
s	= solid state

Literature Cited

- 1) Arad-Yellin, R., B. S. Green, M. Kossow and G. Tsoucaris: *J. Am. Chem. Soc.*, **105**, 4561 (1983).
- 2) Bender, M. L. and M. Komiyama: “Cyclodextrin Chemistry,” Springer-Verlag (1987).
- 3) Davy, R. J.: *J. Colloid and Interface Science*, **108**, 189 (1985).

- 4) Kitamura, M., E. Wakabayashi and T. Nakai: *Kagaku Kogaku Ronbunshu*, **7**, 50 (1981).
- 5) Kitamura, M. and T. Nakai: *J. Chem. Eng. Japan*, **15**, 105 (1982).
- 6) Kitamura, M.: *Separation Process Engineering*, **16**, 160 (1986).
- 7) Lipkowski, J., A. Bylina, K. Duszczuk, K. Lesniak and D. Sybilska: *Chem. Anal. (Warsaw)*, **19**, 1051 (1974).
- 8) McMullan, R. K., W. Saenger, J. Fayos and D. Mootz: *Carbohydr. Res.*, **31**, 37 (1973).
- 9) Mullin, J. W.: "Crystallization," Butterworths, London (1972).
- 10) Takemoto, K.: "Hosetsukagobutsu no Kagaku," Tokyo-kagakudojin, Tokyo (1969).
- 11) Toda, F.: "Topics in Current Chemistry," Vol. 140, p. 44, Springer-Verlag, Berlin and Heidelberg (1987).

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MODELING AND DESIGN METHOD FOR INTERNAL HEAT-INTEGRATED PACKED DISTILLATION COLUMN

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Key Words: Distillation, Energy, Film Theory, Heat Integration, Heat Pump, Packed Column, Process Design, Simulation, SRV Distillation

A mathematic model for an internal heat-integrated packed distillation column (IHIPAC) is developed on the basis of interphase mass transfer theory. A new method for design of an IHIPAC is proposed using the newly developed model. The binary system of methanol-water is adopted for the simulation work. The results show that an IHIPAC can be operated at a reflux ratio smaller than the minimum reflux ratio of a conventional distillation column, and that an energy saving of approximate 30% can be achieved under various operating conditions.

Introduction

Distillation is the biggest energy consumer among unit operations in chemical plants. Various methods for energy saving in distillation have been proposed during the last two decades, such as multi-effect method, heat-pump method, intermediate heating-cooling method, and secondary reflux and vaporization [SRV] method. The first three methods have already been applied to actual processes.⁶⁾ In particular, the heat-pump method has been widely used and found effective not only in distillation but also in other heat recovery processes.¹¹⁾ The SRV method, however, has not yet been applied to actual processes.

The SRV method was first proposed by Mah *et al.* (1977).¹⁰⁾ Fitzmorris *et al.* (1980)³⁾ presented a thermodynamic availability analysis of an ethylene-ethane splitter using the SRV method. Nakaiwa *et al.* (1984)^{12,13)} proposed a design method for a plate-to-plate heat-integrated distillation column by modi-

fying the McCabe-Thiele method. Shimizu *et al.* (1985)¹⁴⁻¹⁶⁾ presented a control scheme for binary distillation with SRV, and other techniques have been proposed.^{1,17)}

In this paper we propose a new design method for a packed distillation column in which energy saving is realized by the SRV method. This system is hereafter called an internal heat-integrated packed distillation column (IHIPAC).

1. Structural Description of an IHIPAC

Figure 1 shows a schematic diagram of an IHIPAC. The rectifying section is operated at a higher pressure and a higher temperature than those of the stripping section. For adjusting the pressures, a compressor and a throttling valve are installed between the two sections. A certain amount of heat is differentially transferred from the rectifying section to the stripping section along the heat-integrating section. As a result, flow rates are decreased along the column upward in the rectifying section and downward in the stripping section. The vapor flow rates at the top of the rectifying section and at the bottom of the stripping

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