TEMPERATURE EFFECT ON THE PRECIPITATION PROCESS OF POLYMORPHOUS CLATHRATE CRYSTALS OF Ni-COMPLEX

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***Key Words*:** Crystallization, Nucleation, Polymorph, Transformation, Clathrate, Inclusion Compound, Adductive Crystallization

Introduction

Two polymorphous clathrate crystals of β- and γ-type precipitate from methylcellosolve (MCS) solution containing Ni-complex ($Ni(C_6H_7N)_4(SCN)_2$) and 1-methylnaphthalene (1-MN) at 293 K.[2,3] It was shown in the previous paper[2] that the precipitation behaviors of both polymorphs depend notably on the 1-MN concentration and that their behaviors are controlled by the competitive nucleation rates of the polymorphs, according to supersaturation ratio.

In this paper the temperature effect on the precipitation behaviors of the polymorphs is shown.

1. Experimental

Crystallization was carried out at constant temperatures between 283 and 303 K by the same method as in the previous study.[2] The initial concentration of Ni-complex was changed with crystallization temperature to keep the slurry densities nearly the same, e.g. 0.0749 and 0.106 mol/l at 283 and 303 K, respectively. During the crystallization, small amounts of slurry were periodically sampled and subjected to microscopic observation, X-ray diffraction measurement and analysis by pyrolysis gas chromatography. Solubility measurements of Ni-complex of each polymorph were also made at several temperatures between 283 and 303 K.

Received August 10, 1988. Correspondence concerning this article should be addressed to M. Kitamura.

2. Results and Discussion

2.1 Temperature effect on the relative nucleation behaviors of polymorphs

Dependencies of the weight fraction of γ-type in the precipitate, Y_r, on 1-MN concentration at 283 and 303 K are shown in **Fig. 1** together with the result at 293 K, which was reported in the previous paper.[2] It

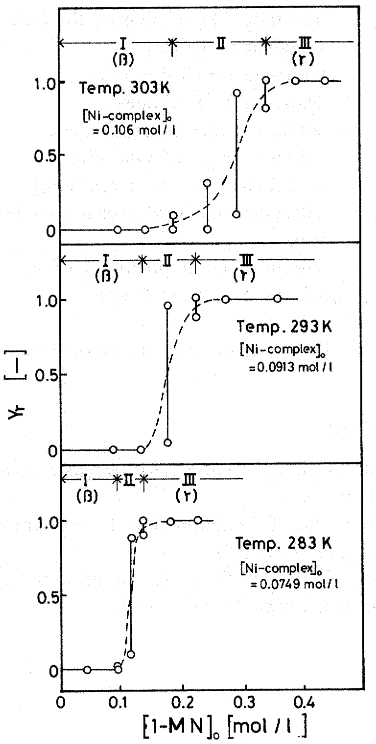

Fig. 1. Dependence of weight fraction of γ-type in precipitates on 1-MN concentration at different crystallization temperature

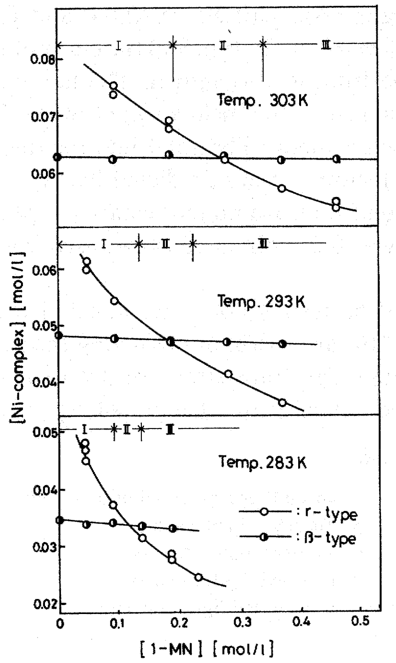

Fig. 2. Solubilities of Ni-complex forming β- and γ-type crystals at each temperature

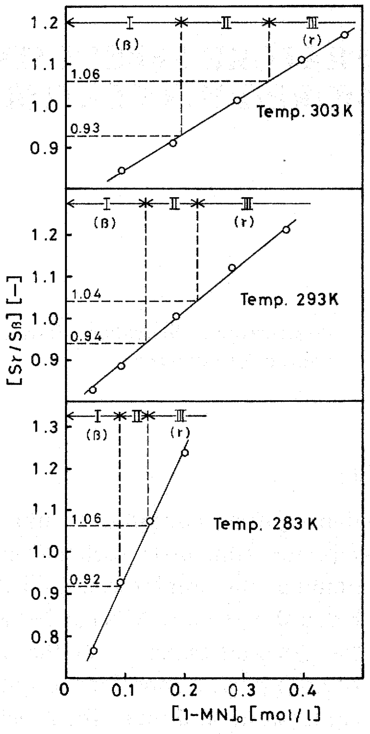

Fig. 3. Dependence of ratio of supersaturation ratios of polymorphs on 1-MN concentration at each temperature

can be seen that the precipitation behaviors at 283 and 303 K are also divided into three parts, as is that at 293 K. In Parts I and III, only β- and only γ-type respectively nucleated and grew. However, both polymorphs nucleated and grew independently in Part II. On the other hand, it appeared that Part II shifts to the higher concentration range of 1-MN and its width increases with operating temperature.

Solubilities of Ni-complex host forming β- and γ-type crystals were measured at 283 and 303 K, and the results are shown in **Fig. 2** together with that at 293 K. The concentration ranges of Parts I, II and III for each temperature in Fig. 1 are also denoted in the figure. As shown in the previous work,[2] the solubilities correspond to the free energies of each host lattice. The cross point of both solubility curves can be regarded as the transition point, where the stable form changes. Figure 2 indicates that in Parts I and III the stable form precipitates and in Part II both stable and metastable forms precipitate competitively at each temperature. It can also be seen that the transition point moves to a higher concentration of 1-MN as the temperature rises. This may suggest that the dissociation of γ-type clathrate proceeds more easily than that of β-type at higher temperatures, and that higher concentration of 1-MN is necessary for γ-type crystals to suppress dissociation and exist stably. From these results the shift of Part II with temperature in Fig. 1 can be attributed to the shift of the transition point.

The ratio of the supersaturation ratios of each polymorph that are driving forces of their nucleations, S_r/S_β,[2] obtained at 283 and 303 K are plotted against the 1-MN concentration with the result at 293 K in **Fig. 3**. Linear relationships are obtained in every case and the slope decreases with temperature. It can be

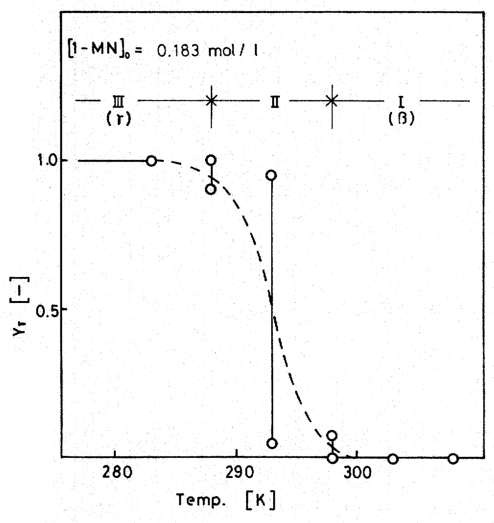

Fig. 4. Effect of crystallization temperature on weight fraction of γ-type in precipitates

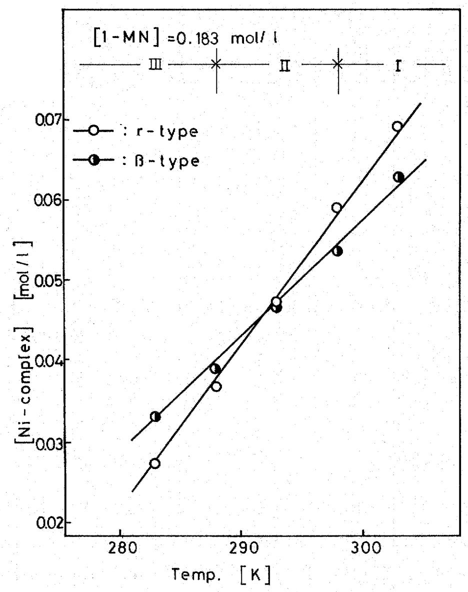

Fig. 5. Dependence of solubilities of Ni-complex forming β- and γ-type crystals on temperature

seen that the values of S_r/S_β in Part II have almost the same ranges for each temperature, i.e. 0.92–1.06 at 283 K, 0.94–1.04 at 293 K and 0.93–1.06 at 303 K. These facts reveal that the increase in width of Part II in Fig. 1 with temperature is due to the decrease of the ratio of S_r/S_β and 1-MN concentration.

In **Figs. 4** and **5**, dependences of Y_r and solubilities of the polymorphs on the temperature at the same concentration of 1-MN (0.183 mol/*l*) are shown. It appeared that precipitation behaviors can be also divided into three Parts of I, II and III in respect to the operating temperature in the same manner as in Fig. 1, and that Part II includes the transition point with respect to the temperature as shown in Fig. 5.

2.2 Transformation of clathrate crystals

Although both polymorphs were present in the solutions in Part II in Fig. 1, no transformation could be observed for at least 48 hours after the completion of crystallization at each temperature. On the other hand, when metastable crystals were added in the saturated solution of the stable form in Parts I and III, the solution-mediated transformation occurred soon,[2)] if the 1-MN concentration was far from the transition point. It is considered that in Part II both the dissolution rate of the metastable crystals and the growth rate of the stable crystals are small because the solubility difference between β- and γ-type is small, and the rate of solution-mediated transformation is too slow to be observed in this experiment.

Transformation from γ- to β-type crystals was observed when the temperature was raised to 303 K after γ-type was crystallized at 283 K. This may be due to the change of the stable form with increase in temperature. The transformation mechanism was also confirmed to be solution-mediated[1,2)] by the microscopic observation. These facts indicate the importance of temperature control in the separation process of adductive crystallization.

Conclusion

1. Precipitation behaviors are divided into three parts with respect not only to 1-MN concentration but also to temperature. Part II shifts to higher concentration of 1-MN with temperature because of the shift of the transition point.

2. The slope of S_r/S_β versus 1-MN concentration decreases with temperature and the increase in width of Part II with the operating temperature is attributed to the slope decrease.

3. The solution-mediated transformation from γ- to β-type crystals occurs by increasing the temperature on account of the change of the stable form.

Nomenclature

S	= supersaturation ratio	[—]
Y_r	= weight fraction of γ-type in crystals	[—]
⟨Subscript⟩		
o	= initial concentration in batch crystallization	
β	= β-type structure	
γ	= γ-type structure	

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