Novel Crystallization based on Design of Nano-Crystal Structure for Separation of Bioproducts

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Introduction

Separation of individual components from mixture solution has been concerned long time in chemistry, pharmaceutics and chemical engineering fields and many techniques and processes such as distillation, crystallization, chromatography, extraction etc have been developed to achieve the goals of separations. Even though above techniques and processes for the separations are most traditional and common unit operations in industries, they are frequently frustrated to separate the individual components from mixtures, especially in case of molecular isomer mixtures, because the isomers have very similar physical properties on which the traditional separation methods rely. Thus, it prompts to develop new method exploiting a distinctive property between molecular isomers to effectively perform separation of individual components from the isomer mixture.

Based on the recognition of molecular configuration (shape) of isomers the selective inclusion into host materials is counted as most prospective way to attain the goal of isomer separations. In this method the host structure is tailored to preferentially adopt a certain shape of isomers as a guest in the structure and to form a solid inclusion compound. To perform this kind of functionality of the host materials for the isomer separation, the host framework of guanidinium organosulfonate has been designed on the base of hydrogen bond in our research group. This noncovalent framework is created by virtue of hydrogen bonding between the N-H moiety of the guanidinium cations (**G**) and the sulfonate moiety of the organosulfonate anions (**S**), as shown in Fig. 1. The guanidinium and sulfonate ions are arranged to form a quasi-hexagonal lamellar motif being pillared with organic residue of the organodisulfonate anions in third dimension of the arrangement to create a space to include a guest molecules during assembly of the host framework. Since the noncovalent bonding in the host framework allows the **GS** lamellar sheet to pucker along to the **GS** ribbon direction, the **GS** host framework is endowed with ability to adopt the different configuration of the guest molecules by changing the shape and volume of inclusion space

within the host framework.

For performance of separation of the mixture, the solid-liquid reaction system is schemed, as displayed in Fig. 2. The solid host powder directly contacts the mixture of guests to include selectively a guest within his framework of the inclusion compound and it produces the two phases of the selected-guest rich solid phase and raffinate liquid phase. Then, the separation of the each component from the mixture is completely attained just after a filtration of the inclusion compound from the suspension and an extraction of the guest from the inclusion compound. This solid-liquid reaction system provides us with several advantages of high potentials for industrial application and process scale-up, in addition to the reuse of the host material and the easiness in handling of solid inclusion compound and retrieval of including guest.

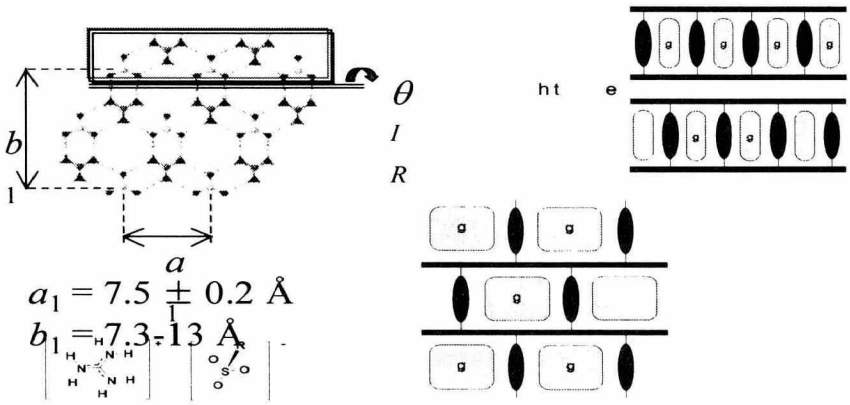

Figure 1. Crystal structure of GS host for inclusion compound

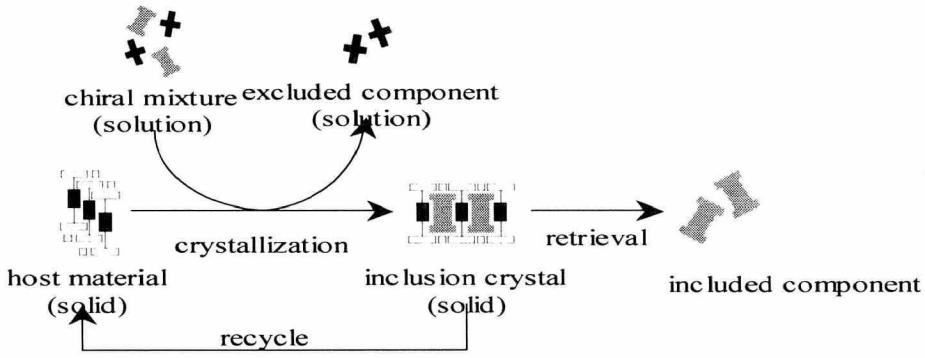

Figure 2. Conceptual diagram of selective separation based on shape recognition

Results and Discussion

Separation of mixture with solid hosts. In the present experiment, the **G_2NDS** and **G_2BPDS** host in solid state are applied to separate the three xylenes and ethylbenzene from pairwise mixtures. As displayed in Fig. 3, the propensity of selectivity of guest within **G_2NDS** host framework exhibits a competition behavior varying with composition in the binary mixture of the ortho-xylene and para-xylene. Below 0.2 of the ortho-xylene composition in the binary mixture ($X_{ortho\text{-}xylene} < 0.2$), the para-xylene is extremely selective to inclusion compound. In this range the selectivity factor, defined as $K_{AB} = (Y_A/Y_B)*(X_B/X_A)$, reaches up to 41, where Y_A and Y_B indicate the composition of components A and B in the solid inclusion compound, respectively and X_A and X_B are in mixture solution. This selectivity value imply that 20 : 80 of ortho-xylene and para-xylene mixture is separated to 0.994 : 0.006 by the selective inclusion. From the TGA (thermal gravitational analysis), in addition, the inclusion ratio of guest to host is estimated as 1.0, which corresponds to that of a single para-xylene within the bilayer **G_2NDS** host framework. This result is reasonably expectable with accounting for the high selectivity of para-xylene in the host; that is, the para-xylene templates the bilayer architecture dominantly and then the architecture selects the para-xylene for inclusion preferentially, again. As the composition of the ortho-xylene in the mixture increases up to 0.4, the preference of the guest inclusion into the host is suddenly shifted from para-xylene selection to ortho-xylene selection and the selectivity of ortho-xylene in the solid inclusion compound is enhanced up to about $Y_{o\text{-}xylene} = 0.8$. It also brings a consequence of increase of the inclusion ratio (guest to host) up to 3.0, which is equivalent to inclusion ratio of the single guest of ortho-xylene within the brick architecture of **G_2NDS** host framework. It is also due to dominant role of the ortho-xylene molecules to template host framework to form the isomeric brick architecture. Above 0.4 of $X_{o\text{-}xylene}$, it is most interesting to note that the ortho-xylene composition selected in the inclusion compound is almost independent of its composition in the liquid mixture; that is, the guest ratio in the simple brick structural compound is always approximately 4 :1 of ortho-xylene and para-xylene. In terms of the selectivity, in this range of the composition, the selectivity factor for the o-xylene is rather than reduced with increasing the concentration of o-xylene in the mixture and then becomes less than unity. This may be due to the less exclusiveness of the guest inclusion in the larger cavity space of the simple brick architecture than of the bilayer one.

From above experimental results it can be suggested that the separation of para-xylene and

ortho-xylene relies predominantly on the competition of architecting isomeric structures rather than of selective inclusion. It means that the guest composition of the inclusion compound is predetermined by a type of architecture of the compound, which is controlled by the mixture solution of the guests. For example, the bilayer architecture is exclusively containing the para-xylene and the simple brick structure is including both para-xylene and ortho-xylene with approximately fixed selectivity. Then, the apparent separation of ortho-xylene and para-xylene is the result of competition of architecting the bilayer and brick structures.

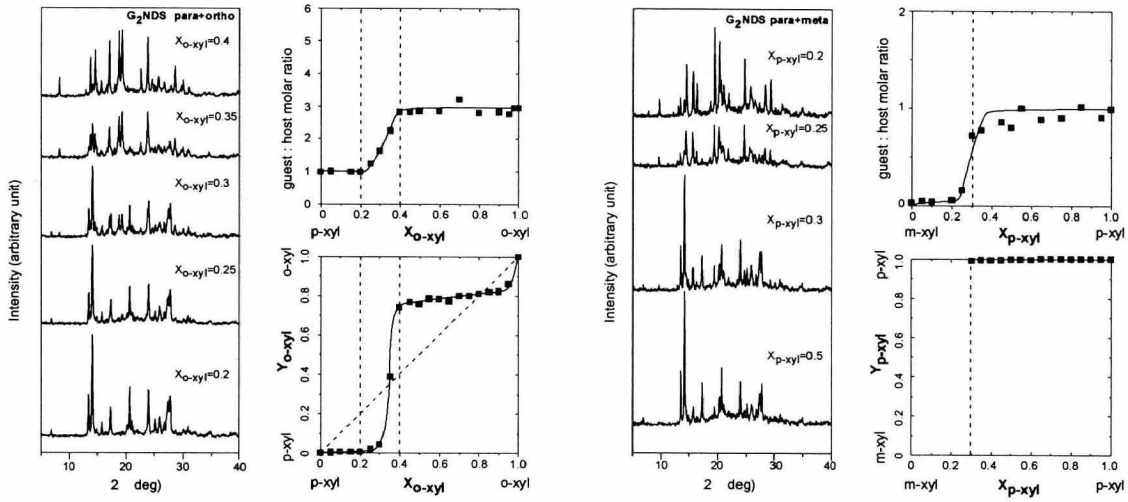

Figure 3. Selective separation of isomer by host inclusion

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