

CHAPTER II

LITERATURE SURVEY

2.1 Inclusion compound: history and development

Inclusion phenomenon was firstly reported by Schlenk (1951) that proposed the honeycomb structure of urea and thiourea. The concept of inclusion polymerization was then proven when Clasen (1956) applied urea and thiourea as a host molecule for butadiene monomer and proceeded the polymerization in room temperature for the nine months of a long period time. Brown and White (1960) adopted γ -rays for the polymerization in the system of 1,3-butadiene and 2,3-dimethyl butadiene in urea to obtain the stereoregularity polymer in a good yield. Meanwhile, C.J. Pedersen reported the alkaline and alkaline earth metal interaction with crown ether of which can be proven by the analytical techniques. Hydrotriphenylene was also recognized as a host compound for diene polymerization by Farina *et al.* (1964).

However, the inclusion phenomenon was not as much recognized until in the year 1987, when D.J. Cram, J.M. Lehn and C.J. Pedersen were awarded the Nobel Prize for their carriers and scientific fundamental researches to establish inclusion chemistry (Frängsmyr and Malmström, 1992). With the development of the analytical instruments, the understanding of inclusion chemistry has grown up rapidly and received much attention to concern it as a molecular assembly or supramolecular structure in the extended area of polymer science.

The most useful methods of checking the host guest composition are gas chromatography, X-ray diffraction, density measurements, thermal analysis, NMR, and single crystal X-ray crystallography. Miyata *et al.* studied crystal structure of steroid compounds such as cholic acid,

deoxycholic acid, apocholic acid, and its derivatives and reported the unique guest responsive property of cholic acid (Miyata *et al.*, 1990).

2.2 Deoxycholic acid as a host molecule in host-guest compound

Deoxycholic acid (3 α , 12 α -Dihydroxy-5 β -cholan-24-oic acid, DCA) is a steroidal compound with a molecular weight of 392.6, corresponding to the formula C₂₄H₄₀O₄. The chemical structure and schematic representative are shown in Figure 2.1.

This typical bile acid of chiral character, isolated from the bile of some animals by saponification and subsequent processing, has perhydro-1,2-cyclopentanophenanthrene ring system. DCA has a polar site, characterized by two secondary hydroxyl groups, and an apolar site, characterized by two singular methyl groups. The molecule consists of two sites of hydrophilic and hydrophobic and features the remarkable chemical behavior including the assembly formation. A short aliphatic chain, with another methyl group, sticks out from the cyclopentane ring and terminates in the carboxyl group.

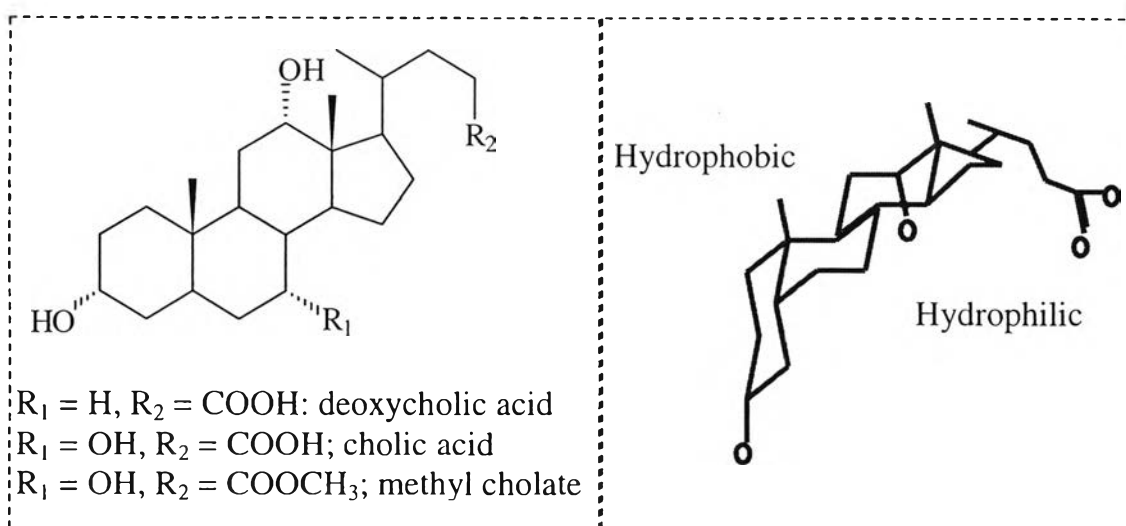


Figure 2.1. Chemical structure and schematic representative draw of deoxycholic acid.

Latschinoff isolated the first DCA inclusion compound from ox bile in 1885. Wieland and Sorge reported that DCA compound will be found as a stable complex with fatty acid. The related stable complex were also reported in the case of aliphatic, aromatic and alicyclic hydrocarbons, alcohols, ketones, fatty acid, esters, ethers, phenols, azo dyes, nitriles, peroxides, and amines. In 1972, Craven and DeTitta reported the first crystal structure of 1:1 compound of DCA with acetic acid to conclude as a host guest compound. Subsequently, x-ray studies have established that almost all DCA compounds have crystal structures composed of bilayers involving channels. Gilglio (1984) reviewed the structures known in mid-1980s, and discussed the flexibility of bilayers on the basis of energy calculations. The bilayers involving channels of DCA are depicted in Figure 2.2.

Cerrini *et al* (1993) reported the crystal of DCA with *o*-xylene that the crystals belong to the monoclinic system and the host/guest ratio is 2/1 by using single crystal crystallography. However, the presence of pseudo-two-fold screw axes among the host molecules makes the structure to be the bilayers, which is close to orthorhombic system. The guest molecules fill the space in the channels almost completely, occupy well-defined positions and interact with the surrounding host molecules at distances close to the sum of Van der Waals radii. The arrangement of the host and guest molecules in the channel is also shown in Figure 2.2.

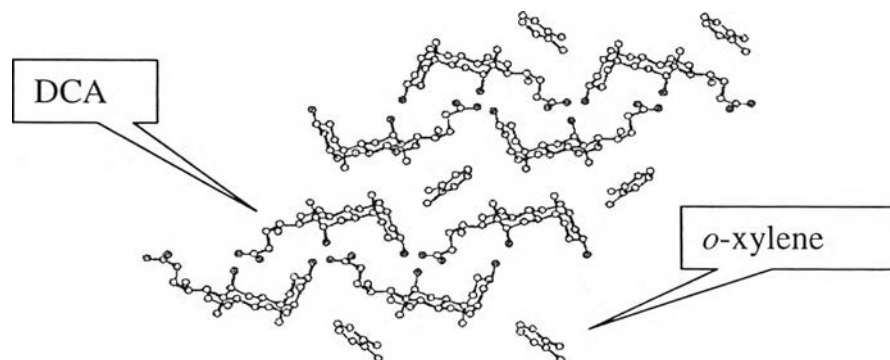


Figure 2.2. Bilayer involving channels of DCA with *o*-xylene guest molecule.

Four types of DCA host-guest compound crystal structure are reported, i.e., orthorhombic, tetragonal, monoclinic and hexagonal. Most of the guests yield orthorhombic crystal ($P2_12_12_1$). Figure 2.2, shows the monoclinic crystal of DCA-*o*-xylene. DCA host-guest compounds were summarized in Table 2.1.

Table 2.1. Crystal data and composition of DCA

| Guest | DCA/guest | a(Å) | b(Å) | c(Å) | Space group |
|-------------------|-----------|-------|-------|-------|--------------|
| Acetic | 1:1 | 25.55 | 13.81 | 7.11 | $P2_12_12_1$ |
| Acetone | 5:3 | 25.81 | 13.61 | 7.23 | $P2_12_12_1$ |
| Diethyl ketone | 2:1 | 25.83 | 13.56 | 7.24 | $P2_12_12_1$ |
| Aceptophenone | 5:2 | 25.59 | 13.71 | 7.25 | $P2_12_12_1$ |
| Cyclohexanone | 2:1 | 26.99 | 13.35 | 14.16 | $P2_12_12_1$ |
| Phenathrene | 3:1 | 26.81 | 13.60 | 21.66 | $P2_12_12_1$ |
| <i>d</i> -Camphor | 2:1 | 27.35 | 13.81 | 7.32 | $P2_12_12_1$ |
| Water | 2:3 | 14.00 | 14.00 | 48.90 | $P4_12_12_1$ |
| Ethanol,Water | 3:2:1 | 15.12 | 15.12 | 18.68 | $P6_5$ |

Gallese *et al.* (1992) studied the isomerization processes of xylene in the channel of DCA. From crystallographic study, the inclusion compound of DCA-*o*-xylene and DCA-*p*-xylene belong to the monoclinic system ($P2_1$), while DCA-*m*-xylene shows orthorhombic ($P2_12_12_1$) as shown in the Table 2.2.

Table 2.2. Crystal data of DCA with various isomers of xylene

| | DCA/ <i>o</i> -xylene | DCA/ <i>p</i> -xylene | DCA/ <i>m</i> -xylene |
|------------------|-----------------------|-----------------------|-----------------------|
| Space group | $P2_1$ | $P2_1$ | $P2_12_12_1$ |
| a | 7.24 | 7.27 | 7.20 |
| b | 26.17 (unique axis) | 13.38(unique axis) | 13.69 |
| c | 13.51 | 27.08 | 25.75 |
| β | 90.9 | 91.0 | 90.0 |
| Z | 2 | 2 | 2 |
| Host/guest ratio | 2:1 | 2:1 | 2:1 |

Nasimbeni *et al.* (1986) studied the inclusion compound of DCA with ethyl acetate by using single crystal X-ray crystallography. The crystal is found to belong to the orthorhombic type with $P2_12_12_1$ space group having four molecules of DCA in the unit cell. The ethyl acetate molecules exhibit different degree of disorder at low temperature and room temperature structures suggesting that it is both statistical disorder and dynamic disorder in nature. The molecular packing of DCA with ethyl acetate is shown in Figure 2.3.

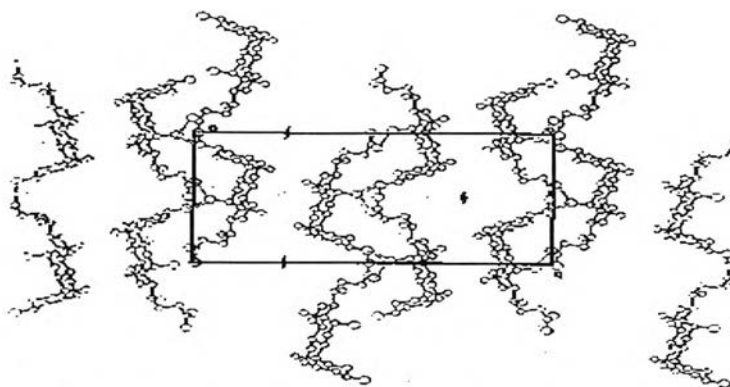


Figure 2.3. Molecular packing of DCA with ethyl acetate molecule.

2.3 Inclusion polymerization: history and development

Inclusion polymerization is one of the applications for inclusion compound when guest compound is a monomer. Here, the host molecule forms as a molecular assembly. Because of the specific size and shape of cavities provided by host molecules, the entrapped guest monomer is forced to align in an order making monomer guest molecules lose their ability to move or rotate contrary to the case of monomer in conventional solution. Clasen was firstly applied thiourea as a host molecule for butadiene monomer and proceeded the polymerization at room temperature for long time. The partial success was improved by Brown and White, by using high-energy radiation, such as γ -ray for initiating reactive species to find that the reaction gave the high stereoregularity polymer in a good yield in 1960. Inclusion polymerization was further reported by Fanira *et al.* in preparation of trans-

anti-trans-anti-trans-perhydrotriphenylene as a host for synthesis a series of highly stereoregularity polymers from butadiene.

2.4 Deoxycholic acid and the inclusion polymerization

DCA form inclusion compound with a wide variety of organic substances, including monomers. Thus, inclusion polymerization can be claimed as a space-dependent reaction, which contributes the stereoregularity polymer corresponding to the low-dimensionality spaces derived by the host molecular assembly.

In the late 1980s, Miyata *et al.* clarified the general aspects of inclusion polymerization for DCA and apocholic acid (APA). Inclusion polymerization is shown as a space-dependent polymerization (Miyata *et al.*, 1984).

In the case of DCA, Miyata *et al.* (1987) summarized various kinds of diene and diacetylene monomer in DCA and APA. Miyata *et al.* showed that diacetylene, butadiene, and vinyl monomer can be polymerized in the channel of DCA and APA. Tsutsumi *et al.* (1990) reported that 1-chlorobutadiene can be polymerized in DCA channel with 100% of head to tail to obtain trans-1, 4 poly(1-chlorobutadiene). Heyes *et al.* (1992) characterized the obtaining polymer from inclusion polymerization of 2,3-dimethylbutadiene in DCA by using ^{13}C CP/MAS NMR technique to investigate the polymer inside the channel. Nowadays, inclusion polymerization is not concern only in organic compound but also in inorganic host such as zeolite and substituted cyclophosphazene. The obtained polymers from inclusion polymerization of inorganic hosts give highly stereoregularity polymers as well.

2.5 PVC from inclusion polymerization

Yoshii *et al.* (1975) studied broad line NMR on radiation-induced polymerization of vinyl chloride and 1,3-butadiene in urea canal complex. It

is found that the obtaining poly(vinyl chloride) is rich in syndiotactic under the effect of radiation time, temperature and post polymerization. The polymer is highly insoluble without being swollen in any known solvent for PVC such as tetrahydrofuran, cyclohexanone, nitrobenzene, and benzene-acetone mixed solvent.