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学位論文の概要及び要旨

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題　　目　Molecular Encapsulation of Gases by Cyclodextrin
（シクロデキストリンによる気体状物質の分子包接）

学位論文の概要及び要旨

Molecular encapsulation refers to the confinement of a guest molecule inside the cavity of a host molecule based on the concept of molecular recognition, which relies upon the complimentarity of size, shape, and chemical functionalities. Molecular encapsulation by cyclodextrins (CDs) is not, like most of the encapsulation techniques, limited to modifying liquid compounds to powders, providing protection against deteriorative reactions and imparting controlled release features toward guest molecules. It is also employed for solubility enhancement of various scarcely soluble compounds, odor and color masking, and stabilization of reactive compounds. Selection of preparation method depends on the capacity of preparation and sometimes on the physicochemical property of the intended guest. A vast and expanding array of solid, liquid, and gaseous compounds has been found a suitable guest for encapsulation by CDs, among which solids and liquids prevail. The first molecular encapsulation of gaseous compounds by CDs dated back to half a century ago. Nonetheless, the subject is poorly explored to date.

In this research, the aim is to study the molecular encapsulation reaction by CDs. Emphases were placed on two main aspects: the formation and dissociation of the inclusion complexes. More specifically, the study encompasses the molecular encapsulation of different guest compounds, the release or dissociation of their inclusion complexes, and the stability of the inclusion complexes against heat and humidity. Generally, the encapsulation reactions were characterized in terms of enhancement of guest aqueous solubility or inclusion ratio of the obtained inclusion complexes. Since the suitable encapsulation method varies with guest compound, the encapsulation parameters of study also differed accordingly. These parameters include the pressure of guest compound, length of encapsulation time, and guest concentration. As for the dissociation, the stability of the inclusion complexes was evaluated in response to two primary factors, namely the relative humidity of storage atmosphere and heat.

Our primary research interest lies in the molecular encapsulation of gaseous compounds, which leads us to carbon dioxide (CO_2) and 1-methylcyclopropene (1-MCP). Besides, a solid and a liquid compound have also been included. The guest compounds of interest include CO_2 and 1-methylcyclopropene (gaseous compounds), iodine (subliming compound), and 10-undecyn-1-ol (volatile compound). All these guest

compounds shared a common feature: the molecular encapsulation reaction and/or the release or dissociation reaction involved a transition of the guest compounds to or from the gaseous state.

This work started off with molecular encapsulation of CO_2 into α-CD. In addition to its availability, CO_2 interested us as a subject of study by its beneficial physiological effects and its increasingly unacceptable level in the atmosphere. CO_2 was encapsulated by pressurizing moistened or aqueous α-CD. The effects moisture content and CO_2 pressure were investigated. The stability of CO_2/α-CD inclusion complex was assessed with regards to release in response to storage humidity.

While 1-MCP is an effective ethylene response inhibitor that depends solely upon molecular encapsulation with α-CD for practical application at present, it is of utter importance to understand the mechanism of encapsulation as well as the stability of the inclusion complex formed. The encapsulation reaction was performed in a closed, agitated vessel with a flat gas–liquid interface. The reaction was kinetically characterized by monitoring the decrement of 1-MCP headspace concentration with reaction time from different initial values. The encapsulation was explained quantitatively by gas adsorption theory with a pseudo-first-order reaction between 1-MCP and α-CD. On the other hand, the kinetic study on the thermal stability of the inclusion complex has also been carried out. The dissociation reaction was found describable by the unimolecular decay law. The initial inclusion ratio (molar ratio of 1-MCP to α-CD) was varied to study the effect on inclusion complex stability, which in turn leads to the establishment of the so-called "true" kinetic parameters that account for the dissociation reaction.

Iodine also makes an interesting subject of study due to its fungicidal properties and the feasibility for molecular encapsulation in the gas phase by CDs. The solubilizing and stabilizing power of various CDs (natural and derivatized) on iodine in the aqueous phase were examined. α-CD, the one found with the highest stabilizing power, was further studied at different concentrations and the apparent stability constant of the inclusion complex was deduced with a model developed based on mass transfer theory.

Finally, a volatile compound with antifungal properties called 10-undecyn-1-ol was included. As a naturally occurring compound exhibiting high antifungal activity, the study on the inclusion complex of 10-undecyn-1-ol with CD derivatives aimed for a replacement of the currently-in-use synthetic fungicides to reduce soil pollution. Solubility of 10-undecyn-1-ol in solutions of CD derivatives was determined, from which the apparent stability constant was subsequently computed. The solid inclusion complexes were prepared at various host to guest ratios and characterized. The improvement of antifungal activity of 10-undecyn-1-ol in the aqueous phase on *Rosellinia necatrix* by molecular encapsulation with CD derivatives was digitally evaluated.