論文の内容の要旨

論文題目 「Study on the reactivity of active oxygen species with the composite films of methylene blue/water-soluble polymers using quantum chemical calculation」

（量子化学計算を用いた活性酸素種と
メチレンブルー／水溶性ポリマー複合膜との反応性に関する研究）

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Active oxygen species (AOS) play a pivotal role in the oxidation reactions of organic compounds. Previous studies have reported the preparation of indicators that decolorize under specific AOS generation conditions. The indicators are composite thin films based on methylene blue and water-soluble polymer such as pullulan and sodium alginate. The decolorization occurs only under high humidity condition that produces a large amount of hydroxyl radical (OH*), which is known to have the strongest oxidative ability among AOS.

In this thesis, the index for AOS detection using the decolorization phenomenon that occurs between AOS and composite membranes was explored at the atomic interaction level. To approach the goal, the quantum chemical calculation techniques were used to clarify the molecular interactions between AOS and a methylene blue/pullulan or methylene blue/sodium alginate composite thin film. This thesis consists of the following five chapters:

In Chapter 1, effectiveness of the molecular orbital theory and the computational chemistry methods was explained. After introducing the manipulation of the program including input and output data, the objectives of this thesis were described.

In Chapter 2, the intermolecular interaction between methylene blue and pullulan was investigated using a model complex of a methylene blue/pullulan composite thin film, which is useful for detecting highly oxidative OH*. Although the accuracy and the computation time of calculation are in a trade-off relation depending on a molecular size, the size of the model should be kept in a reasonable range in the calculation. Therefore, the pullulan model was represented by five glucose units. Molecular orbital (MO) calculations were performed to identify the interaction modes between methylene blue and pullulan at the HF/6-31G(d) level. Ten methylene blue/pullulan complex structures were characterized, and their complexation energies were evaluated. The detailed structure analysis suggested the formation of hydrogen-bonds between the OH group of pullulan and the sulfur, carbon, or nitrogen atoms of methylene blue.

In Chapter 3, the decolorization mechanism of methylene blue was investigated by using sodium

alginate as a water-soluble polymer. The density functional theory (DFT) calculations at the B3LYP/6-31G(d) level were carried out to identify the positions of methylene blue, at which AOS attacks, as well as to get information about the decolorization mechanism. This chapter also provided theoretical evidence for understanding why the indicators made of sodium alginate or pullulan mixed with methylene blue are not decolorized by the ozone exposure while ozone causes decolorization of methylene blue. The results indicated that stable methylene blue/sodium alginate complex possesses intermolecular interactions between the carboxylates (–COO) of sodium alginate and sulfur, carbon, or nitrogen atoms of methylene blue. The interactions would contribute to suppressing the decolorization by ozone.

In Chapter 4, geometrical properties, the highest occupied molecular orbital (HOMO), and the lowest unoccupied molecular orbital (LUMO) have been studied for better understanding the reaction mechanism of OH* with methylene blue and water-soluble polymers (pullulan and sodium alginate). The binding energy was also calculated by using the DFT method at the B3LYP/6-31G(d) level. As a result, it was rationalized that ozone and hydrogen peroxide do not react with the complex of methylene blue with pullulan or sodium alginate whereas OH* can decolorize these complexes.

Chapter 5 summarizes the results obtained in Chapters 2-4.

Based on the above results, this thesis clarified the molecular interaction between methylene blue and water-soluble polymers and identified the interaction modes that would be responsible for the decolorization of the methylene blue-doped thin films in the exposure to OH*. Thus, we could construct a theoretical model of the chemical indicators that specifically react with OH* among AOS.